Methane Photochemistry in the Outer Planets

By

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Acknowledgements

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Abstract

Chapter I

  Historical summary is given for the theoretical and observational works so far made on hydro-carbons in the outer planets and Titan. The significance of the present research is stated through a critical evaluation of the previous theoretical studies.

Chapter II

  Photoprocesses involving hydrocarbons (C_1 to C_4) are widely compiled for preparation of the present research and for future reference. Description is given of:
  a)   absorption features *vs* wavelengths
  b)   states responsible for absorption
  c)   Primary and secondary decompositions by photoabsorption
  d)   quantum yields for the processes *(c)*.
  They are reviewed with stress being placed on aeronomical applications, that is, on the processes that have possible importances on the longer wavelength side of the solar *UV*. Description is further given for short-lived radicals and, for some of them, the dissociation rates due to the solar *UV* are evaluated.

Chapter III

  This chapter deals with the modeling of (neutral-neutral and ion-neutral) chemical reactions that are very likely to occur in the upper atmospheres of the outer planets. Description is first given about what types of reactions would progress in these environments. The coverage of the pressure range is so large that most of reactions are neither purely of a second-order nor are they purely of a third-order. (For example, recombination rates are determined by a competition between a stabilization by third bodies and several unimolecular processes inherent to the reaction system.) For such a necessity of evaluating the decomposition rates of the latter, the classical *RRK* theory is extensively used in the present work where no available information is obtained.
  For a majority of neutral reactions, a detailed explanation is given in the Remarks of Table 7, of the underlying chemical reaction models and of the rates adopted (or calculated). Several methods to evaluate the rate coefficients in the high pressure limit and the fundamental assump-tions introduced on dealing with ion-neutral reactions are also described.

Chapter IV

  This chapter deals first with a mathematical formulation of our present problems and next with a discussion on the physical parameters that appear in the relevant system of equations,

such as temperature, eddy diffusion coefficient and mixing ratio of methane. All these parameters required for actual calculations are made definite in this chapter. The effect of the atmospheric constituents other than methane whose existence is already known, is also discussed. Finally, computational procedures and some contrivances to improve numerical stability are described.

Chapter V

Calculations including hydrocarbons heavier than C_2-compounds are done for the first time in the present work. Results are presented for the several possible models of the Jovian atmosphere and for the model atmospheres of Saturn, Uranus and Neptune. The elementary photochemical processes occurring in these atmospheres are widely discussed in this chapter. The following is the outlines of the matters described in each section and the main results attained therein.

§ 1. *solutions in local photochemical equilibrium*

The abundance of ethane, ethylene, acetylene and free hydrogen dominates in this case. Principal chemical reactions in producing these and some C_3 and C_4-hydrocarbons are discussed and, relating to it, particular importance of hydrogen addition reactions and that of unimolecular processes are indicated. It is further shown that there are several catalytic reaction systems, very efficient in recombining a pair of hydrogen atoms, and that acetylene plays a peculiar role in our present chemistry, since there are many processes that lead to its restoration (namely, effective destruction of acetylene is very slow).

§ 2. *effect of eddy diffusion*

The effect of eddy diffusion is discussed, compared with the results obtained in § 1. Discussion is also given for the different magnitudes of its coefficient. The abundance decrease of atomic hydrogen and the resulting increase of hydrocarbons are described.

By inclusion of such an eddy diffusion, molecules with longer lifetimes (particularly, such as saturated hydrocarbons) come to attain large abundances. With increasing eddy diffusion co-efficient, the abundance increase of ethane and thence that of most hydrocarbons are caused. This is owed essentially to the extreme deficiency of atomic hydrogens resulting from its strong downward transport.

§ 3. *ion chemistry*

The present calculations for ions are new in that the reactions with C_2H_2, C_2H_4 and C_2H_6 (principal neutral products expected in methane photochemistry) are taken into account. Density profiles of ionic species consistent with that of neutral hydrocarbons (§ 1 and § 2) are presented and the flows of ion-molecule reactions are examined.

As far as hydrocarbonic ions are concerned, the species such as $C_2H_3^+$, $C_3H_3^+$, $C_3H_5^+$ and $C_4H_5^+$ constitute a group of dominant ions. Which ion, however, becomes a principal one is largely dependent upon the relative abundance among the above neutrals (C_2H_2, C_2H_4, C_2H_6) and free hydrogen.

§ 4. *lower boundary condition and associated stability problem of methane atmosphere*

The implication of our assumption of fixing methane content is examined in relation to the stability problem of methane atmosphere, and also to the lower boundary conditions to be im-posed on those hydrocarbons with long lifetimes. A numerical example is given for the latter case.

Downward fluxes at the lower boundary cause a general reduction of the abundance of saturated hydrocarbons near the lower boundary in a way as predicted from a simple theory.

§ 5. *temperature effect*

A temperature increase is favorable to the reactions with high activation energies to progress, while it is less favorable to the stabilization of excited intermediates in reaction. These two opposing effects in producing heavier hydrocarbons yield a peculiar density profile in every different case of temperature. Here, discussions are made on the Jovian case where a high temperature of 300 K is assumed and on the Uranian and Neptunian cases with much lower temperatures adopted. In any case, characteristic features in the abundance profile of hydrocarbons and photochemical processes responsible for it are indicated.

In the tentative Jovian atmosphere of 300 K, overall increase of hydrocarbon abundances (especially, of some C_4-compounds) are brought about, essentially due to the delay of the reaction,

$H + CH_3 + M \rightarrow CH_4$, and due to that more efficient chemical cycles are then used for a restoration process of acetylene. In the Uranian and Neptunian cases, despite the quite small mixing ratios of methane given, heavier compounds are abundantly produced. (C_2-hydrocarbons are, on the contrary, rather reduced.) This is due to the greatly enhanced role of the reactions that result in combination, since the unimolecular decompositions involved in the reaction systems are largely suppressed in such low temperatures.

§ 6. *comparison with observational results and theoretical implications for future research*

In this last section, a comparison is made between observational results and those obtained from the present calculations and plausible atmospheric models on temperature and eddy diffusion coefficient are sought. At this point, high eddy diffusion coefficient ($\sim 10^8$ cm^2 s^{-1}) is more favorable in explaining the abundance of hydrocarbons suggested from observations. For some (currently not observed) hydrocarbons whose existence is indicated in this work, argument is given about the possibility of detection. A brief discussion is finally added about C_5- and C_6-hydrocarbons, which may be produced through the '*solar photolysis*' on such C_1- to C_4-hydrocarbons as studied in the present work.

Chapter I. INTRODUCTION AND OVERVIEW

1. Introduction

In the last decade, planets have become an object full of interest for many researchers belonging to a variety of scientific fields. This is entirey due to a number of spacecraft so far directed to planets, which have successfully ended their missions by elucidating many features once not understood by scientists, and at the same time, by providing new data that require future studies. In particular, the results brought about by the Pioneers and the Voyagers on the Jovian and Saturnian systems were remarkable: Vivid pictures of violent atmospheric motions on Jupiter and Saturn, close-up surface views of the Galilean satellites suggesting the past tectonic activities, especially the still active volcanism on Io, features on several satellites that show cratering events in the early times of their formations, an innumerable number of ringlets revolving around Saturn (even reported as *"grooves in a record disk"* or described as *"rings within rings within rings within"*), queer morphology of F ring, first direct observation of Titan (giving a clue for its atmospheric compositions and temperatures, which have long been a theme full of debate), identification of sulfur dioxide frost on *Io*, detection of several UV emissions characteristic to some atomic species such as H, S and O in the magnetospheres, and discovery of decametric radiation from Saturn.

All the above facts strongly suggest that the study of the outer planets and their satellites are now more closely related to the geophysical science, rather than to the classical planetary astronomy. This is not exceptional for *aeronomy*, too. Photochemical calculations for the outer planets, once thought as purely of an academic interest, have become a theme that deserves more sincere discussions, due to the increasing knowledge of the atmospheric constituents, which was obtained from the earth-based observations of the past ten years and from such direct observations by the Pioneers and Voyagers.

The spectra of the outer planets are dominated by the absorption by methane, as seen in Fig. 1. Indeed, it is well known that methane is the third most abundant constituent next to hydrogen and helium. The latter two molecules, however, are chemically very inactive and spectroscopically, highly transparent. In this sense, *methane* is one of the most interesting and important gaseous constituents in the atmospheres of those planets, when the photochemical processes are considered. Observationally, the infrared spectra with high dispersion have gradually become possible to be taken for the outer planets owing to the development of large interferometric system, and such molecules as acetylene (C_2H_2) and ethane (C_2H_6) were proved to exist in Jupiter and Saturn, and ethylene (C_2H_4) in Titan. Not only the existence of these hydrocarbons was reaffirmed by direct observations on board the Pioneers and Voyagers, but also the heavier compounds as methylacetylene (C_3H_4) and propane (C_3H_8) were shown to exist in Saturn and Titan by the recent space
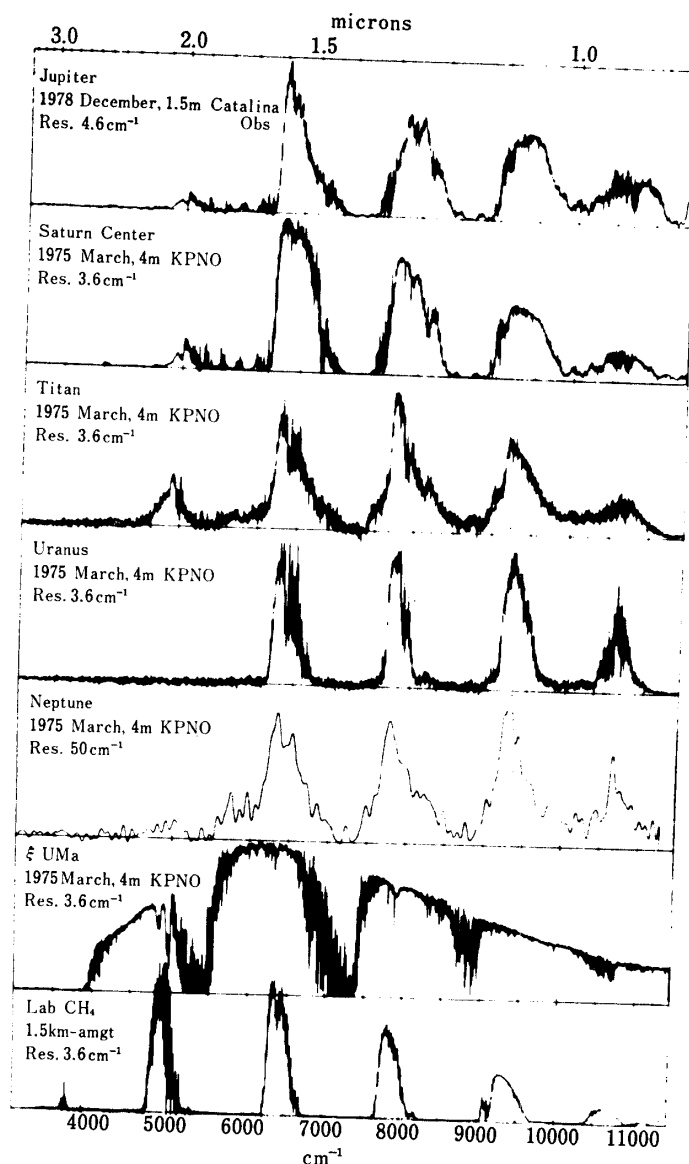
Fig. 1. Absorption spectra of Jupiter, Saturn, Neptune and Titan in the near-infrared wavelengths. The spectrum of comparison star, ξ UMa (spectral type of G0 V) provides the strength of the telluric absorptions. The bottom is methane spectrum in laboratory (1.5 km·amag). From Fink & Larson (1979).

mission (Voyager 1). It is to be noted that all of these hydrocarbons were observed *in emission* at rather high altitudes with elevated temperatures, a result strongly suggesting that their formations are done by *photochemical processes* which have an origin to the solar *UV* irradiation on methane.

Currently available theoretical studies of hydrocarbons in the outer planets are all based upon rather simple chemical models, purposing to calculate the concentrations of those observed small hydrocarbons as C_2H_2 and C_2H_6. These models, however, appear to have been oversimplified and have missed several important chemical reaction paths. Furthermore, there are no theoretical investigations which

have extended the scope of research to heavier compounds as C_3 and C_4-hydrocarbons, despite so many data on the photoprocesses and chemical processes of hydrocarbons being now available experimentally, and also despite some recent observations have hinted at the exstence of heavier hydrocarbons in the outer planets and Titan. Of course, we know that there are some difficulties to overcome for this purpose. It is just with such a view that the present study has been started.

The rough contents described in the present article are:

In Chap. I (remaining part), historical summaries of theoretical and observational studies made on hydrocarbons.

In Chap. II, extensive compilation on the photoprocesses (absorption feature, its strength, decomposition mode, quantum yield etc.) for C_1-to C_4-hydrocarbons.

In Chap. III, modeling of chemical reactions and several accompanying probems. Detailed comments are added to most neutral-neutral reactions.

In Chap. IV, description of governing equations and numerical procedures, and selection of plausible atmospheric models regarding temperature, eddy diffusion coefficient and mixing ratio of methane.

In Chap. V, results and discussions for several atmospheric and chemical models on Jupiter and those for typical atmospheric models of the other outer planets (Saturn, Uranus and Neptune). An emphasis is placed on analyzing the elementary photochemical processes essential to determining hydrocarbon abundance.

2. Historical summary of theoretical studies of methane photochemistry

The first study of photochemistry in planetary environments can be traced back to Wildt (1937), where he briefly discussed a stability problem of methane atmosphere in Jupiter as follows:

UV radiation on methane acts to produce a pair of radicals, methyl and free hydrogen,

$$CH_4 + h\nu \longrightarrow CH_3 + H$$

and in principle these radicals can form, by a self-combination, molecular hydrogen and ethane, respectively,

$$H + H + M \longrightarrow H_2$$
$$CH_3 + CH_3 + M \longrightarrow C_2H_6 \ .$$
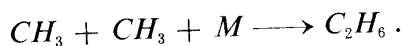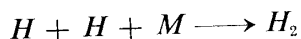
However, the concentration of methane is to be maintained through the much faster reaction shown below because of the ample supply of molecular hydrogen,

$$CH_3 + H_2 \longrightarrow CH_4 + H \ . \qquad\qquad (**)$$
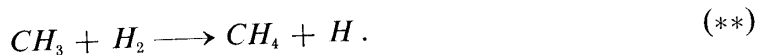
He further states *". . . . hydrogen atoms are known to attack violently all hydrocarbons,*

methane excepted, ... , it should have led to complete destruction of the higher hydrocarbons within a time which is short compared with the age of the planets." In a current viewpoint, however, such a reaction as (**) is almost completely prohibitive in the low temperature conditions of the outer planets because of the high activation energy of the system ($\sim 5000K$). Furthermore, free hydrogen does not attack all hydrocarbons and rather is highly preferential with respect to the reaction partner (see, Chap. III, § 3, ii)).

About a quarter century later, Cadle (1962) carried out a crude, time-dependent photochemical calculation on the upper atmosphere of Jupiter, where he derived a somewhat perplexing result that methane and ammonia concentrations drop to zero after a sufficient time in the zone of active photolysis. In his calculation, all the initially given methane and ammonia were converted to C_2H_6, CH_3, NH_2, N_2H_4 and CH_3NH_2. To avoid such a catastrophe, he explained that molecular hydrogen might undergo a slow photolysis to a considerable depth in the atmosphere and that methane would be recycled, if the resultant free hydrogen could, though probably with a very slow rate, react with ethane, *via* $H + C_2H_6 \longrightarrow CH_3 + CH_4$. It, however seems evident that the failure may be due to an insufficient treatment of the photodissociation processes in his model. This is particularly true in the treatment of an atomic hydrogen. Since he did not take account of the photodissciation processes capable of producing atomic hydrogen essentially except from CH_4 and NH_3, the extreme deficiency of H, we believe, caused the above result.

Saslaw & Wildey (1967) carried out an experiment which simulated the upper atmospheres of the outer planets by irradiating UV at 584A, and suggested several ion-molecule reactions that might be responsible for producing such molecules as C_2H_4, C_2H_6 and C_3H_8 and also for making the chain reactions of polymer formations initiating there. The obtained result, however, is not quantitative at all. We will show in a later chapter that ion-molecule reactions, after all, contributed much less in forming these products than neutral-neutral reactions.

The photochemistry on Jupiter was again overviewed by McNesby (1969), where he developed an interesting but controversial argument about some chemical reactions which coud be effective in the atmospheric environments of the outer planets. Particularly as to the methane photochemistry, he suggested that the reaction, $CH_3 + H_2 \longrightarrow CH_4 + H$, once abandoned by Cadle (1962) because of the high activation energy, might be rapid if the methyl radical would become metastably-excited by absorbing the solar radiation in longer wavelength. If the reaction should really proceed through such a mechanism as speculated, it is clear that the methane photochemistry would be greatly simplified: because no sooner methyl radical is produced than it is recycled to methane and there is no room left for further reactions, namely, for producing higher hydrocarbons. We would then, as a matter of fact, need not worry about such a stability problem of methane atmosphere as will be discussed in Chap. V, § 4. Fact, however, appears to deny his assertion, since the hydrocarbons, which have been found to exist abundantly on the outer planets from the infrared observations of these ten years, are known to originate in

the photolysis region high in the atmospheres. In viewpoint of elementary chemical reaction process too, no evidence is as yet obtained to support the hypothesis.

All the preceding studies are more or less of qualitative nature in that a realistic calculation based on the transport equation was not carried out. The first attempt to formulate reliable photochemcal model for methane atmosphere was performed by Strobel (1969). The study was followed by Strobel (1973a, d, 1974a, 1975) and Yung & Strobel (1980), in which the various photochemical processes responsible for producing C_2H_2, C_2H_4 and C_2H_6 were repeatedly discussed with the chemical data being replenished by newer ones. As the present research is closely

Table 1. Photodissociation processes in Jupiter adopted by Strobel (1973a)'s work

	probability		reference
	at Ly α	at all other λ	
$CH_4 + h\nu \longrightarrow CH_3 + H$	0.0	0.0	Strobel (1969)
$^1CH_2 + H_2$	0.92	1.0	Rebbert et al (1972)
$CH + H + H_2$	0.08	0.0	Rebbert & Ausloos (1972/73)
$C + 2H_2$	0.0	0.0	
$C_2H_2 + h\nu \longrightarrow C_2H_2^*$	1.0	1.0	Takita et al (1968, 1969)
$C_2H_4 + h\nu \longrightarrow C_2H_2 + H_2$	0.35	1.0	Strobel (1969)
$C_2H_2 + 2H$	0.65	0.0	
$C_2H_6 + h\nu \longrightarrow C_2H_2 + 2H_2$	0.45	0.9	Strobel (1969)
$C_2H_4 + 2H$	0.30	0.1	Lias et al (1970)
$CH_4 + {}^1CH_2$	0.25	0.0	

Table 2 Chemical reaction processes in Jupiter adopted by Strobel (1973a)'s work

reaction	rate coefficient $(cm^3 \cdot s^{-1})$[++]	reference
$^1CH_2 + H_2 \longrightarrow CH_4^* \longrightarrow CH_3 + H$	7.0(-12)	Braun et al (1970)
$^1CH_2 + CH_4 \longrightarrow C_2H_6^* \longrightarrow CH_3 + CH_3$	1.9(-12)	Braun et al (1970)
$CH + CH_4 \longrightarrow C_2H_4 + H$	2.5(-12)	Braun et al (1970)
$CH + H_2 + M \longrightarrow CH_3$	~1.0(-30)[M]	Braun et al (1970)
$H + CH_3 + M \longrightarrow CH_4$	8.5(-29)[M]	Barker et al (1970)
$CH_3 + CH_3 + M \longrightarrow C_2H_6$	~6.0(-29)[M]	{Kristiakowski & Roberts (1953) Dodd & Steacie (1954)}
$H + H + M \longrightarrow H_2$	8.0(-33)(T/300)$^{-0.6}$	Ham et al (1970)
$H + C_2H_2 + M \longrightarrow C_2H_3$	4.0(-14) at high pressure 2.5(-30)[M] at low pressure	Volpi & Zocchi (1966)
$H + C_2H_3 \longrightarrow C_2H_2 + H_2$	7.0(-12)	Benson & Haugen (1967b)
$H_2 + C_2H_3 \longrightarrow C_2H_4 + H$	5.0(-12)$e^{-3200/T}$	Benson & Haugen (1967b)
$H + C_2H_4 + M \longrightarrow C_2H_5$	3.9(-13) at high pressure ~4.0(-30)[M] at low pressure and at 300K activation energy=1.5 kcal	{Barker et al (1970) Rabinovitch & Setser (1964) Penzhorn & Darwent (1971)}
$H + C_2H_5 \longrightarrow C_2H_6^* \longrightarrow 2CH_3$	6.0(-11)	Kurylo et al (1970) Heller & Gordon (1962)

[++] For third-order reactions, unit is $cm^6 s^{-1}$.

related to the sequence of Strobel's work, it would greatly benefit understanding of our subsequent arguments to give an overview of his works here.

In his model calculation (Strobel, 1973a), nine species of hydrocarbons (C_1, and C_2)* plus atomic hydrogen were considered: CH_4, CH, $^1CH_2$, CH_3, C_2H_2, C_2H_3, C_2H_4, C_2H_5, C_2H_6 and H. The photodissociation processes and the chemical reactions incorporated into his model are shown in Tables 1 and 2. It is evident that a drastic simplification is being made there of the chemical reactions associated with the problem, as is readily noticed when a reference is made for our corresponding table in Chap. III (Table 7). Since his purpose has been confined to revealing the chemistry of forming C_1- and C_2-hydrocarbons under the atmospheric environments of the outer planets, the reaction paths of his interest were limited to only those which did not result in the production of C_3- and C_4-compounds. Nevertheless it appears that the calculation which was carried out on the twelve reactions alone is oversimplified even in describing C_2-hydrocarbon chemistry. The principal routes were explained as:

On absorbing the solar *UV*, methane is mainly dissociated to $^1CH_2$ (singlet ethylene radical) plus H_2.

$$CH_4 + h\nu \longrightarrow {}^1CH_2 + H_2 .$$
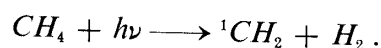
And the former is immediately changed to methyl radical by reacting with H_2, the predominant atmospheric constituent.

$$^1CH_2 + H_2 \longrightarrow CH_3 + H .$$

This methyl radical, if not returned simply back to methane due to

$$H + CH_3 + M \longrightarrow CH_4 ,$$
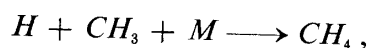
yields ethane by a self-combination,

$$CH_3 + CH_3 + M \longrightarrow C_2H_6 .$$
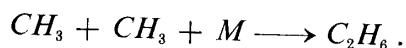
The ethane thus formed is reduced by absorbing the solar *UV* to smaller unsaturated hydrocarbons like acetylene and ethylene,

$$C_2H_6 + h\nu \longrightarrow C_2H_2 + 2H_2$$
$$C_2H_4 + 2H .$$
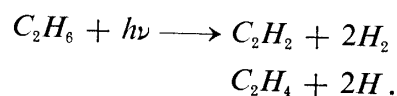
Photolytic act on these products is again a simple reduction of molecular dimension. More important effect played by such unsaturates is to supply radical species through an addition reaction by free hydrogen as,

$$H + C_2H_2 + M \longrightarrow C_2H_3$$
$$H + C_2H_4 + M \longrightarrow C_2H_5 .$$

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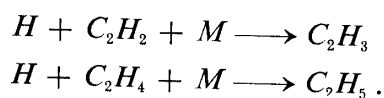
* Here and in the followings, C_i designates hydrocarbons that consist of i carbon atoms.

As to these radicals, only reactions with (atomic and molecular) hydrogen are considered and the immediate result is reproduction of the molecules of which a description has already been made,

$$H + C_2H_3 \longrightarrow C_2H_2 + H_2$$

$$H_2 + C_2H_3 \longrightarrow C_2H_4 + H$$

$$H + C_2H_5 \longrightarrow 2CH_3 .$$
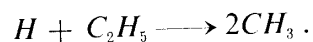
There are additional included reactions, which begin with dissociation of methane and affect preferentially the abundances of acetylene and ethylene,

$$CH_4 + h\nu \longrightarrow CH + H + H_2$$

$$CH + H_2 + M \longrightarrow CH_3$$

$$CH + CH_4 \longrightarrow C_2H_4 + H .$$
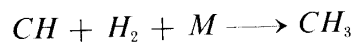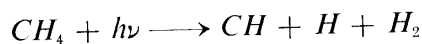
All the above chemical reactions complete those which were incorporated into his model calculations. One example of his results and the flow diagram of photochemical processes used there are shown in Fig. 2 and Fig. 3, respectively.
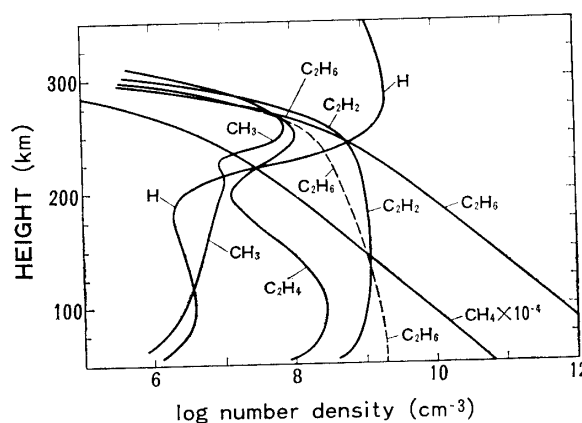
Fig. 2. Hydrocarbon densities in Jupiter for $K = 5 \times 10^5 \text{cm}^2 \text{ s}^{-1}$, $f_{CH_4} = 7 \times 10^{-4}$: $\phi(C_2H_6$; downward flux at the lower boundary)=0 (solid line), and $\phi(C_2H_6) = -4 \times 10^8 \text{cm}^{-2} \text{ s}^{-1}$ (dashed lines). From Strobel (1973a).
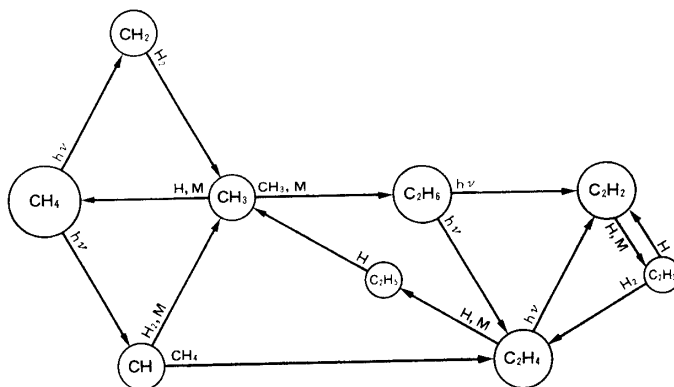
Fig. 3. Principal chemical reactions in the Jovian hydrocarbon photochemistry From Strobel (1973a).

The fact particularly noted by Strobel is that acetylene works as an efficient catalyst for recombining a pair of free hydrogen atoms,

$$H + C_2H_2 + M \longrightarrow C_2H_3$$
$$H + C_2H_3 \longrightarrow C_2H_2 + H_2$$

sum; $\quad H + H + M \longrightarrow H_2$
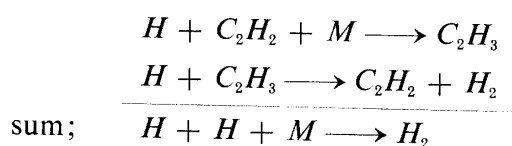
and also noted is the decisive importance of ratio between the rates of the following two reactions by which methyls are principally consumed,

$$H + CH_3 + M \longrightarrow CH_4$$
$$CH_3 + CH_3 + M \longrightarrow C_2H_6 .$$
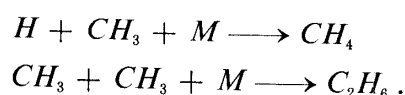
The immediate result of the former reaction is a restoration of methane and serves to keep atmosphere stable against the solar UV radiation, while as to the latter, it provides a virtual entry to a number of (known and unknown) chemical reactions which are required for yielding hydrocarbons. Accordingly, it is to be understood that the concentration of free hydrogen has a large influence on determining the abundances of such heavier hydrocarbons. It must be added that Strobel further studied the effect of eddy diffusion on the abundance distribution of C_2H_2, C_2H_4 and C_2H_6, variously changing the profile (magnitude at maximum and shape with altitude) and also the effect of lower boundary condition for these major C_2-hydrocarbons.

Strobel's reaction models, unquestionably insufficient, were supplemented by Prasad *et al* (1975) where the models were reinforced by introducing several reactions for acetylene and those compounds closely related to it chemically (C_2H, $C_2H_2^*$, C_2H_3, $C_2H_3^*$). Although they introduced a few of the processes capable of yielding C_4-compounds into chemical model, their calculation still remained to be the one made within a framework of C_2-hydrocarbon chemistry (*i.e.*, C_4-producing reaction was taken into account only as a loss term for C_2-compounds). After all, it is true that no effort has been made in the last decade to investigate the photochemical processes of hydrocarbons essentially beyond the scope which Strobel imposed on himself.

Now we shall turn our subject to the study of ion chemistry in the outer planets. From old times the Jovian ionosphere has aroused a special interest, obviously associated with the radio emission which this planet was believed to emanate. The earlier models of ionosphere almost all constructed upon the neutral atmosphere consisted of H_2 and He (Rishbeth, 1959, Zabriskie, 1960, Shimizu, 1964, Gross & Rasool, 1964, Hunten, 1969, Shimizu, 1971, Prasad & Capone, 1971, McElroy, 1973, Tanaka & Hirao, 1973, Capone & Prasad, 1973, Atreya & Donahue, 1975a). Stimulated by the progress of laboratory experiment on ion-molecule reactions, these models were steadily enlarged in scale with some older data being replenished by newer ones. We may say that our current understanding of the ion chemistry on H_2/He atmosphere has been considerably deepened compared with that in the

1960's (for the recent data compilation, see, *e.g.*, Albritton, 1978).

The common feature found in those studies is the predominancy of H^+ ion in the topside ionosphere. This is simply due to H^+ not being able to find a suitable reaction partner other than electron and that such a recombination as between electron and atomic ion is exceedingly slow. Originally the ion comes from dissociative ionization of H_2, a minor event that is accompanied in the photoionization of the molecule. On the other hand, the major product ion, H_2^+ is rapidly converted to H_3^+ via $H_2^+ + H_2 \longrightarrow H_3^+ + H$, and the resulant ion, H_3^+ is readily neutralized by recombining with electrons. Hence no molecular ions become dominant in these environments. Incluson of He into model is unlikely to cause an essential change in the above story of principal chemical flows, if it is made of moderate (near-solar) abundance. Quite complicated, multiply branched, chemical flows appear rather when an inclusion is made for the neutral species as methane and its derivative hydrocarbons. On this point we shall discuss details in Chap. V, § 3.

Following the studies as mentioned, calculations which include the chemistry of hydrocarbon ions have become prevalent, partly stimulated by successive discoveries of hydrocarbons in the outer planets, and partly supported by accumulated reaction rate data that have been made available experimentally, and also partly associated with interpretation of the Jovian electron density profiles that were brought about by Pioneer 10. Shown below is the major ions derived from such calculations.

investigators	planets	dominant hydrocarbon ions
Prasad & Tan (1974)	Jupiter	CH_5^+, $C_2H_5^+$
Atreya & Donahue (1975a)	Jupiter & Saturn	CH_5^+, $C_2H_5^+$
Tan & Capone (1976)	Jupiter	CH_5^+, $C_2H_5^+$
Ashihara & Shimizu (1977)	Jupiter	CH_5^+, $C_2H_5^+$
Capone *et al* (1976)	Titan (lower ionosphere)	$C_2H_9^+$, $C_3H_9^+$
Whitten *et al* (1977)	Titan (upper ionosphere)	CH_5^+
Capone *et al* (1977)	Saturn, Uranus, Neptune	$C_2H_9^+$, CH_5^+
Waite *et al* (1979)	Saturn	CH_5^+, $C_2H_5^+$

All these studies, however, have considered only methane as a neutral counterpart of ion-molecule reaction except for the work of Titan's ionosphere by Capone *et al* (1976) where inclusion was made for CH_3 and C_2H_6—whose densities were roughly estimated based on the simple photochemical model as Strobel (1974a) adopted. Fig. 4 is an example of such calculations, which was taken from Ashihara & Shimizu (1977). Here we only note that the ion chemistry of hydrocarbons is liable to suffer a change to the altered distributions of C_2H_2, C_2H_4 and C_2H_6 which are photochemically produced from methane.
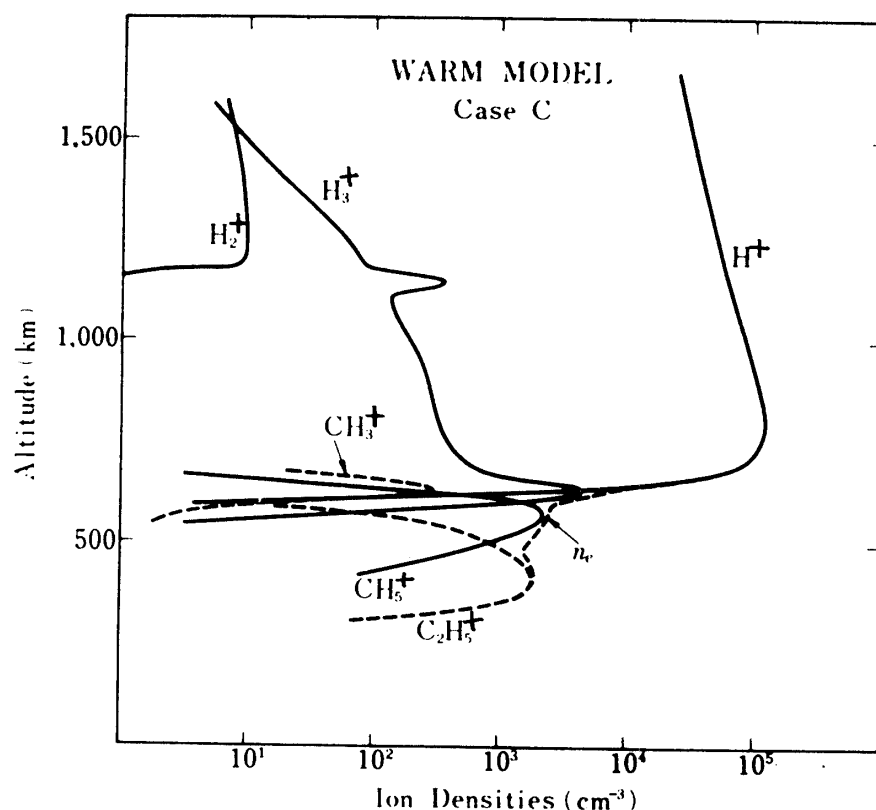
Fig. 4. Ion and electron density profiles in Jupiter calculated upon the warm (neutral) atmospheric model. From Ashihara & Shimizu (1977).

3. Historical Summary of Observational Studies of Hydrocarbons

Table 3 summarizes observations which have brought about some information on hydrocarbons in the outer planets and Titan. Before a high dispersion spectrum of Jupiter was taken by Ridgway (1974), several observations of low and/or medium dispersions had already revealed a bulge around 12μ in the infrared spectra of those celestial objects, giving a hint of discoveries to come. The bulge was usually interpreted as indicating the existence of a warmer region above the tropopause (temperature inversion). For Titan this radiation at 12μ was predicted by Caldwell *et al* (1973) as an emission of ethane (C_2H_6) existing in such a high temperature region. The identification was soon achieved by Ridgway (1974), where he observed Jupiter in the wavenumber range of 750 to 1300 cm^{-1} at a high resolution of 1.3 cm^{-1} and obtained spectra that consisted of prominent emission lines of ν_9 band of C_2H_6 and ν_5 band of C_2H_2 (Fig. 5). Since then, a number of studies have followed up to the present time for this and other outer planets and for Titan as is seen in Table 3. A notable fact is that all these molecular bands (in the infrared) have been observed *in emission* except for the only one case where acetylene was, though in the *UV* region, observed *in absorption* by Moos & Clarke (1979).

For remote planets such as Uranus and Neptune, the observations listed in the table cannot, in a strict sense, be regarded as having given identifications of C_2H_6

Table 3.   Observational studies of hydrocarbons in the outer planets and Titan

Investigators	Planet	Observed Wavelength interval	Resolution	Suggested or Identified Hydrocarbons	Abundance (Mixing ratio)	Comments
Gillett et al (1973)	Titan	8~13 μm				suggests strong temperature inversion and existence of at least one or more spectroscopically active component in addition to H_2 and CH_4
Gillett & Forrest (1974)	Saturn	7.5~13.5 μm	$\Delta\lambda/\lambda=0.015$			strong temperature inversion suggests possible emission from C_2H_6 around 12 μm
Ridgway (1974)	Jupiter	750~1300 cm⁻¹	1.3 cm⁻¹	C_2H_6 C_2H_2	4×10^{-4} 8×10^{-5}	first identification of C_2H_6 and C_2H_2 in the planetary atmospheres C_2H_6 (ν_9), C_2H_2 ($\nu_5(R)$)
Combes et al (1974)	Jupiter	11~13.5 μm	1.3 cm⁻¹	C_2H_6 C_2H_2	0.5 cm atm, 0.01 cm atm for $T=250K$; 1.5 cm atm, 0.03 cm atm for $T=200K$	
Gillett & Orton (1975)	Saturn	11.7 μm		C_2H_6		center to limb observation confirms the presence of thermal inversion and supports that 12 μm feature is due to emission from C_2H_6
Gillett (1975)	Titan	7.8~13.3 μm	$\Delta\lambda/\lambda=0.02$	C_2H_6 C_2H_4	2×10^{-3} cm atm	in addition to C_2H_6, evidence is found for emission by C_2H_2 and C_2H_4. tentative assignment to C_2H_4. ($\nu_1(Q)$)
Tokunaga et al (1975)	Saturn	800~850 cm⁻¹		C_2H_6	$C_2H_6(\nu_9)$	first identification of C_2H_6 in Saturn
Aumann & Orton (1975)	Jupiter	12~24 μm	4 cm⁻¹	C_2H_2	$10^{-6\pm0.5}$	C_2H_2 ($\nu_5(Q)$)
Tokunaga et al (1976)	Jupiter	755~850 cm⁻¹		C_2H_6 C_2H_2	3×10^{-5} (3.6 cm atm) $\leqslant7.5\times10^{-8}$ ($\leqslant1.6\times10^{-2}$ cm atm)*	*) not positively detected
Orton & Aumann (1977)	Jupiter	near 750 cm⁻¹	6.34 cm⁻¹	C_2H_2	5×10^{-8}~6×10^{-9}	C_2H_2 (ν_5 (Q, R))
Gillet & Rieke (1977)	Neptune	8~12 μm		C_2H_6	5×10^{-7} (assuming T~150K)	strong temperature inversion. a hump at 12 μm, possibly ascribed to C_2H_6 temperature inversion is weak
Macy & Sinton (1977)	Uranus Neptune			C_2H_6		warm thermal inversion layer, ascribed to C_2H_6 not observed a thermal inversion
Caldwell (1977)	Uranus Titan			C_2H_6 C_2H_2	0.5 cm atm 1.0 cm atm	for 160K assumed. analysis of the data obtained by Gillett et al (1973)

Reference	Planet	Spectral range	Resolution	Species	Abundance / Mixing ratio	Remarks
Encrenaz *et al* (1978)	Jupiter	720~1010 cm⁻¹	1.5 cm⁻¹	C_2H_6, C_2H_2		no evidence for C_2H_4. C_2H_4 is estimated at maximum to be 1/2000 of C_2H_6
Moos & Clarke (1979)	Saturn	7A		C_2H_2	column abundance $<7\times10^{17}\,\mathrm{cm}^{-2}$	detection in *UV* region (~1750A) *IUE* satellite observed in absorption
Tokunaga *et al* (1979)	Jupiter	744~980 cm⁻¹	0.05 cm⁻¹	C_2H_6, C_2H_2, C_2H_4	$<4\times10^{-9}$	peak brightness temperature of C_2H_6 ~145K. from not detecting C_2H_4 (ν_7) band, mixing ratio of C_2H_4 is estimated to be less than 4×10^{-9}
Hanel *et al* (1979a)	Jupiter			$(CH_3)_2CCH_2$ isobutene		speculates 889.7 cm⁻¹ emission feature to be Q-branch of isobutene
Hanel *et al* (1979b)	Jupiter			C_2H_6, C_2H_2		Voyager 1 (IRIS) Voyager 2 (IRIS) abundance ratio of C_2H_6 to C_2H_2 is three times larger in the polar region than at lower latitudes
Macy (1980)	Neptune			C_2H_6, C_2H_2	10^{-6}, 10^{-8}	
Tokunaga *et al* (1980)	Jupiter			C_2H_6		emission intensity at 12μ is 30% weaker at the GRS than at the NTZ or NEB
Tokunaga (1980)	Titan			C_2H_2		identification (referenced as private communication in Capone *et al*, 1980)
Hanel *et al* (1981)	Saturn, Titan			C_2H_6, C_2H_2, C_3H_4 (methylacetylene), C_3H_8 (propane)	5×10^{-6}, 2×10^{-8}	Voyager 1(IRIS) Saturn Saturn & Titan, tentative identification C_3H_4 (ν_9) C_3H_8 (ν_{26})
Broadfoot (1981)	Jupiter	500–1700A		C_2H_6	2.5×10^{-6}	Voyager 2 (UVS) artifitial star occultation of αLeo. at the height level where CH_4 mixing ratio is 2.5×10^{-5}.
Bjoraker *et al* (1981)	Saturn	2800–6000 cm⁻¹	0.5 cm⁻¹	C_2H_6		3.0±1.4 cm-amagat. detect in absorption (3μ). mixing ratio profile ~2.3×10^{-7} exp (z/90), where z(km) is measured from cloud top.
Maguire *et al* (1981)	Titan			C_3H_8, C_3H_4	2×10^{-5}, 3×10^{-8}	Voyager 1 (IRIS) ν_7, ν_{15}, ν_{16}, ν_{21} ν_9, ν_{10}
Kunde *et al* (1981)	Titan			C_4H_2		Voyager 1 (IRIS) ν_8, ν_9
Hanel *et al* (1982)	Saturn, Titan					Voyager 2 (IRIS) spectra similar to those obtained by Voyager 1. inferior *S/N* ratio to Voyager 1.
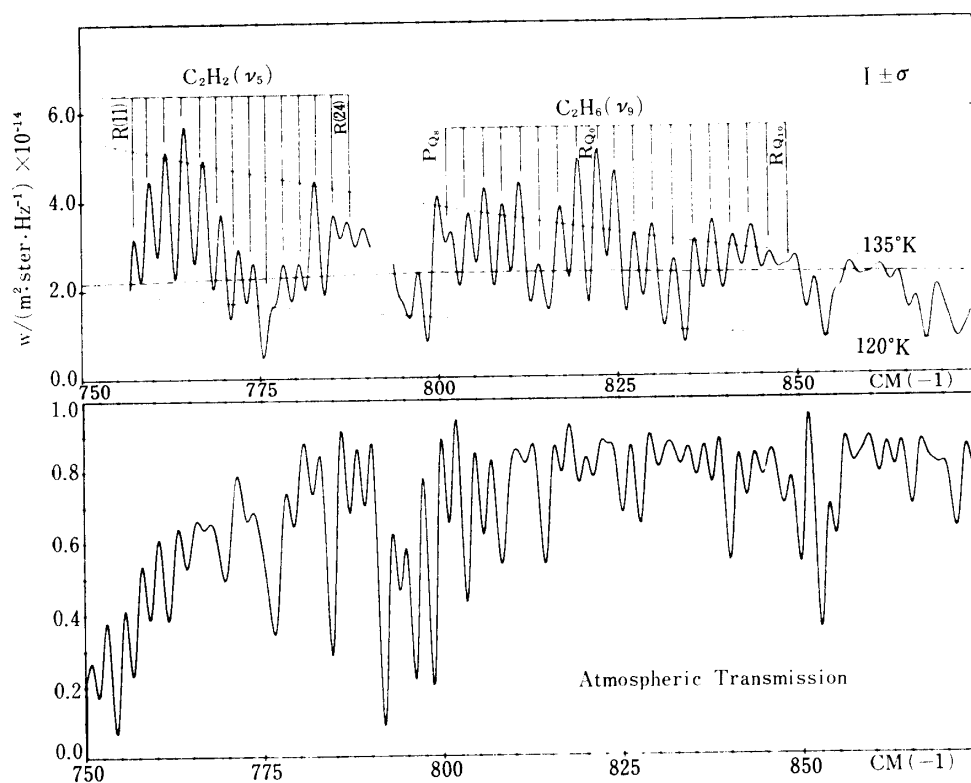
Fig. 5.   Thermal emission spectrum of Jupiter corrected for absorption in the earth's atmosphere. The dashed line is the predicted form of the H_2 continuum. From Ridgway (1974).
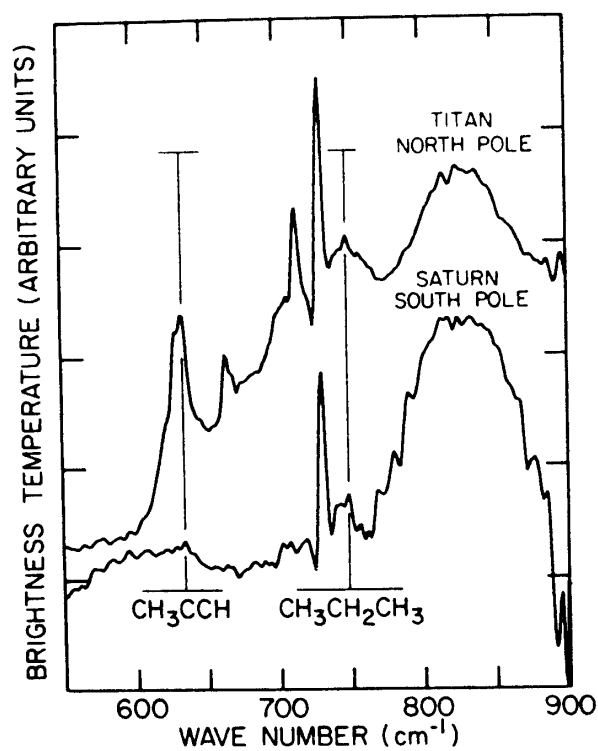
Fig. 6.   Tentative identification of C_3H_4 and C_3H_8 features on Saturn and Titan. From Hanel *et al* (1981).

and C_2H_2, because of the insufficient spectral resolutions. They, however, strongly suggest (particularly for Neptune) that the emission peaks observed arise from the above hydrocarbons because a spectral similarity exists in the infrared brightness profiles *vs* wavelength between these remote planets and the objects closer to the sun, as Jupiter, Saturn and Titan.

Among the mixing ratios listed in the table, there are considerable discrepancies (ranging from one to two orders of magnitudes). This is mostly due to the reason that an emission intensity is rather sensitively dependent on the temperature of the layer whence radiation comes. In the outer planets, the temperature in such an altitude region (upper stratosphere and mesosphere) is still most ambiguous.

Until quite recently, all the hydrocarbons observed or discussed were those pertaining to C_2-compounds. However, identifications, though tentative, have been newly given for the C_3-compounds as methylacetylene (C_3H_4) and propane (C_3H_8) by the latest Saturn encounter of Voyager 1 (Hanel *et al*, 1981, see Fig. 6). This would be an encouraging result for the present study that attempts to make clear the formation routes of numerous heavier hydrocarbons other than C_2-compounds in the outer planets. But we must also keep in mind that these hydrocarbons appear to distribute rather differently planet by planet in not only quantitative but also qualitative ways, in spite of the apparently (compositionally) similar environments of
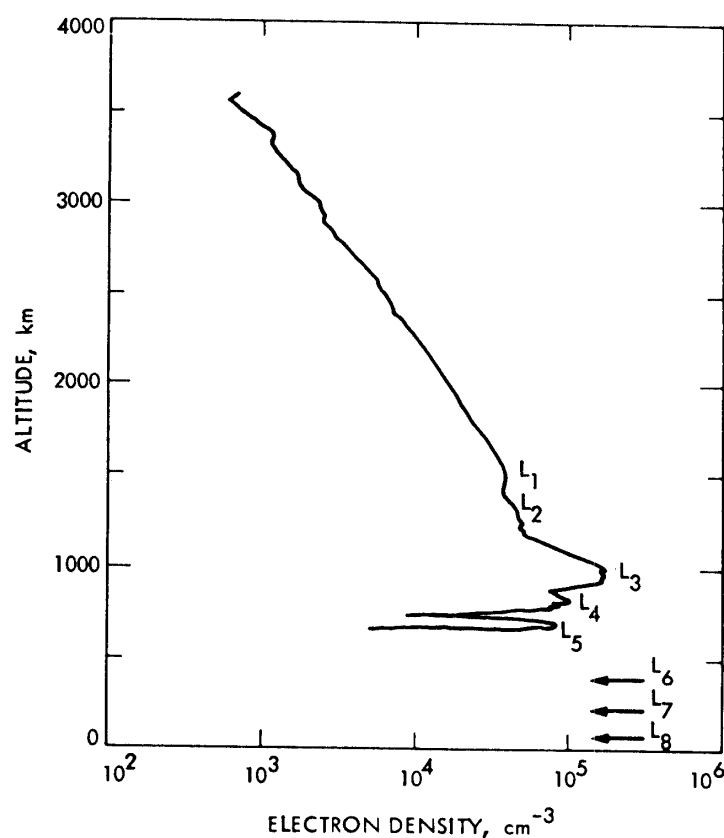
Fig. 7, Electron density in the Jovian ionosphere obtained from Pioneer 11 taken during entry ($\Phi=79°$S, $\chi=93°$). From Fjeldbo *et al* (1976).

Table 4.   Radio Occultation Experiments (relevant to Ionosphere) by Space Missions

Investigators	Missions	Planets	Observed Sites	Results
Kliore et al (1974) Fjeldbo et al (1975)	Pioneer 10	Jupiter	entry $A=26°N^{1)}$ $\chi=81^{°2)}$ exit $A=58°N$ $\chi=95°$	$H^{3)}\sim975$ km $H\sim800$ km $n_p^{4)}\sim3\times10^5/cm^3$ assuming H^+, $T_p^{5)}\sim900\pm400K$ detectable ionosphere extends over an altitude range of more than 3000 km
Kliore et al (1975b)	Pioneer 10	Io	entry $\chi=81°$ exit night	$T_p\sim400K$ for Na^+ 500K for N_2^+ $n_p\sim6\times10^4/cm^3$ at an altitude of 100 km $T_p\sim130K$ for Na^+ 160K for N_2^+ $n_p\sim9\times10^3/cm^3$ at an altitude of 50 km
Fjeldbo et al (1976)	Pioneer 11	Jupiter	entry $A=79°S$ $\chi=93°$ exit $A=20°N$ $\chi=79.1°$	$H\sim540\pm60$ km $T_p\sim850\pm100K$ for H^+ $n_p\sim1.5\times10^5/cm^3$ not available
Eshleman et al (1979a)	Voyager 1	Jupiter	entry $A=12°S$ $\chi=82°$ exit $A=1°N$ $\chi=98°$	$H\sim590$, 950 km, below and above 3500 km, respectively $T_p\sim1100K$ for H^+ $n_p\sim2.2\times10^5/cm^3$ $n_p\sim1.8\times10^4/cm^3$
Eshleman et al (1979b)	Voyager 2	Jupiter	entry $A=66.7°S$ $\chi=87.9°$ (evening) exit $A=50.1°S$ $\chi=92.4°$ (morning)	$H\sim1040$ km³ $T_p\sim1600K$ $n_p\sim2.2\times10^5/cm^3$ $H\sim880$ km $T_p\sim1200K$ no peak in electron density profile
Kliore et al (1980a, b)	Pioneer 11	Saturn	entry $A=11.6°S$ $\chi=89.2°$ exit $A=9.7°S$ $\chi=90.9°$	$T_p\sim1150K$ for H^+ $n_p\sim1.1\times10^4/cm^3$ not available
Tyler et al (1981)	Voyager 1	Saturn	entry $A=73.0°\sim79.5°N$ $\chi=89°$ exit	$H\sim560$ km $n_p\sim2.3\times10^4/cm^3$ H is markedly less than the corresponding interpretation of Pioneer 11 (Saturn) not available
Tyler et al (1982)	Voyager 2	Saturn	exit $A=31°S$ $\chi=93°$ (predawn) entry $A=36.5°N$ $\chi=87°$ (evening terminator)	$H\sim1100$ km at upper portions $H\sim260$ km at lower portions $n_p\sim1.7\times10^4/cm^3$ $H\sim1000$ km $n_p\sim6.4\times10^3/cm^3$

1) geocentric latitude, A
2) solar zenith angle, χ
3) topside plasma scale height above main peak, $H=k(T_e+T_i)/mg$
4) electron density at the peak, n_p
5) plasma temperature, $T_p=(T_e+T_i)/2$
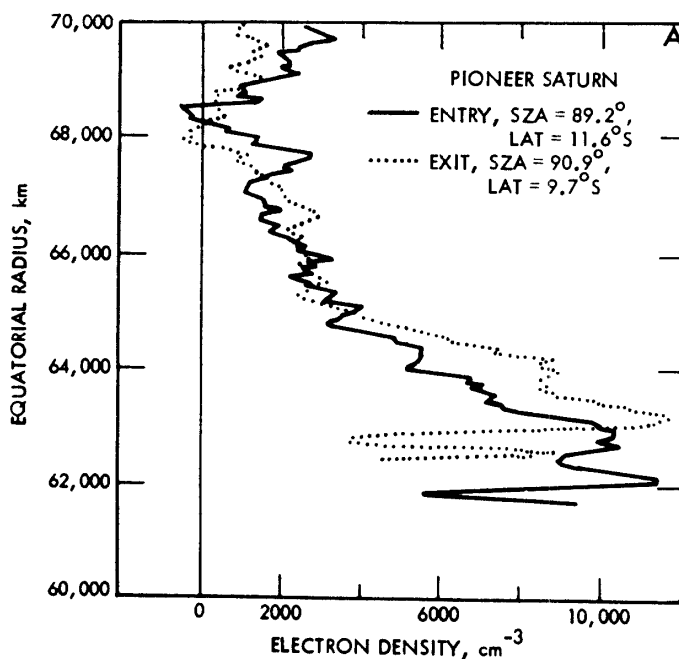
Fig. 8. Electron density in the Saturnian ionosphere. Solid curve is a profile produced from the closed loop data taken during entry. From Kliore *et al* (1980b).

the planetary atmospheres (see, Table 3). Currently we have no idea of what makes them so different. Presumably several factors intrinsic to each planet (which eventually have origins in its formation history) may be acting on the photochemical processes which are universally expected for those planets under the solar radiation.

All the observational knowledge on the ionospheres of the outer planets has been derived from the deep-space missions of Pioneers and Voyagers. A spacecraft can, as it passes behind a planet, convey useful information of the ionosphere to us, if it is possible to measure the slightly changing Doppler shift in frequency of the radio signal transmitted between the earth and the spacecraft, which is associated with the deflection of its ray path caused by the intervening ionospheric electrons. Table 4 summarizes the results obtained from such *radio occultation experiments*.

A remarkable feature commonly found in them is the existence of ionosphere over a greaty extended altitude range (Fig. 7), which was unexpected in the theoretical studies of those ionospheres *prior* to the Pioneer missions. This suggests that the underlying neutral atmosphere may be substantially heated by some internal mechanisms intrinsic to the planet of which we do not know exactly or by strong interaction with the upper-lying plasmasphere. Also unexpected is the much lower peak electron density found in Saturn's ionosphere by Pioneer 11, when compared with that in Jupiter (Fig. 8). Although a ring shadowing effect (screening of sunlight by rings) has been introduced for explanation, it would not promise enough success since the subsequent radio occultation experiment by Voyager 1 has also derived similar poor ionospheric feature in the *polar* region.

Chapter II. PHOTOPROCESSES

Molecules dissociate more or less under the action of the solar ultraviolet radiation. It has been pointed out in the previous chapter that numerous hydrocarbons are possibly being created in the upper atmospheres of the outer major planets through a variety of photo- and chemical processes. These processes would, however, immediately stop operating as soon as the continuous supply of energy comes to its end. This makes us visualize the two aspects of the same process performed by the solar ultraviolet radiation on atmosphere.

One is the role of supplying free radicals through dissociation of molecules. Very often, these free radicals, together with some kind of metastable-excited molecular species, are quite efficient to form molecular compounds of higher complexity by mutual combinations—of such radical combination processes will be given a full detail in the next chapter.

The other aspect is concurrent with the first event but opposing in effect. Splitting of larger stable molecules that have already been formed, also results from the same ultraviolet absorption. It is known that a molecule, by irradiation, dissociates in various ways, for instance, '(atomic) hydrogen elimination' such as $C_3H_8 \xrightarrow{h\nu} H + C_3H_7$, 'radical decomposition' such as $C_3H_8 \xrightarrow{h\nu} CH_3 + C_2H_5$, '(molecular) hydrogen elimination' such as $C_3H_8 \xrightarrow{h\nu} H_2 + C_3H_6$, and 'molecular decomposition' such as $C_3H_8 \xrightarrow{h\nu} CH_4 + C_2H_4$. The first two modes of dissociation, and also the simple excitation to fairly long-lived state, usually contribute to producing higher hydrocarbons, and the last two modes contribute to returning a molecule to a pair of smaller hydrocarbon molecules, respectively.

To incorporate the photoprocesses into calculation, we need knowledge on how molecule dissociates by the UV insolation and at the same time on how the absorption cross section varies over the important wavelength regions of the solar UV spectra. The required information is not always available, particularly for those molecules with a high degree of unsaturation (C_3H_2, C_4H_2, C_4H_4, etc.). Furthermore, the situation becomes worse for free radicals and there are only a limited number of species of which the information of oscillator strength, dissociation mode and so forth are all precisely known. Although most radicals have a shorter lifetime for chemical reaction rather than for photodissociation in the substantial parts of the atmospheres, it should not necessarily be excluded *a priori* from consideration.

In what follows, we describe the photophysical and photochemical knowledge obtained with those hydrocarbon molecules whose carbon atoms are, in number, four or less: absorption intensities, the spectral features, the ;states responsible for absorption, dissociation modes, the yields of products in specific processes, the wavelength dependences etc.. These descriptions contain, for future reference, molecules which will not be included in the actual calculations and discussions more than that is necessary for the purpose. The author, however, believes that it would be worthy to compile, at this point of time, our knowledge of a series of those mole-

cules which may stem from methane photochemistry. Currently there are no available bibliographies arranged for that purpose. The impression is strengthened when we take into account the recent successive discoveries of hydrocarbons in the major planets by the earth-based observations and by the deep-space missions, and also
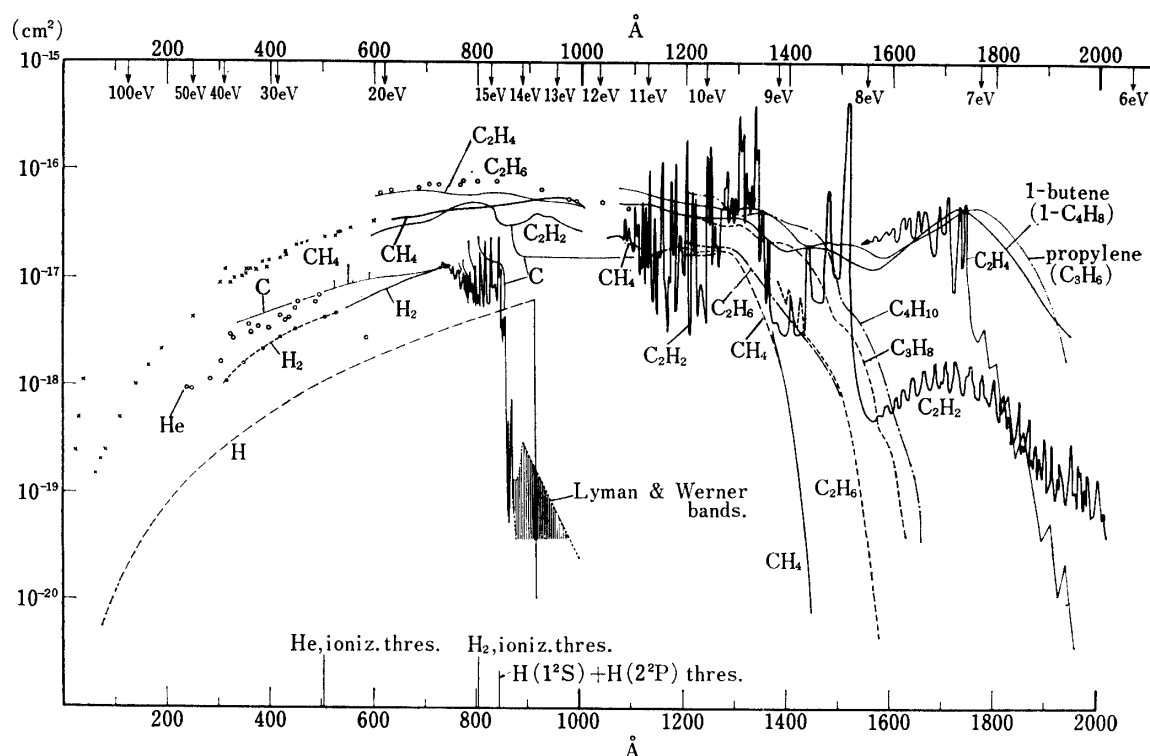
Fig. 9. Photoabsorption cross section of hydrocarbons (I).

H:	Burgess (1965)		
He:	Lee & Weisler (1955)	(∘ c ∘)	
C:	Burke & Taylor (1979)		
H_2:	Cook & Ching (1965)		$550 < \lambda < 1050$A
	Samson & Cairns (1965)	(———)	
CH_4:	Watanabe *et al* (1953)	(------)	$\lambda < 1300$A
	Okabe & Becker (1963)		$\lambda > 1200$A
	Metzger & Cook (1964)		$\lambda < 1000$A
	Rustgi(1964)	(× × ×)	
	Mount *et al* (1977)		$1400 < \lambda < 1850$A
C_2H_2:	Nakayama & Watanabe (1964)		$1050 < \lambda < 2000$A
	Metzger & Cook (1964)		$\lambda < 1000$A
C_2H_4:	Zelikoff & Watanabe (1953)		$\lambda > 1550$A
	Metzger & Cook (1964)		$\lambda < 1000$A
C_2H_6:	Schoen (1962)	(∘ ∘ ∘)	$\lambda < 1200$A
	Okabe & Becker (1963)	(—·—·—)	$\lambda < 1500$A
	Mount & Moos (1978)	(———)	$\lambda > 1400$A
C_3H_6 (propylene):	Samson *et al* (1962)		
C_3H_8:	Okabe & Becker (1963)		
C_4H_2 (diacetylene):	Georgieff & Richard (1958)		
1-C_4H_8 (1-butene):	Samson *et al* (1962)		
C_4H_{10}:	Okabe & Becker (1963)		
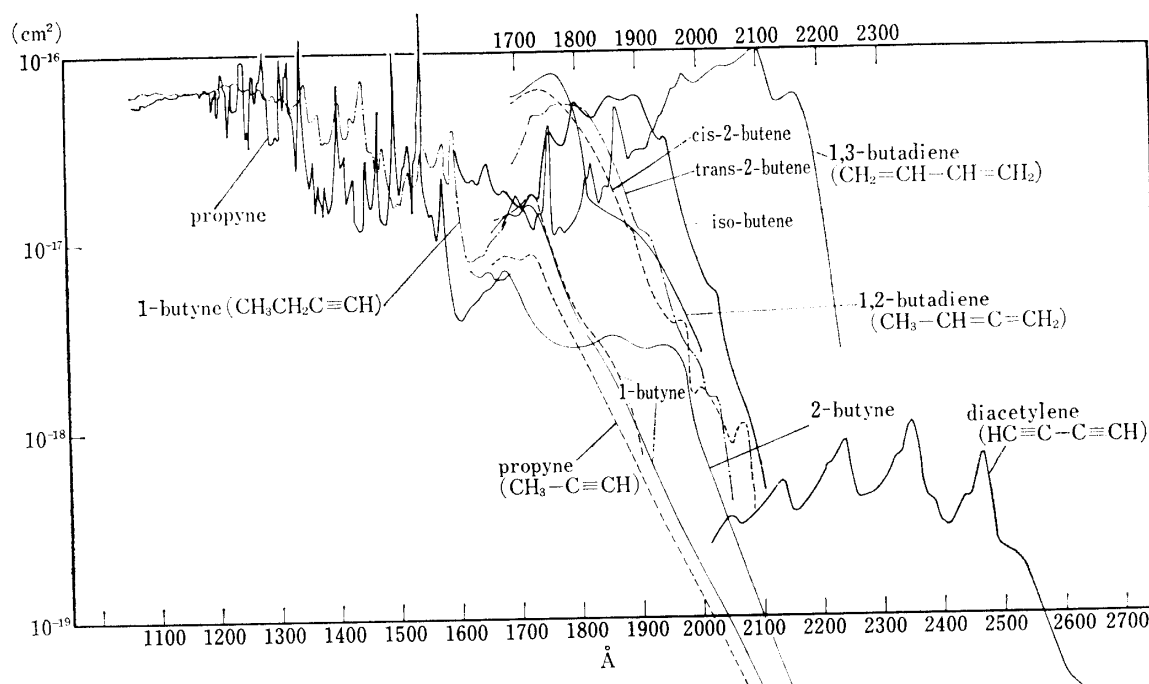
Fig. 10.   Photoabsorption cross section of hydrocarbons (II).

C_3H_4 (propyne):   Nakayama & Watanabe (1964) $\lambda < 1700A$
                        Hamai & Hirayama (1979)   (— — —) $\lambda > 1650A$
1-C_4H_6 (1-butyne):   Nakayama & Watanabe (1964) (— · — ·)
                        Jones & Taylor (1955)   (— — — —) $\lambda < 1900A$
                        Hamai & Hirayama (1979) $1650 < \lambda < 2100A$
2-C_4H_6 (2-butyne):   Hamai & Hirayama (1979)
$1,3$-C_4H_6 (1,3-butadiene):   Jones & Taylor (1955)
$1,2$-C_4H_6 (1,2-butadiene):   Jones & Taylor (1955)
i-C_4H_8 (isobutene):   Gary & Pickett (1954)
cis-2-C_4H_8:   Jones & Taylor (1955)
$trans$-2-C_4H_8:   Jones & Taylor (1955)
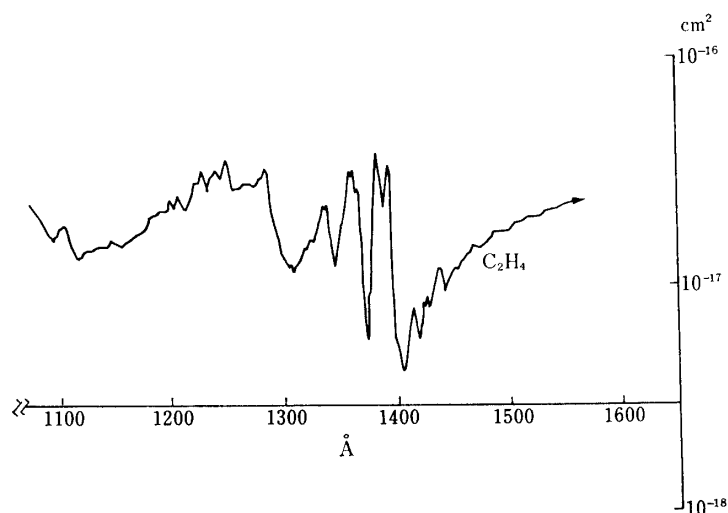
Fig. 11.   Photoabsorption cross section of hydrocarbons (III).
C_2H_4: Zelikoff & Watanabe (1953) $1100 < \lambda < 1550A$

when we consider the present states of the theoretical studies of methane photo-chemistry in those planets.

The descriptions wll be given first of H_2 and next of stable hydrocarbons in the sequence of the saturated to the unsaturated and the smaller to the larger species, and cyclocompounds, and finally of free radicals (where those of atomic species such as H, He and C are not included in this chapter since ionization is *practically* the only one possible event for UV radiation). Fig. 9 to Fig. 11 illustrate the available cross secton data of hydrocarbons of our interest (they have been reproduced from the original forms represented in a variety of different units).

2.1 Hydrogen (H_2)

H_2 is one of the most transparent gases to the ultraviolet light and the photo-absorption starts only at the extreme ultraviolet (EUV), where H_2^+ is the major product. A very minor fraction of the absorption results in the production of atomic species like H and H^+. For these minor species, it is necessary for the quantum yield to be evaluated with great caution, since they will play an important role in the successive reactions.

Free hydrogen is produced by three mechanisms:

i) 1050—850A: through an excitation to the Lyman band system followed by radiative transition to the vibrational continuum $(v'' > 14)$ of the ground state of H_2. The absorption spectrum shows a fine band structure. Since the solar radiation is more intense in the lines than in the continuum around these wavelength regions, the effect of the band absorption would be much more increased, if it should happen that vibro-rotational lines characteristic to the band system *did* coincide with one of the strong solar lines. Contribution from the Werner band system is negligibly small.

ii) 860–770A: through an excitation to the Hopfield band system.

iii) $\lambda < 685A$: through a dissociative ionization $(H_2 \xrightarrow{h\nu} H + H^+)$.

Ratio of the yield to that of $H_2 \xrightarrow{h\nu} H_2^+$, is 0.02, which is nearly independent of wavelength.

2.2 Methane (CH_4)

The most complete arguments must be devoted to this compound, since our article intends to have an insight into the physico-chemical processes prevailing over the production of various hydrocarbon molecules. All the carbon atoms as a constituent material of hydrocarbons originate from methane eventually.

Absorption

In general, saturated hydrocarbons $(CH_4, C_2H_6, C_3H_8, C_4H_{10})$ show appreciable absorption only at the wavelengths below $1400 \sim 1700A$—It is known that there is a systematic shift of the absorption edge towards the longer wavelength with increase of molecular size.

The absorption coefficient for CH_4 was measured by Watanabe *et al* (1953). Specifically to this molecule, the very small absorption underlying beyond the edge (around 1400A) must be taken into account in the present work. The required

data are taken from the more recent measurements (Mount *et al*, 1977 and Mount & Moos, 1978), where the absorption coefficient has been obtained up to the order of 10^{-23} cm^2 (close to that of Rayleigh scattering).

In the wavelength region important to ionization, data have been taken from Metzger & Cook (1964) and also from the Hudson's review (1971).

Photolysis

Lyman α (1216A) occupies about 80% as much as the solar UV photons which are capable of dissociating or ionizing CH_4. Hence, photolysis experiments made at Ly α would be the most adequate to provide data relevant to the present work. This is usually substituted by the experiment at Kr resonance line (1236A), very close to Ly α.

The experimental works performed on CH_4 can be traced back to the 1930's, when it was already known that the species like H_2, C_2H_6, C_3H_8 were the main products and to a less extent the species like C_2H_2, C_2H_4, C_3H_4, C_3H_6, C_4H_{10}. It was, however, not until the 1960's that the principal route of decomposition was clearly established as $CH_4 \longrightarrow CH_2 + H_2$.

Mahan & Mandal (1962) first demonstrated that the dominant primary process at 1236A is a molecular elimination ($CH_4 \longrightarrow CH_2 + H_2$). Since then, extensive studies have been done from a variety of aspects: Magee (1963), Ausloos *et al* (1964), Braun *et al* (1966, 1967), Golden & Ausloos (1967), Laufer & McNesby (1968), Rebbert *et al* (1971a), Welch & Judge (1972) and Rebbert & Ausloos (1972/1973). For example, Ausloos *et al* (1964) found at 1236A that,

$$CH_4 \longrightarrow CH_2 + H_2 \qquad 0.85$$
$$\longrightarrow CH_3 + H \qquad 0.15$$
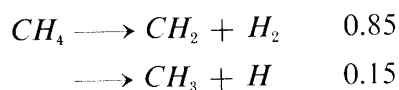
(The latter had once been suggested to be a dominant primary process.) and Rebbert & Ausloos (1972/73) obtained for minor channels,

$$CH_4 \longrightarrow C(^1D) + H_2 + H_2 \qquad 4 \times 10^{-4}$$
$$\longrightarrow CH(^2\Pi) + H + H_2 \qquad 0.059.$$
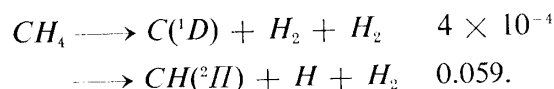
With much more increase of photon energy, secondary decompositions of the fragments like CH_2 and CH_3 produced by the primary decompositions become possible due to the excess energies contained in those fragments, although the processes have not been taken into account in our calculations: the reason would become evident in the course of developing arguments over the subsequent chemical reactions. It is noted that, because of the special importance it plays, CH_2, the major decomposition product of methane, is created in a singlet state (b^1B_1).

As for an ionization, an equal probability has been assigned to the following processes (Rebbert & Ausloos, 1973)

$$CH_4 \longrightarrow CH_4^+$$
$$\longrightarrow CH_3^+ + H .$$
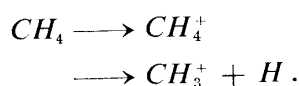
2.3 Ethane (C_2H_6)

Absorption

Absorption coefficient has been taken from Okabe & Becker (1963) and Mount & Moos (1978) at the energies below the ionization threshold while above it from Metzger & Cook (1964) and Hudson's review (1971).

Photolysis

C_2H_6 is one of the molecules most extensively studied in the past photolysis experiments (C_2H_2 is another such molecule). Okabe & McNesby (1961) photolyzed C_2H_6 at 1470 and 1295A (*Xe* lines) and suggested the following molecular elimination process,

$$C_2H_6 \longrightarrow CH_3CH(\text{ethylidene}) + H_2$$
$$C_2H_4 + H_2$$
$$CH_4 + CH_2 .$$
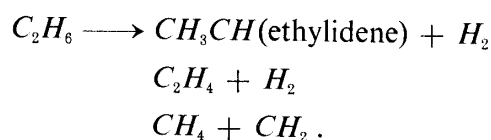
The resuts, confirmed later by Laufer & Sturm (1964), are in contrast to those obtained from a photosensitized experiment in which C_2H_6 is almost completely led to radical decomposition, $C_2H_5 + H$ (Back, 1959)—thus it would be worth while to note that a photosensitized experiment can not always correctly take the place of a photolysis experiment, for the purpose of deducing reliable information on photodissociation.

A number of works have followed not only at 1470A but also at the shorter wavelengths and the dissociation mechanisms have been clarified more fully: Hampson *et al* (1964), Hampson & McNesby (1965a, b), Laufer & McNesby (1965a), Akimoto *et al* (1965), Von Bünau *et al* (1969), Ogata *et al* (1971), and Lias *et al* (1970). It was shown that C_2H_4, major primary decomposition product, retains energy sufficient for the secondary decomposition so that a substantial portion of it tends to a unimolecular decomposition ($\longrightarrow C_2H_2 + H_2$) in the low pressure region. Moreover, an atomic hydrogen elimination, $H + H + C_2H_4$ and a radical decomposition, $CH_3 + CH_3$ were proven to exist as minor events. These product yields show rather steep increases with increasing photon energy.

2.4 Propane (C_3H_8)

The absorption of propane starts in the neighborhood of 1600A and it was measured by Okabe & Becker (1963) in the *VUV* region and by Koch & Skibowski (1971) in the *EUV* region.

Photolysis

Introduction of some radical scavengers or deuterated molecules into the system is a powerful tool in photolysis experiment. However, as the molecular dimension increases, it often becomes difficult to obtain reliable results. This is due to the increasing number of modes open to the primary and secondary decompositions.

The first reliable study was made at 1470 and 1236A by Okabe & McNesby (1962b), who presented the following molecular detachments as the major processes

$$C_3H_8 \longrightarrow CH_3CCH_3 \text{ (isopropylidene[*]) } + H_2$$

$$CHCH_2CH_3 \text{ (propylidene[*]) } + H_2$$

$$CH_2CHCH_3 \text{ (propylene) } + H_2$$

$$\longrightarrow CH_3CH \text{ (ethylidene[*]) } + CH_4$$

$$CH_2CH_2 \text{ (ethylene) } + CH_4$$
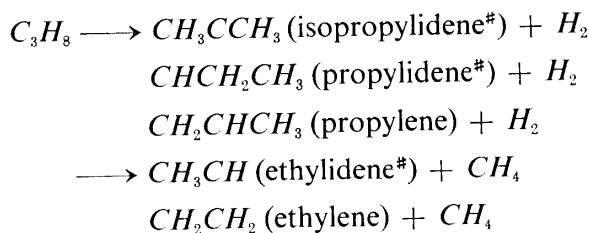
and additional radical decompositions

$$C_3H_8 \longrightarrow C_3H_7 + H$$
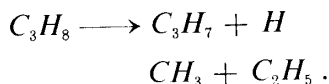
$$CH_3 + C_2H_5 .$$

Ausloos & Lias (1966a) showed at 1236A that the internally excited C_3H_6, C_2H_4, C_2H_5, C_3H_7 species formed in these primary processes decompose to form H, CH_3, C_2H_2, C_2H_3 and C_2H_4 unless they are collisionally stabilized. Ausloos & Lias (1968a) also experimented at higher energies, 1067–1048A (which is about 0.5 eV above the ionization energy) and showed that although the modes of decomposition are unchanged, the free radical producing processes occur with high probability.

One other radical process proven to occur is the formation of allyl radical (C_3H_5) (Voraschek & Koob, 1970). Although the actual route is not certain, more than one precursors are probably related to it.

CH_2, ethylidene radical—which plays a peculiar role in our hydrocarbon chemistry owing to the small energy separation between the excited singlet and the ground triplet states and also owing to their quite different natures in reaction to each other—has been studied to clarify the energy partitioning between the products observed in the reaction $C_3H_8 \xrightarrow{h\nu} CH_2 + C_2H_6$ (Dhingra & Koob, 1970, and Koob, 1972). They concluded that the radical is probably produced in a singlet, not in a triplet state, and most likely in $^1B_1$ (first excited state in the singlet system).

All those experiments described above are more or less qualitative in nature and not necessarily useful directly to the present purpose.

Voraschek & Koob (1973) estimated the primary yields at 1236A,

$$
\begin{aligned}
C_3H_8 \longrightarrow C_3H_6 + H_2 \quad &0.42 \\
C_2H_4 + CH_4 \quad &0.47 \\
CH_2 + C_2H_6 \quad &0.09,
\end{aligned}
$$
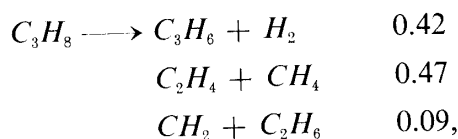
and they further analyzed the secondary decomposition processes of these primary fragments, obtaining the results as follows,

$$
\begin{aligned}
C_3H_8 \longrightarrow C_3H_6 + H_2 \quad &0.11 - x + y \\
C_3H_6 + H + H \quad &0.15
\end{aligned}
$$
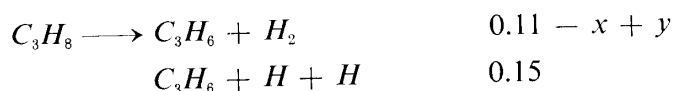
[#] These radicals may or may not isomerize, respectively, to propylene and ethylene in the actual photolytic act. However, we have, in our calculations, made an implicit assumption that the isomerizations to stable molecules are instantaneous. The one reason is to simplify our calculations and the other is for the fact that the fragments produced in the photolysis very frequently contain enough internal energy capable of going across the isomerization barrier.

$$C_3H_4 + H_2 + H_2 \qquad x$$
$$C_3H_5 + H_2 + H \qquad 0.068$$
$$C_2H_2 + H_2 + CH_4 \qquad 0.092$$
$$C_2H_3 + H + CH_4 \qquad 0.006$$
$$C_2H_4 + CH_4 \qquad 0.125 - y$$
$$C_2H_4 + CH_3 + H \qquad 0.339$$
$$CH_2 + C_2H_6 \qquad 0.086,$$

where y is the yield of the path, $C_3H_8 \longrightarrow CH_4 + C_2H_4^* \longrightarrow CH_4 + C_2H_2 + H_2$ and is smaller than 0.092.

As for ionization, the quantum yields of the product ions ($C_3H_8^+$, $C_3H_7^+$ and $C_2H_4^+$) and the related ionic chemistries were investigated by Ausloos & Lias (1968a) and Rebbert *et al* (1971b).

2.5 Butanes (n-C_4H_{10}, i-C_4H_{10})
Absorption

The absorption features do not essentially differ between n- and i-butane. It starts in the neighborhood of 1700A, as measured by Okabe & Becker (1963) and Lombos *et al* (1967). In the *EUV* region it was measured by Koch & Skibowski (1971).

Photolysis (n-C_4H_{10})

Sauer & Dorfman (1961) indicated that a molecular detachment is the major primary process at 1470A

$$n\text{-}C_4H_{10} \longrightarrow C_4H_8 + H_2$$
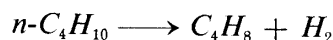
and suggested that an atomic hydrogen was also produced, possibly by the process

$$n\text{-}C_4H_{10} \longrightarrow C_4H_8 + H + H .$$

Any other primary process, as well as the isomeric identification of the above products, namely, butenes, were not established.

A more quantitative result was obtained by Okabe & Becker (1963), who postulated several probable modes of molecular and radical decomposition and assessed the relative yields as

	Xe(1470)	*Kr*(1236)
$n\text{-}C_4H_{10} \longrightarrow C_4H_8 + H_2$	0.41	0.18
$2C_2H_4 + 2H$	0.12	0.20
$CH_4 + C_3H_6$ (propylene)	0.01	0.03
$CH_3 + H + C_3H_6$	0.07	0.07
$C_2H_6 + C_2H_4$	0.02	0
$C_2H_6 + C_2H_2 + H_2$	0.06	0.15
$n\text{-}C_4H_{10} \longrightarrow CH_3 + C_3H_7$	$\gtrsim 0.24$	$\gtrsim 0.27$
$C_2H_5 + C_2H_5$	$\gtrsim 0.07$	$\gtrsim 0.10,$

where the butenes produced in the primary event consist isomerically of 1- and 2-butenes (negligible amount of i-butene).

With increasing photon energy free radical production becomes more important, similar to the case of C_3H_8, as demonstrated by Ausloos & Lias (1968a). They investigated photolytic mechanism at the wavelengths 1067—1048A, which is about 1.0eV above the ionization energy of n-C_4H_{10}, suggesting the possibilities of another decomposition mode

$$n\text{-}C_4H_{10} \longrightarrow H + C_2H_4 + C_2H_5$$
$$CH_3 + C_2H_4 + CH_3 .$$
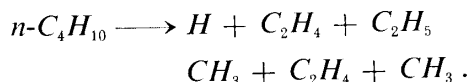
These dissociative processes, however, account for only about 40% of the superexcited n-butane molecules (the quantum yield of the superexcited n-C_4H_{10} is 0.68 and the rest, 0.32 is the yield leading to ionization).

At such a short wavelength, it is not necessarily an easy matter, to not only postulate every plausible decomposition route but also to evaluate simultaneously the yields, because a substantial portion of the fragments produced in the primary act would tend to further decompositions and also because radical processes would be relatively more enhanced compared with molecular processes. However, so far as an application to our present calculation is concerned, this kind of uncertainty does not cause any practical difficulty by virtue of the spectral characteristics of the solar UV light.

Ogata *et al* (1971), at 1470A, argued exclusively the processes in which C_2H_4— abundant product next to C_4H_8 at this wavelength—takes part at any (primary or secondary) stage of decomposition, evaluating the lifetime of an excited ethylene and at the same time the relative yields of these processes.

The first quantitative determination of quantum yield was contrived by Jackson & Lias (1974), introducing more efficient radical scavenger HI into the system of deuterated n-butane (n-C_4D_{10}). The results appear to be a significant revision o' Okabe & Becker (1963). In fact, while hydrogen elimination $H_2 + C_4H_8$ is the major primary process as ever, it differs from Okabe & Becker (1963) in that the yield is relatively much more enhanced, the radical decomposition $CH_3 + C_3H_7$ is greatly suppressed and the decomposition route into $2C_2H_4 + 2H$ is not a favorable one and also in that the secondary fragmentations are pursued, with the branching yields estimated as

	1470	1236A
$n\text{-}C_4D_{10} \longrightarrow CD_4 + C_3D_6$	0.006	0.040
$\longrightarrow C_3D_8 + CD_2$	0.0036	0.018
$\longrightarrow C_2D_6 + C_2D_4$ (pressure independent)	0.12	0.20
$\searrow\longrightarrow CD_3 + CD_3$	0.021	0.040
$\longrightarrow CD_3 + C_3D_7^* \xrightarrow{M}$ stabilize	0.0078	0.013
$\searrow\longrightarrow CD_3 + C_2D_4$	0.021	0.055

$$\longrightarrow C_2D_5 + C_2D_5^* \longrightarrow C_2D_5 + D + C_2D_4 \qquad 0.10 \qquad 0.14$$

$$\longrightarrow D + C_4D_9^* \longrightarrow D + C_3D_6 + CD_3 \qquad 0.038 \qquad 0.092$$

$$\longrightarrow D_2 + C_4D_8^* \xrightarrow{M} \text{stabilize (1- or 2-butenes)} \quad 0.656 \qquad 0.268$$

$$\searrow \longrightarrow C_3D_5 + CD_3 \qquad 0.023 \qquad 0.050$$

$$\searrow \longrightarrow C_2D_3 + C_2D_5 \qquad 0.021 \qquad 0.052$$

$$\text{total} \quad 1.02 \qquad 0.97$$

Their major conclusions are; the quantum yield of the process $(C_4D_{10} \rightarrow C_4D_8 + D_2)$ diminishes from 0.70 to 0.37 when the photon energy increases from 1470 to 1236A; relative overall importance of direct $C–C$ bond cleavage, alkane elimination, and hydrogen atom elimination do not significantly change as a function of energy; processes involving breakage of the 2, 3 $C–C$ bond strongly predominate over processes involving the 1, 2 $C–C$ bond at both energies.

Photolysis $(i\text{-}C_4H_{10})$

Okabe & Becker (1962) postulated the following primary processes at 1470 and 1236A,

$$i\text{-}C_4H_{10} \longrightarrow (CH_3)_2CHCH \text{ (isobutylidene)}[\#] + H_2 \qquad \Phi_1$$

$$(CH_3)_2C{=}CH_2(i\text{-}C_4H_8) + H_2 \qquad \Phi_2$$

$$(CH_3)_2CHCH_2 \text{ (isobutyl)} + H \qquad \Phi_3$$

$$(CH_3)_3C(t\text{-butyl}) + H \qquad \Phi_4$$

$$CH_4 + CH_3CCH_3 \text{ (propylidene)} \qquad \Phi_5$$

$$CH_4 + C_3H_6 \text{ (propylene)} \qquad \Phi_6$$

$$CH_3 + (CH_3)_2CH \text{ (isopropyl)} \qquad \Phi_7$$

$$2CH_3 + C_2H_4 \qquad \Phi_8$$
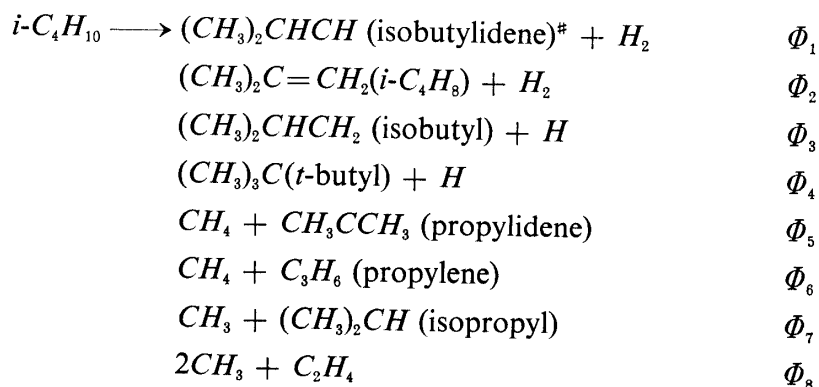
and estimated the yields as

$$\Phi_2/\Phi_1 \sim 1.7, \quad \Phi_1 + \Phi_2 \simeq \Phi_3 + \Phi_4, \quad \Phi_3 \simeq 8\Phi_4, \quad \Phi_2 > \Phi_1 \quad \text{and} \quad \Phi_5 \simeq \Phi_6 \quad \text{at 1470A}$$

and

$$\Phi_1 > \Phi_2 \quad \text{and} \quad \Phi_5 \simeq \Phi_6 \qquad \text{at 1236A.}$$

This indicates that considerable hydrogens are produced by an atomic process, in contrast to the case of $n\text{-}C_4H_{10}$.

Analogous experiment was performed at 1470 and 1236A by Lias & Ausloos (1968) in which $i\text{-}C_4D_{10}$ was photolyzed in the presence of H_2S. They confirmed most of the reaction paths postulated by Okabe & Becker (1962) and also the occurrence of the following process by observing C_3D_8

[#] It was shown that almost all the isobutylidene formed in the primary carbene elimination iso-merizes to *i*-butene (~95%) and that a very minor fraction of it, by intramolecular process, cyclizes to *MCP* (methylcyclopropane) and/or further to various butenes (1- and 2-butenes), (Tschuikow-Roux & McNesby, 1966).

$$i\text{-}C_4D_{10} \longrightarrow C_3D_8 + CD_2 \qquad \Phi_9$$
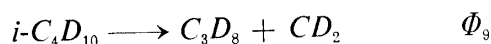
and gave an estimate, $\Phi_9 \sim 0.1 \cdot (\Phi_5 + \Phi_6)$ at the both wavelengths. In addition, propyl radical (produced in the primary step, $i\text{-}C_4H_{10} \longrightarrow CH_3 + C_3H_7$) was shown to accept further decompositions

$$C_3H_7 \longrightarrow C_3H_6 + H$$

and

$$CH_3 + C_2H_4 .$$
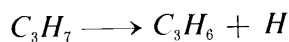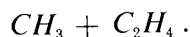
An experiment was done by Rebbert *et al* (1975) at the longer wavelength, 1633A as well as at those of *Kr* and *Ar* lines—the former has an importance more directly to our calculations than the latter due to the reason previously mentioned. In their discussions, particular emphasis was placed on the study of the molecular eliminations such as $i\text{-}C_4H_{10} \longrightarrow CH_4 + C_3H_6$ and $i\text{-}C_4H_{10} \longrightarrow C_4H_8 + H_2$. They deduced the following results on the fractional percentages of major isomers,

$i\text{-}C_4H_{10} \longrightarrow H_2 + C_4H_8$	$i\text{-}C_4H_8$ fraction	
	$\gtrsim 88\%$	at 1633A
	63%	at 1470A
	33%	at 1236A
$\longrightarrow CH_4 + C_3H_6$	propylene fraction	
	$86 \sim 89\%$	at 1633A
	40%	at 1470A
	38%	at 1236A

Compared with the current knowledge of the photolytic mechanism itself, we are possibly deficient in the quantitative data too much on this molecule.

We have so far described the photoabsorptions and the photochemical processes for a series of the saturates, alkanes, and found their absorptive property to be characterized by its onset at the very short wavelength side of UV. Photophysically, this extinction corresponds to an allowed transition of a σ-electron to a non-bonding σ^* orbital. The most common transition in organic molecules is promotion of an electron from a bonding π electron to antibonding π^* orbital and with unsaturated hydrocarbons they are the only type to be considered in the visible and UV regions. Such transition $\pi \rightarrow \pi^*$ in these unsaturate species brings about broad absorption over the extended wavelength region of UV. The overall absorption feature is expected to be subject to the bonding property of carbon atoms constituting a molecule. In fact, hydrocarbon molecules show similar profile in extinction for each subset classified according to the bonding property (*e.g.*[*], alkene, alkyne, alkadiene, enyne, etc. in aliphatic hydrocarbons) and with an increasing number of carbon atoms,

---

[*] They are defined as chain hydrocarbon compounds with one double bond, one triple, two double and, one double and one triple, respectively.

systematic shifts have been found in the quantities characterizing the absorption, such as $\varepsilon_{max}^{\#}$, $\lambda_{max}^{\#}$, and wavelength of the onset.

2.6 Ethylene (C_2H_4)

Absorption

Although there are not a few experiments on the absorption spectra of ethylene (Scheibe & Grieneisen, 1934, Snow & Allsopp, 1934, Price, 1935, Price & Tutte, 1940, Platt *et al*, 1949, Wilkinson & Johnston, 1950, Zelikoff & Watanabe, 1953, Metzger & Cook, 1964, and Hudson, 1971), older ones are restricted in energy to rather longer wavelength regions ($\lambda > 1800$A) and their spectral dispersions are quite low.

Zelikoff & Watanabe (1953) measured the absorption coefficients in the region 1065–2000A and their results are to be considered most standard from a current viewpoint. The absorption features are:

It commences weakly near 2000A and rises to the first strong absorption which begins at 1744A and extends to 1405A (most intense ~ 1400 cm^{-1} at 1700A). Strong absorption commences abruptly again at 1393A and continues to a minimum at 1125A. The spectrum contains two continua with maximum at about 1620 and 1250A, respectively (the former is due to transition $'A_{1g} \rightarrow 'B_u (N \rightarrow V)$). Superposed on the continuum, there are a strong banded structure arising from a series of vibrational transitions of first and second Rydberg members $('A_{1g} \rightarrow 'B_{3u} (N \rightarrow R))$, and weaker structures, possibly arising from other weaker Rydberg transitions. Each band is rather diffuse and no rotational line structure discernible.

In the *EUV* region, the absorption data can be utilized from the compilations by Metzger & Cook (1964) and Hudson (1971).

Photolysis

Sauer & Dorfman (1961) concluded that at 1470A the following two processes occur with nearly equal probabilities

$$C_2H_4 \longrightarrow C_2H_2 + H_2$$
$$\longrightarrow C_2H_2 + H + H$$
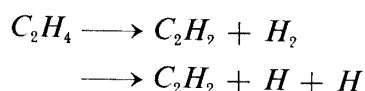
and that the rupture of only a single carbon hydrogen bond (*i.e.*, vinyl radical (C_2H_3) production) is not an important primary process.

The dissociation mechanism was examined in more detail at the wavelengths of 1849, 1470 and 1236A by Okabe & McNesby (1962a), photolyzing CH_2CD_2 and $CHDCHD$. The following primary processes were postulated,

$$CH_2 = CH_2 \longrightarrow CH_2C \text{ (ethenylidene)} + H_2 \qquad \Phi_1$$
$$\searrow \longrightarrow HC = HC$$
$$\nearrow$$
$$CH_2C + H + H \qquad \Phi_2$$
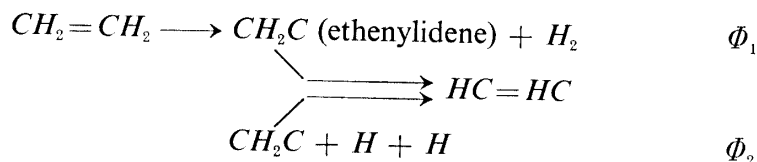
[#] ε_{max} and λ_{max} are traditionally used by photochemist to designate absorption strength at the maximum extinction, and its wavelength position, respectively. This molar extinction coefficient ε_{max}, defined in terms of decadic power, is connected with the absorption cross section σ(cm^2) used by photophysicist as σ(cm^2)$=3.824 \times 10^{-21} \varepsilon$ (l/mole·cm).

$$HC \equiv CH + H_2 \qquad\qquad \Phi_3$$

$$HC \equiv CH + H + H \qquad\qquad \Phi_4$$

$$CH_2CH + H \qquad\qquad \Phi_5$$
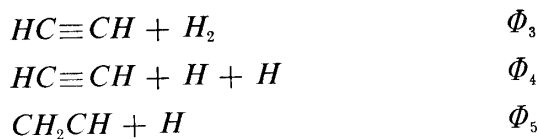
with $\qquad (\Phi_2 + \Phi_4)/(\Phi_1 + \Phi_3) \simeq 1$ at $1470A$, 1.4 at 1236A, and $\Phi_5 \leqslant 0.05$.

These results were also confirmed by the flash photolysis experiment (broad spectral distribution from about 1550 to 1950A) by Back & Griffiths (1967) with the estimates of

$$\Phi_1 + \Phi_3 \sim 0.51 \quad \text{and} \quad \Phi_2 + \Phi_4 \sim 0.49,$$

in which they suggested that rearrangements (isomerization) or decomposition of CH_2C is rapid enough to preclude successive reactions.

The yields of the primay processes were quantitatively determined by Borrell *et al* (1971) at 1849A, the longest wavelength used in the Okab? & McNesby's (1962a) experiment where no information of the primary yields was presented,

$$\Phi_1 + \Phi_3 = 0.68, \quad \Phi_2 + \Phi_4 = 0.20, \quad \text{and} \quad \Phi_5 = 0.16\dagger.$$

The most recent and detailed study was made by Potzinger *et al* (1972) at the wavelengths of 1930, 1849, 1634 and 1470A in which they deduced results, somewhat different in the yield values from the previous ones, and the reaction scheme as,

$$C_2H_4 \longrightarrow C_2H_4^* \xrightarrow[k_1]{} C_2H_4$$

$$\xrightarrow[k_2]{} C_2H_2 + H_2$$

$$\xrightarrow[k_3]{} C_2H_4^\ddagger \xrightarrow[k']{} C_2H_3 + H$$

$$\xrightarrow[k'']{} C_2H_2 + H + H$$

$$\xrightarrow[k_4]{} C_2H_4^{\ddagger\ddagger} \xrightarrow[k''']{} C_2H_2 + H + H$$

$$\xrightarrow[k_\omega, M]{} C_2H_4 \,,$$
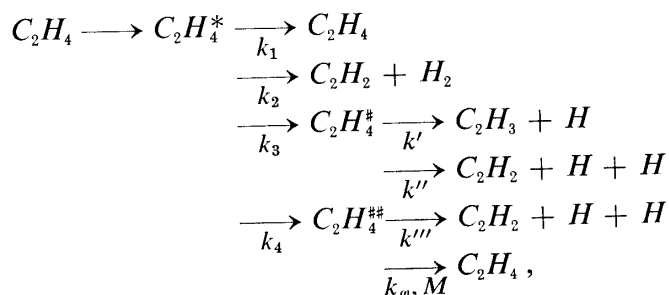
where $C_2H_4^*$, $C_2H_4^\ddagger$ and $C_2H_4^{\ddagger\ddagger}$ indicate three intermediate states that show distinct behaviors from each other to the variations of pressure and photon energy. They derived,

	Φ			
	1930	1849	1634	1470A
k_1		0.21	0.13	0.17
k_2		0.42	0.49	0.375
k_3	0.43	0.24	0.38	0.54
k_4		0.13		0.015
k'/k''		0.25	0.08	0.01

and $k_\omega/k''' = 6.7 \times 10^{-18} \, \text{cm}^3$.

$\dagger$ Excess deviation from unity of the summation $\sum_i \Phi_i$ is to be regarded as a measure of experimental accuracy.

2.7 Propylene $(CH_2=CHCH_3)$

Absorption

Absorption spectrum of propylene was investigated by Ashdown *et al* (1936), Price & Tutte (1940), Samson *et al* (1962) and Iverson *et al* (1972). Propylene, a methyl-substituted ethylene, has a first strong absorption at the position shifted to longer wavelengths than that corresponding to ethylene and the absorption pattern found in ethylene is obliterated there. To wavelengths shortward of 1300A the spectrum is essentially continuous while in the longer wavelength region it shows some structure arising from Rydberg transitions. The two maxima are clearly seen in the spectrum, peaked at 1720 and 1450A, respectively. The former is assigned as $\pi \rightarrow \pi^*$ transition and the latter is believed to be associated with a $\sigma \rightarrow \sigma^*$ transition of the methyl group.

Propylene $(IP=9.73\,\mathrm{eV})$ suffers ionization to the $Ly\ \alpha$ photons. Resulting production of $C_3H_6^+$, with the yield value of 0.32 (Samson *et al*, 1962), has been incorporated in the present calculation.

Photolysis

A number of photosensitized reactions were made for propylene in the 1950's and the dissociation processes concluded from their analyses have a close resemblance to those derived from photolysis experiments which were performed long after that time.

Becker *et al* (1965) carried out photolysis of propylene at 1470 and 1236A and found that acetylene dominates the products. It suggests that $C_3H_6 \longrightarrow CH_3 + C_2H_3$ $(\longrightarrow C_2H_2 + H)$ is the major primary process. The same conclusion was succesively obtained at 1849A by Okabe *et al* (1966). Other primary decompositions postulated in these experiments are: $CH_4 + C_2H_2$, C_3H_4 (allene) $+ H_2$, $C_3H_5 + H$ and $CH_2 + C_2H_4$.

Tschuikow-Roux (1967) pointed out at 1470A the occurrence of another mode of decomposition, C_3H_4 (allene and/or propyne) $+ H + H$ and at the same time the importance of methane elimination, $CH_4 + C_2H_2$ more than it had been thought.

The foregoing works, however, are not relevant to our present purpose since information of the primary yields was not given at all. This is made possible by the more recent experiments performed at 1850A (Borrell *et al*, 1971) and at 1630A (Collin *et al*, 1979).

	1850	1630A
$C_3H_6 \longrightarrow C_3H_5 + H$	0.41	⎫
$\searrow$		0.565
C_3H_4 (allene) $+ H$	0.02	⎭
$CH_3 + C_2H_3$	0.36	⎫
$\searrow$		0.335
$C_2H_2 + H$	0.04	⎭
$CH_4 + C_2H_2$	0.04	
$CH_2 + C_2H_4$	0.03	0.02
$C_2H + (CH_4 + H)^{+)}$		$\simeq 0.05$

$^{+)}$ or $(CH_3 + H_2)$

2.8   Acetylene ($HC\equiv CH$)

Absorption

Acetylene is one of those organic molecules whose physical and chemical properties have been most extensively studied. Earlier absorption experiments—a complete bibliography was given in the article by Platt & Klevens (1944)—however, are hardly useful for the problems relevant to aeronomy, since most of them are either limited in wavelength to fairly longer parts of the *VUV* region, or confined in extinction to relative measurement of the intensities. Furthermore the spectral dispersions are sometimes too coarse to attempt an application.

Absolute measurements of the absorptivity are found in the works; Platt *et al*, 1949 (1400–2400A, law dispersion), Nakayama & Watanabe, 1964 (1050–2000A) and Hamai & Hirayama, 1979 (1600–2400A).

Acetylene shows very complex spectral features, particularly between 1950 and 1550A—it has been even regarded as unpromising for analysis. Wilkinson summarized—*"the spectra in this region appears extremely complicated and very diffuse—"*. Weak absorption begins at 2380A and the overall absorption increases up to the maximum value at about 1700A. In this wavelength region, weak, comparatively diffuse bands superposed on a continuum are observed, now assigned to a transition from the linear ground state to a trans-bend first excited singlet state ($^1\Sigma_g^+\rightarrow{}^1A_u$). The transition is, in high dispersion spectrum, shown to consist of a few progressions (each spectral progression consists of a number of subbands characterized by the vibrational angular quantum number which is indicated by vibrational quantum number of lower level and symmetry type of upper level).

In the spectral region mentioned above (1950–1550A), a new electronic transition ($X^1\Sigma_g^+\rightarrow\tilde{B}^1B_u$) is suggested to be involved (Foo & Innes, 1973). To shorter wavelengths, there appear two outstanding series of Rydberg bands, both converging to the same ionization potential 11.35 eV and three more non-Rydberg band systems, in which 0-0 transition is the strongest (Price, 1935, Wilkinson, 1958 and Nakayama & Watanabe, 1964).

Photolysis

A noticeable feature revealed in acetylene photolysis would be its relatively long lifetime with respect to dissociation. This property, as inferred from the absorption features by Nakayama & Watanabe (1964), had been suggested by some of the preceding photolytic experiments and was recently confirmed by measuring natural lifetime ($\tau\sim6.2\,\mu$sec) of the excited acetylene from its fluorescent decay curve (Becker *et al*, 1971).

It has been already known since about the beginning of this century that acetylene vapor, when irradiated by the *UV* light, yields gaseous products as vinylacetylene (C_4H_4), benzene, ethylene, hydrogen, diacetylene (C_4H_2) and a white amorphous polymer called *"cuprene"* (*e.g.*, see Zelikoff & Aschenbrand, 1956). In the 1960's, there was a controversy about the formation mechanisms of these substances: One is the so-called *excited molecular mechanism* in which C_4H_4 and C_6H_6 are consecutively produced by the following reactions,

$$C_2H_2 + h\nu \longrightarrow C_2H_2^*$$

$$C_2H_2^* + C_2H_2 \longrightarrow C_4H_4^*$$

$$C_4H_4^* + C_2H_2 \longrightarrow C_6H_6^* \text{ etc,}$$
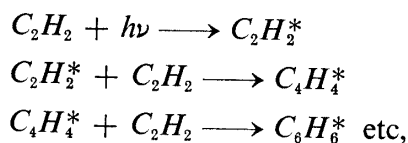
(Zelikoff & Aschenbrand, 1956, Shida *et al*, 1958, Stief *et al*, 1965, Tsukada & Shida, 1966, Shida & Tsukada, 1970, Tsukada & Shida, 1970).

The other is the so-called *free radical mechanism* in which ethynyl radical (C_2H), a decomposition product of $C_2H_2^*$, plays an important role in the successive reactions, for example,

$$C_2H + C_2H \longrightarrow C_4H_2$$

$$C_2H + C_2H_2 \longrightarrow C_4H_3 \text{ etc,}$$
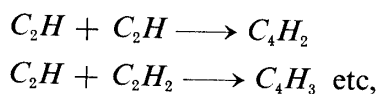
(LeRoy & Steacie, 1944, Mains *et al*, 1963, Sherwood & Gunning, 1965, LeRoy, 1966).

At present this problem appears to have been settled down in a somewhat compromising way that both mechanisms could be effective in producing those higher hydrocarbons. Thus the excited molecular mechanism taking advantage of its long-lived excited state of acetylene would be a unique and promising one, in the case where one considers the problem of polymer formation in the tenuous planetary upper atmospheres, because existence of such a long-lived excited state as found in acetylene seems not so much known in other kinds of unsaturated molecules, for which, therefore, the excited molecular mechanism would be less operative. The rate values of the series of these reactions are unfortunately unknown.

On the other hand, the free radical mechanism in acetylene photolysis was previously mentioned as being initiated by C_2H radical. But this is not the unique mode of decomposition in acetylene and we would briefly survey the possible decompositions of $C_2H_2^*$ which were experimentally suggested.

Zelikoff & Aschenbrand (1956) studied the photolytic mechanism of acetylene at 1849A and explained the products partially in terms of ethynyl radical (C_2H) produced by

$$C_2H_2 + h\nu \longrightarrow C_2H + H.$$
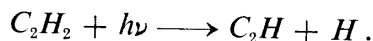
Stief *et al* (1965) photolyzed acetylene at Kr(1236, 1165A) and Xe(1470, 1295A). From fluorescence observation suggestive of the Swan band emissions of $C_2(d^3\Pi_g \rightarrow a^3\Pi_u)$, they concluded a decomposition

$$C_2H_2^* \longrightarrow C_2(d^3\Pi_g) + H_2$$
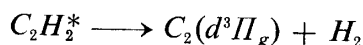
where the emissions due to chemical reactions (*e.g.*, $2CH \longrightarrow C_2(d^3\Pi_g) + H_2$) was excluded due to isotopic analysis. Furthermore, the decompositions to $C_2(X^1\Sigma_g^+$ and $a^3\Pi_u) + H_2$ were also suggested in the experiment. No evidence, however, was given there for or against the occurrence of $C_2H_2^* \longrightarrow C_2H + H$, an initiation process most commonly posed in the above free radical mechanism. Central splitting of acetylene, *i.e.*, $C_2H_2^* \longrightarrow CH + CH$, was negatively argued.

As for the origin of the fluorescence just mentioned, however, it was inferred later by Becker *et al* (1971) that it might be attributed to $C_2H_2^*$ or C_2H^*—possibly the former according to the authors—but not to the C_2 Swan band emissions.

The situation appears to have become more confused by another experiment of Okabe (1975), where he could not recognize the fluorescence in acetylene photolysis as due to the Swan band emissions but rather attributed it to C_2H^* emissions. Okabe (1975) explained the photolytic mechanism as follows

$$C_2H_2 + h\nu \longrightarrow C_2H_2^* \xrightarrow{\text{rapid internal conversion}} C_2H_2^{**} \text{ (not optically combine with ground state)}$$

$$C_2H_2^{**} \xrightarrow{\text{long lifetime}} \begin{cases} C_2H^*(B^2A) + H \\ C_2 + H_2 \end{cases}$$

$$\text{or} \quad C_2H_2^{**} + M \longrightarrow \text{quench}$$

$$C_2H_2^{**} + C_2H_2 \longrightarrow C_4\text{-compounds}$$
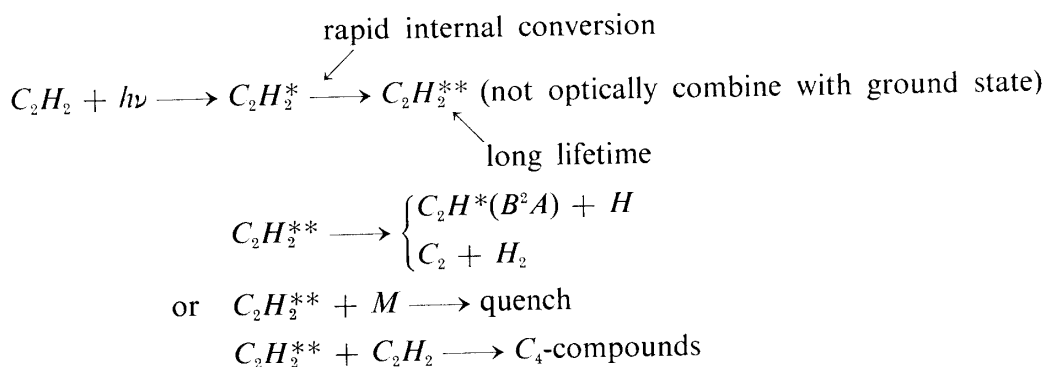
and the lifetime of $C_2H_2^{**}$ is roughly estimated as $2\,\mu s$ at 1236A and $6\,\mu s$ at 1305A.

Recently Laufer & Bass (1979) stated in flash photolysis that while the major decomposition path is $C_2H_2 \longrightarrow C_2H + H$, there is another, minor channel

$$C_2H_2 \longrightarrow C(^3P) + CH_2(X^3\Sigma_g^-)$$
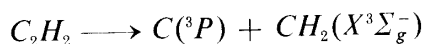
producing methylene radical (CH_2), a possible precursor to the observed C_3H_4 products.

Summarizing the foregoing arguments, a quantitative knowledge of the relative importance of the primary decomposition processes is badly needed for acetylene and further experimental studies are desirable.

2.9 Butenes (1-butene, $CH_3CH_2CH=CH_2$; cis- & trans-2-butene, $CH_3CH=CHCH_3$; isobutene, $(CH_3)_2C=CH_2$)

Absorption

Butenes (C_4H_8) are classified into four isomers (1-butene, *cis* or *trans*-2-butene, *isobutene*) depending on the way alkyl groups attach themselves to the carbon atoms of the double bond and, in particular, in 2-butene the two conformations (*cis* & *trans*) are possible.

Absorption measurements were done; for 1-butene by Carr & Stücklen, 1936 (2300–1500A), Price & Tutte, 1940 (2200–1100A, photograph), Gary & Pickett, 1954 (2200–1560A) and Samson *et al*, 1962 (2000–1050A).

for *cis*-2-butene by Carr & Stücklen, 1936 (2300–1500A), 1937 (2100–1850A), and Gary & Pickett, 1954 (2220–1560A).

for *trans*-2-butene by Carr & Stücklen, 1936 (2300–1500A), 1937 (2100–1850A), and Gary & Pickett, 1954 (2220–1560A).

and for *iso*butene by Carr and Stücklen, 1936 (2300–1500A) and Gary & Pickett, 1954 (2220–1560A).

Overall characteristics of the absorptions of butenes are that the spectra are composed of the two types of band systems; a series of narrow bands superposed on a broad intense band (ascribed to $N \rightarrow R$ or Rydberg transition, and $N \rightarrow V$ transition, respectively, by Carr & Stücklen, 1939). Butenes can be regarded as derivatives of ethylene, hence it obeys the rule observed by Carr & Stücklen (1936) that the maximum of the main absorption band progressively shifts towards the visible with increasing number of alkyl groups around the double bond.

i) 1-Butene has quite similar absorption spectrum to that of propylene except that the structure is more diffuse. The absorption begins at about 1890A and its maximum (1760A) is shifted towards the red compared with propylene as just mentioned.

ii) *Cis*-& *trans*-2-butenes show rather similar profiles but in more detail differ in that the *cis*-isomer reveals higher band intensity than the *trans*-isomer. This is marked with the first absorption bands which are extremely weak in the *trans*-isomer and hence a significant absorption is brought about in the longer wavelength region for the *cis*-isomer compared with for the *trans*-isomer. The maximum absorption is reached at 1754 and at 1777A for these isomers (*cis* and *trans*).

iii) *Iso*butene has an absorption maximum at 1883A, most longward in wavelength among the butene isomers. Although the absorption onset (around 2100A) is not so different from those of 2-butenes, the rise and the fall before and after the maximum are comparatively steep. This would make *iso*butene a most fragile butene species for the solar *UV* (the intensities of the continuum rapidly increase beyond around these wavelengths).

Photolysis

Although results appear to be considerably scattered in the quantitative values of the decomposition processes on which extensive photolysis experiments have been performed for butene compounds, there seems to be an overall agreement that the radical decompositions such as $C_4H_8 \longrightarrow C_3H_5 + CH_3$ and $C_4H_8 \longrightarrow C_4H_7 + H$ are quite important (just similar to the case of propylene but not to the case of ethylene). Also this is consistent with the results obtained from photosensitization (*e.g.*, Lossing *et al*, 1956). In the photolyses of butenes, ethane generally makes one of the most abundant products, as is naturally expected from the subsequent reaction of thus formed me hyl radicals ($CH_3 + CH_3 + M \longrightarrow C_2H_6$).

i) 1-Butene

Okabe *et al* (1966) carried out mass spectrometric investigation on the photolysis of 1-butene at 1849A and suggested three probable decomposition modes,

$$1\text{-}C_4H_8 \longrightarrow C_3H_4 + (H + CH_3), \qquad C_3H_5 + CH_3, \qquad C_3H_6 + CH_2 .$$
$$\text{allene} \qquad \text{or } CH_4 \qquad\qquad\qquad\qquad \text{propylene}$$
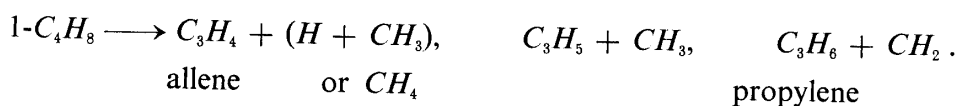
At the same wavelength, Borrell & Cashmore (1968) also photolyzed $1\text{-}C_4H_8$ giving the primary yields as

$$1\text{-}C_4H_8 \longrightarrow C_3H_5 \text{ (allyl)} + CH_3 \qquad 0.71$$

$$C_4H_7 \text{ (α-methylallyl)} + H \qquad 0.12$$

$$C_2H_4 + C_2H_4 \qquad 0.093$$

$$CH_4 + C_3H_4 \text{ (allene)} \qquad 0.044$$

$$C_2H_6 + C_2H_2 \qquad 0.012$$

$$2\text{-}C_4H_8 \text{ (cis \& trans)} \qquad 0.01 .$$
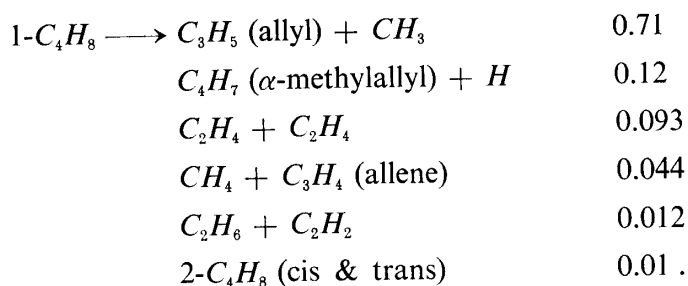
The results are predominantly in favor of the cleavages of the C–C bond and of the C–H bonds in the β position to the double bond.

Since then, a number of experiments have followed, not confined to the primary decompositions alone but extended to the secondary decompositions (Borrell *et al*, 1970, Collin, 1973, Collin & Wiekowski, 1978a, b, Niedzielski *et al*, 1978). An example is shown below (Collin, 1973),

	1849	1470	1237	1064, 1048A
$C_4H_8 + h\nu \longrightarrow C_4H_8^*$				
$C_4H_8^* \longrightarrow C_3H_5 + CH_3$	0.71	0	0	0
$C_3H_4 + H + CH_3$	$0.04^{+)}$	0.38	0.23	0.16
$C_4H_7 + H$	0.12	$\leqslant 0.05$	$\leqslant 0.05$	$\leqslant 0.05$
$C_4H_6 + 2H(H_2)$	—	0.32	0.36	0.17
$C_2H_4 + C_2H_4$	0.09	0.04	0.05	} 0.20
$C_2H_3 + C_2H_4 + H$	—	0.07	0.09	
$C_2H_2 + C_2H_5 + H$	—	0.16	0.12	
$C_2H_2 + C_2H_6$	0.01	0.03	0.02	} 0.33
$C_2H_2 + 2CH_3$	—	0.04	0.05	
$C_3H_6 + CH_2$	—	0.03	0.04	0.05 .

$^{+)} C_3H_4 + CH_4$

It would be readily realized that the secondary decompositions of the primary fragments produced in photolytic act become rapidly important with increase of photon energy.

ii) 2-Butenes (*cis* & *trans*)

Cis-2-butene photolysis was begun by Chesick (1966) at Zn lines (2026 & 2062A) —close to the onset wavelength of the absorption—and the initial stages of the decompositions were explained as follows,

$$cis\text{-}2\text{-}C_4H_8 + h\nu \longrightarrow 2\text{-butene}^* \xrightarrow{M} cis\text{- or } trans\text{-2-butenes}$$
$$(\text{electr. exc.})$$
$$\longrightarrow 1\text{-butene}^*, \text{ (}iso\text{butene}^*)^{\#}$$
$$\longrightarrow 2\text{-butene}^{**} \text{ (highly vib. exc.)}$$
$$\text{very rapid}$$
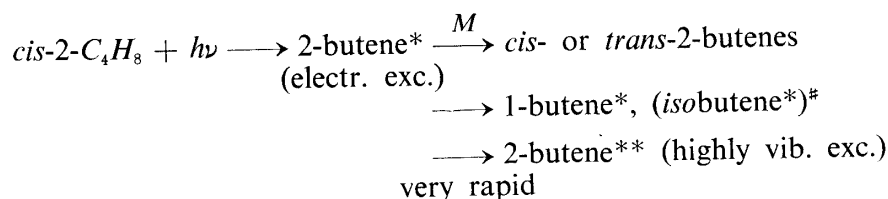
All isomeric species of butenes can be found in the products but it is not certain whether *iso*butene would be formed at this stage of the photolytic processes.

2-butene** $\xrightarrow[5\times 10^8 \text{s}^{-1}]{}$ $\left.\begin{array}{l} CH_3CH=CH \text{ (propenyl)} + CH_3 \\ CH_2CH=CH_2 \text{ (allyl)} + CH_3 \end{array}\right\}$ 59%

$\xrightarrow[3.5\times 10^8 \text{s}^{-1}]{}$ C_4H_7 (γ-methylallyl) + H 41%.
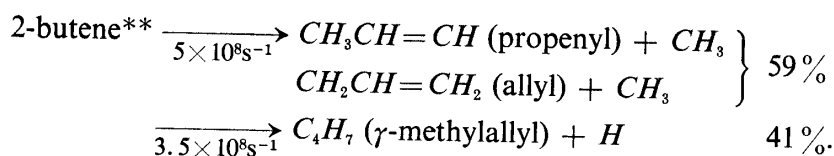
An experiment was carried out for the mixtures of *cis-* and *trans*-2-butenes at 1849A by Borrell & James (1966) at almost the same time. They extended the decomposition processes to consider more minor events and estimated the quantum yields as follows

cis- or *trans*-2-butenes + $h\nu \longrightarrow C_4H_7$ (γ-methylallyl) + H		0.6
$C_2H_2 + 2CH_3$		0.23
$1, 3\text{-}C_4H_6 + H_2$		0.11
C_3H_5 (propenyl) + CH_3		0.085
C_3H_4 (allene & propyne) + CH_4		0.07
$2\text{-}C_4H_6$ (2-butyne) + H_2		0.007
$C_2H_4 + C_2H_4$		0.01
cis-2-butene + $h\nu \longrightarrow$ *trans*-2-butene		0.1
trans-2-butene + $h\nu \longrightarrow$ *cis*-2-butene		indeterminate
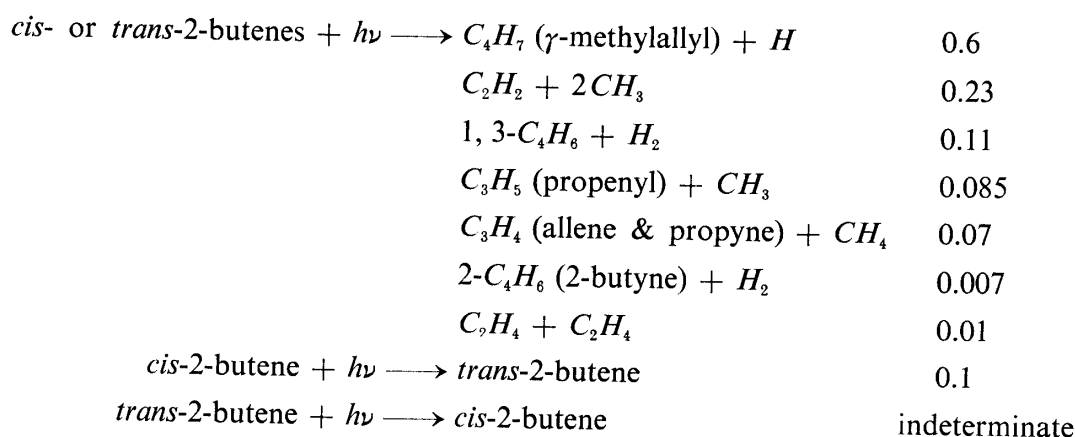
(It was suggested that the above two largest radicals are likely to equilibrate with their isomers,

C_4H_7: γ-methylallyl $\rightleftharpoons$ α-methylallyl

C_3H_5:   propenyl $\rightleftharpoons$ allyl).
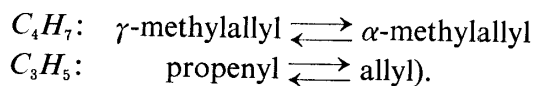
It may be noted at these long wavelengths that the relative importance of the two major radical processes ($C_3H_5 + CH_3$ and $C_4H_7 + H$) is reversed compared with the case of 1-butene.

2-Butene is one of those hydrocarbons for which the quantitative determination of the primary yields have been most successfully performed. The results shown below are taken from the experiments which were recently done at the shorter wavelengths.

	1745		
$2\text{-}C_4H_8 + h\nu \longrightarrow C_4H_8^*$	1743	1470	1236A
$C_4H_8^* \longrightarrow C_3H_4$ (allene, propyne) + $CH_3 + H$	0.026[1]	0.18	0.20
C_4H_6(1, 3-butadiene) + $H + H$	0.40[2]	0.38	0.37
$C_2H_2 + CH_3 + CH_3$	0.07	0.29	0.27
$C_2H_5 + C_2H_2 + H$	0.035	0.02	0.04
C_3H_6 (propylene) + CH_2		<0.02	0.04
$C_4H_7 + H$	0.12	<0.05	indeterminate
$C_3H_5 + CH_3$	0.38[3]	0.08	
$C_2H_4 + C_2H_4$	0.01	<0.02	
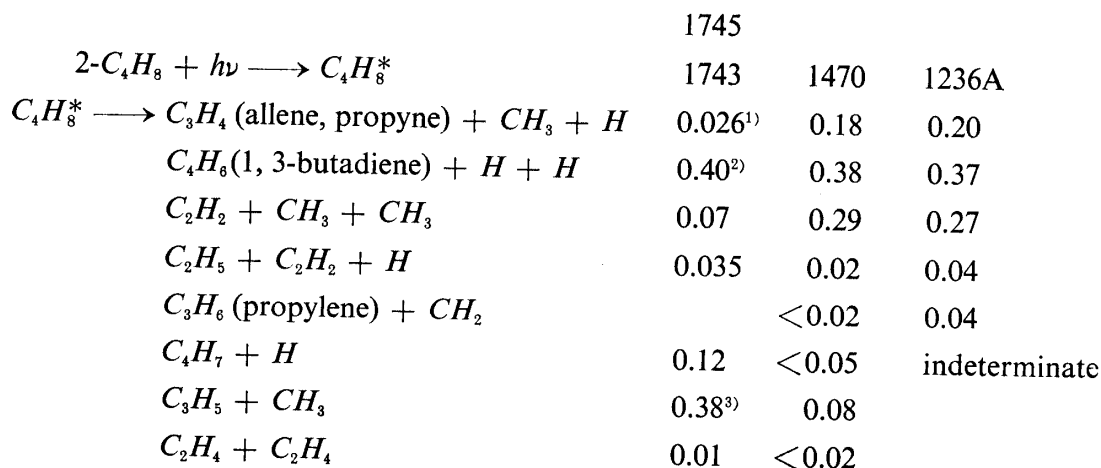
C_4H_8 (isomerization)   0.012   0.02   0.02

1) CH_3+H and CH_4 are both probable at this energy.
2) $H+H$ and H_2 are both probable at this energy.
3) About 42% of C_3H_5 was suggested to undergo further decompositions into $C_2H_2+CH_3$ and
    C_3H_4 (allene) $+H$.

The references are due to Wieckowski & Collin (1977) at 1745, 1743A, Collin & Bukka (1976/77) at 1470A and Collin & Perrin (1972) at 1236A.

iii) *Iso*butene

The photolysis of *iso*butene was carried out earlier by Kieffer & Howe (1942) at about 1900A (nearly monochromatic) and the importance of radical decompositions $(C_3H_5 + CH_3$ and $C_4H_7 + H)$ had been already noted in it.

It was, however, not until the 1970's that the photolytic mechanisms were reexamined in the light of the more advanced present-day techniques. The following results have been compiled from Borrell & Cashmore (1969) at 1850A, Collin & Wieckowski (1978a) at the 1740A and Herman *et al* (1970) at 1470A.

	1849	1740	1470A
$iso\text{-}C_4H_8 + h\nu \longrightarrow C_4H_8^*$			
$C_4H_8^* \longrightarrow C_3H_5^{1)} + CH_3$	>0.26	$0.78^{2)}$	$0.80^{3)}$
C_4H_7 (β splitting)$^{4)}$ $+ H$	>0.23	0.25	
(α splitting) $+ H$		0.05	
$C_2H_2 + 2CH_3$	0.005	0.015	
$C_3H_6 + CH_2$		<0.02	
$C_2H_4 + C_2H_4$	0.002	0.01	
$C_3H_4 + CH_3 + H$	0.07		
$C_3H_4 + CH_4$	0.025		

1) isopropenyl $(CH_3C=CH_2)$.
2) About a half of C_3H_5 is likely to decompose into C_3H_4+H.
3) At 1470A the decomposition of $C_3H_5 \longrightarrow C_3H_4$ (allene & propyne) $+H$ is complete and the product ratio of allene and propyne was estimated to be 3/2.
4) By the symbols α, β, ... , are meant the bond positions which are counted in sequence from the nearest double bond.

Ionization of *iso*butene becomes possible above the energy of 9.32 eV. Photolysis was executed at the wavelengths of 1236 and 1049, 1051A by Herman *et al* (1970), although the results are somewhat of qualitative nature, only except for the measurement of the ionization yields ($\eta \sim 0.26$ and 0.31 at the above wavelengths).

2.10 *Butynes* (1-butyne, ethylacetylene, $CH_3CH_2C{\equiv}CH$
2-butyne, dimethylacetylene, $CH_3C{\equiv}CCH_3$)

Absorption

Absorption coefficients were measured for 1-butyne by Jones & Taylor (1955), Nakayama & Watanabe (1964) in the $2000 \sim 1500$A region and Hamai & Hirayama (1979) in the $2300 \sim 1600$A region, and for 2-butyne also by Hamai & Hirayama (1979) in the $2300 \sim 1600$A region.

Overall spectrum of 1-butyne is quite similar to that of propyne. Very diffuse bands which were identified as Rydberg series from the comparison with those in propyne are discernible at the wavelengths shortward of about 1600A. On the longer wavelength side, the spectrum reveals a broad continuum with maximum at about 1775A.

The absorption feature of 2-butyne is somewhat different from that of 1-butyne. In the fo mer, when compared with the latter, the absorption begins in the relatively longer wavelength region and proportionally the maximum is reached earlier than the latter case. Therefore, the dissociation of 2-butyne due to the solar UV radiation seems to proceed more efficiently than that of 1-butyne. The absorption spectrum of 2-butyne at the wavelengths shortward of 1600A appears to be deficient in literature.

Photolysis (*1-butyne*)

1-Butyne was photolyzed at 1470 and 1236A by Hill & Doepker (1972a). The most important primary process found in the 1-butyne photolysis is $1\text{-}C_4H_6 + h\nu \longrightarrow C_4H_5 + H$. This C_4H_5 radical, at these high energies, is expected to undergo complete secondary decomposition, $C_4H_5 \longrightarrow C_4H_4 + H$ resulting in the formation of vinylacetylene. They also executed an auxiliary photolysis experiment in the much longer wavelength region (2600–2200A) and examined the photolytic products. The vinylacetylene was, in the latter circumstance, observed in only a trace amount. Such a fact would probably imply that the actual decomposition remained in a primary stage alone, $C_4H_6 \longrightarrow C_4H_5 + H$ in these low energy regions. This can well correspond to the situation found in the mercury-photosensitized experiment (Kebarle, 1963), where about a half of the excited 1-butynes was shown to dissociate into $C_4H_5 + H$.

After all in the energy region between 1470 and 1236A, the decomposition yields obtained by Hill & Doepker (1972a) are as follows

$1\text{-}C_4H_6 \longrightarrow C_4H_4$ (vinylacetylene) $+ H + H$	0.34
$CH_2 + C_3H_4$ (allene)	<0.02
$C_2H_4 + C_2H + H$	0.10
$2C_2H_2 + H_2$	0.065
$C_2H + C_2H_3 + H_2$	$\leqslant(0.20\sim0.25)$
$C_2H + C_2H_5$	$\geqslant0.19$
$CH_3 + C_3H_3$ (propargyl)	~0.10.

Here, the overall importance of radical processes would be clearly seen.

To add from the viewpoint of aeronomical applications, the photolytic studies in the longer wavelength region seem to be desirable.

Photolysis (*2-butyne*)

γ-Radiolysis and ultraviolet photolysis for 2-butyne both confirmed $CH_3C=CCH_2$ radical to be involved in the primary act by observing the ESR spectrum (Smirnova *et al*, 1964) and an elimination of hydrogen atom from the methyl group was suggested

$$CH_3C \equiv CCH_3 \longrightarrow CH_3C = CCH_2 + H.$$

A similar experiment followed for liquid 2-butyne by Whitten & Berngruber (1971) but only the final products were shown there.

2.11 *Butadienes* $\left(\begin{array}{l} \text{1, 3-butadiene, divinyl,} \ CH_2 = CHCH = CH_2 \\ \text{1, 2-butadience, methylallene,} \ CH_3CH = C = CH_2 \end{array}\right)$

Absorption

Butadiene, a diolefinic compound, has two isomers of $1, 3\text{-}C_4H_6$ and $1, 2\text{-}C_4H_6$ depending upon whether symmetric configuration of the two double bonds with respect to a certain C–C bond exists (conjugate or nonconjugate).

The spectra for these two isomers were obtained by Jones & Taylor (1955) in the wavelength region of about 2300~1700A. A dramatic alternation of the spectra is seen between the both compounds. The former shows an absorption greatly extended in wavelength towards the longer and enhanced in intensity, compared with that of the latter. This strong absorption arises from the allowed (singlet to singlet) $\pi \rightarrow \pi^*$ transition. Obvious and well-known effect of the conjugation is a shift of the major part of the absorption several hundred angstroms towards the red for every additional $-C = C-$ unit which is added to the chain: in the long conjugated chains, this absorption can move even to the visible, capable of being utilized as a dye material.

Photolysis (1, 3-butadiene)

Srinivasan (1960), Haller & Srinivasan (1964, 1966) carried out photolysis of $1, 3$-butadiene in the MUV region (2600~2200A) and postulated the primary processes. This mechanism may be represented as

$$1, 3\text{-}C_4H_6 + h\nu \longrightarrow 1, 3\text{-}C_4H_6^* \xrightarrow{M} 1, 3\text{-}C_4H_6$$
$$\searrow 1, 2\text{-}C_4H_6^* \xrightarrow{M} 1, 2\text{-}C_4H_6$$

$$1, 3\text{-}C_4H_6^* \longrightarrow \begin{cases} C_2H_2 + C_2H_4 & \Phi_1 \\ C_4H_4 \text{ (vinylacetylene)} + H_2 & \Phi_2 \end{cases}$$

$$1, 2\text{-}C_4H_6^* \longrightarrow \begin{cases} C_2H_2 + C_2H_4 & \Phi_3 \\ C_4H_4 \text{ (vinylacetylene)} + H_2 & \Phi_4 \\ CH_3 + C_3H_3 & \Phi_5 \end{cases}$$

Doepker (1968) photolyzed also 1, 3-butadiene in the same wavelength region as well as in the VUV (1470 and 1236A) region, supporting the scheme as a whole. In these MUV it was estimated that $\Phi_1 \sim 0.14$, $\Phi_2 \sim 0.06$ and $\Phi_3 + \Phi_4 + \Phi_5 \sim 0.3$ (in particular Φ_5 accounts for nearly 75% of the sum, that is, the decomposition yield of the excited $1, 2\text{-}C_4H_6^*$).

The product yield of $1, 2\text{-}C_4H_6$ was observed to increase with increasing $1, 3\text{-}C_4H_6$ pressure. Although this could be interpreted in terms of the existence of long-lived excited state of $1, 3\text{-}C_4H_6^*$, such a behavior was absent at the corresponding experiment in VUV region.

One more distinctive feature found in the $1,3$-C_4H_6 photolysis at the shortward wavelength, contrasted to the longward, is the predominance of the cleavage process of central carbon-carbon bond to produce two vinyl radicals, $1,3$-$C_4H_6 \longrightarrow C_2H_3 + C_2H_3$ (Doepker, 1968). Those fragments (C_2H_4, C_4H_4 and H_2) which were the major decomposition products in the low energy photolysis have this time enough energy to undergo further decompositions and in consequence the overall processes as

$$1,3\text{-}C_4H_6 \longrightarrow C_4H_4 + H_2 \longrightarrow 2C_2H_2 + H_2$$
$$\longrightarrow C_4H_4 + H + H$$
$$\longrightarrow C_2H_2 + C_2H_4 \longrightarrow 2C_2H_2 + H_2$$

are most likely to occur in these high energy photolysis.

Photolysis (1, 2-butadiene)

It was already known in as early as 1957 by the mercury-photosensitized experiment of Collin & Lossing (1957) that 1, 2-butadiene decomposed into $CH_3 + C_3H_3$ (propargyl, $CH_2C \equiv CH$) and $C_4H_4 + H_2$ with the probabilities of $0.53 \sim 0.59$ and the rest, respectively. Although there appears to be a parallelism to some extent between the photosensitization and the direct photolysis for this compound, a basic difference can still be found between their product distributions.

Doepker & Hill (1969) photolyzed 1, 2-butadiene at 1470 and 1236A, and also in the broad region of $2600 \sim 2200$A. They postulated the photolytic mechanism in the longest wavelength region as follows,

$$1, 2\text{-}C_4H_6 + h\nu \longrightarrow 1, 2\text{-}C_4H_6^* \longrightarrow 1, 2\text{-}C_4H_6^{\#} \text{ (fairly long lifetime)}$$

$$\begin{array}{c} M \swarrow \quad \searrow \qquad\qquad \searrow \\ 1, 2\text{-}C_4H_6 \quad 1, 3\text{-}C_4H_6^* \qquad 1, 3\text{-}C_4H_6^{\#} \xrightarrow{M} 1, 3\text{-}C_4H_6 \\ \searrow M \\ 1, 3\text{-}C_4H_6 \end{array}$$

$$1, 2\text{-}C_4H_6^* \longrightarrow C_2H_2 + C_2H_4$$
$$C_4H_4 + H_2$$
$$CH_3 + C_3H_3$$
$$C_4H_5 + H$$

$$1, 2\text{-}C_4H_6^{\#} \longrightarrow CH_2 + C_3H_4 \text{ (allene \& propyne)}.$$

Various decomposition processes at 1470 and 1236A were also reported in that literature. The results obtained in those wavelengths, however, are of qualitative nature after all.
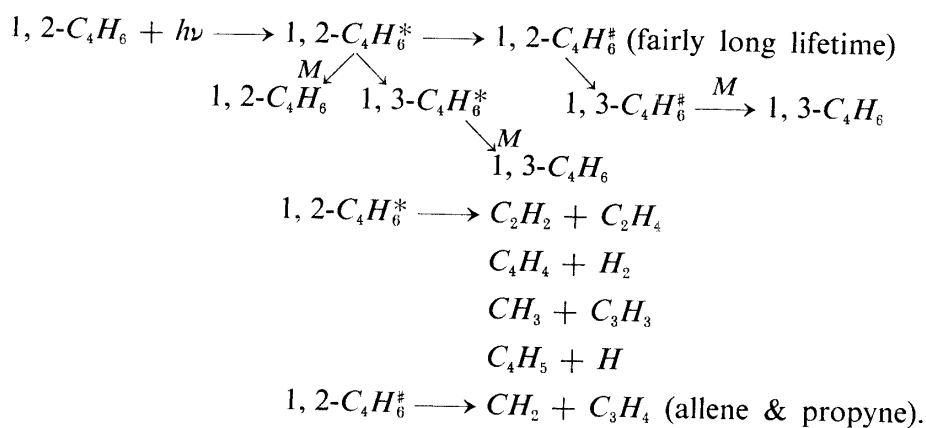
The only experiment to date which gave rise to quantitative results for the primary yields is the one by Diaz & Doepker (1977) at 1470A, which, rather a sophisticated experiment, was performed through the use of various additives such as NO, HI, CH_3I and D_2 in order to identify the radicals involved therein. The yields were estimated for the next nine primary processes,

$$1,\ 2\text{-}C_4H_6 + h\nu \longrightarrow C_4H_4 \text{ (vinylacetylene)} + 2H \qquad 0.30$$

$$C_4H_4 \text{ (butatriene)} + 2H \qquad 0.08$$

$$CH_2 + C_3H_4 \text{ (allene \& propyne)} \qquad 0.02$$

$$C_2H_2 + C_2H_4 \qquad 0.02$$

$$2C_2H_2 + H_2 \qquad 0.05$$

$$C_2H_4 + C_2H + H \qquad 0.02$$

$$C_2H_2 + C_2H_3 + H \qquad 0.03$$

$$CH_3 + C_3H_3 \qquad 0.36$$

$$C_4H_5 + H \qquad 0.09 \ .$$

2.12 Vinylacetylene (1-buten-3-yne, $CH_2 = CHC \equiv CH$)

Absorption

Vinylacetylene is the first member of the *enyne* compounds which in general show fairly strong absorption between the region 2300 to 2190A. To date the absorption spectra obtained with vinylacetylene were restricted to only those in the middle and near UV regions.

Dunicz (1941) photographed the spectrum between the wavelengths of 3305 and 2256A and observed that the sharp bands in the longer wavelength region were followed by diffuse bands in the shorter wavelength region, which finally border on a continuous spectrum. The extinction was not given in the absolute values but presented, in strength, only with the visual estimates classified into the six grades.

Data of the maximum molar extinction and its wavelength position are available due to Brande (1945) and Georgieff *et al* (1954) who reported the values of about $\lambda_{max} \sim 2190\text{A}$ and $\varepsilon_{max} \sim 10^4$.

Photolysis

Vinylacetylene is an important product arising from UV photodissociations of the species like 1, 3-butadiene, 1, 2-butadiene, cyclobutene, methylenecyclopropane and 1-butyne, and also produced in those chemical reactions which were initiated in the photolyses of acetylenic compounds.

At present there appears to be no available photolytic experiment made upon this molecule. In those long wavelength regions beyond 2000A where maximum absorption is observed for vinylacetylene, it may be presumed that the decomposition, if it should happen, would be an elimination of atomic hydrogen, $C_4H_4 \longrightarrow C_4H_3 + H$, as is often seen in the cases of some hydrocarbons like propyne, allene, 1-butyne etc. Doepker & Hill (1969) in fact stated in the photolysis of 1, 2-C_4H_6 that "*It would appear that a second fragmentation process for the $C_4H_4^*$ may be the elimination of a hydrogen atom, $C_4H_4^* \longrightarrow C_4H_3 + H$*".

2.13 Diacetylene (biacetylene, butadiyne, $CH \equiv CC \equiv CH$)

Absorption

The near ultraviolet absorption spectrum of diacetylene was first studied by Woo & Chu (1935, 1937) at the wavelengths longward of 2000A, who observed many sharp and narrow bands in the region between 2970 and 2650A and many more

diffuse bands in the region below 2650A. The very weak intensity and the rich vibrational structure but with no rotational structure would probably suggest that the absorption is due to electronically forbidden transitions and also that predissociation is operative in it.

The studies of the absorption spectra in the wavelength region longward of 2000A have been followed by Price & Walsh (1945), Callomon (1957), Georgieff & Richard (1958), Hardwick & Ramsay (1977) and Haink & Jungen (1979), thereby the configurations of the excited states responsible for the absorption and their molecular constants have been well determined. This absorption, observed in the *MUV* region could be considered as corresponding, in acetylene, to the absorption in the 2000 ~ 1550A region.

On the other hand, in the shorter wave length region there appears to be only a spectrum published in photographic plate (2000 ~ 1000A) by Price & Walsh (1945), where much stronger bands can be seen to occur at around 1630A and other strong (Rydberg) bands to follow them as shorter wavelengths are reached.

In spite of the existing several absorption studies, only available data where the absorption strengths are explicitly given are due to Georgieff & Richard (1958) whose spectrum, however, was derived in solute phase.

Photolysis

Flash photolysis was carried ou by Callomon & Ramsay (1957), where they observed several well-known band spectra due to C_2 (Swan, emission & abs.), C_2 (Phillip, abs.), C_2 (4050A bands, abs.) and CH (3143A bands, abs.). They suggested three possible decomposition modes as

$$C_4H_2 \longrightarrow C_2H + C_2H$$
$$C_3H + CH$$
$$C_4H + H$$
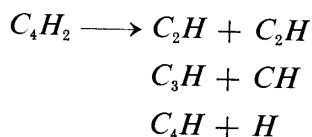
and indicated that the first process would not be important compared with the second (this is to be somewhat abnormal since in diacetylene the central $C\text{-}C$ bond is being thought as weak in the ground state). The formation of C_3 radical, which has a special importance on the classical astronomical problem—how it is produced in comets—was explained either due to the secondary decomposition of C_3H or due to the subsequent reaction with CH

$$C_3H \longrightarrow C_3 + H$$
$$C_3H + CH \longrightarrow C_3 + CH_2 .$$
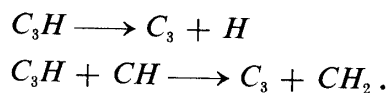
The current status of the knowledge on the decomposition processes of diacetylene appears to have been more confused by two further experiments. Pontrelli (1965) obtained in 2537A photolysis the gaseous products alone, consisted of acetylene and a very small amount of triacetylene (C_6H_2). From an additional experiment for the isotopically substituted material, he excluded the possibility of acetylene formation through C_2H radical in the photolysis above 2500A and alternatively proposed the following decomposition

$$C_4H_2 \longrightarrow C_2H_2 + C_2 \, ,$$
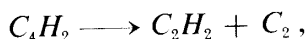
while Graham *et al* (1976) in the flash (H_2/He lamp) photolysis confirmed the existence of radicals, C_4H, C_4H_3 and C_2H (central splitting) as dissociation products of C_4H_2 by virtue of the *ESR* spectra.

Furthermore, there is a suggestion that polymer formation would proceed through the excited molecular mechanism such as (Tarr *et al*, 1965)

$$C_4H_2 + h\nu \longrightarrow C_4H_2^* \xrightarrow[C_4H_2]{} \text{polymer} \, .$$
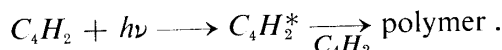
When we take into account the above confusing situation and the fact that in all the foregoing literature no quantitative information on the primary processes was given, it is clear that many more photolysis experiments are needed for this molecule.

2.14 *Propyne* (methylacetylene, $CH_3C \equiv CH$)

Absorption

Absorption spectra of propyne were examined by Price & Walsh, 1945 (2000 ~ 1000A), Nakayama & Watanabe, 1964 (2000 ~ 1050A) and Hamai & Hirayama, 1979 (2200 ~ 1650A). The first, however, was presented in the form of photographic plates which did not provide us with immediate information on the strengths of extinction.

Generally speaking, none of the alkyne spectra reveal any noticeable bands in the wavelength region longer than 2100A. There appears to be a close parallelism in the spectral features between acetylene and propyne (simplest of acetylene's derivatives). In the region from 2000 to 1600A, the spectrum with maximum at 1760A is essentially continuous, probably responsible for a broad dissociation.

On the shorter wavelength side, the spectrum of propyne is very similar to that of acetylene except that the corresponding bands of the former are more diffuse and slightly shifted towards the visible than that of the latter. In addition, two series of Rydberg band systems are prominent, showing a good correspondence to those of acetylene. The strongest band of the whole spectrum occurs at 1540A wth less peak value than in acetylene.

Photolysis

Propyne was photolyzed at 2062A by Galli *et al* (1967), where the yields of the final products alone were reported without analyzing the primary processes at work. The gaseous products—C_6H_6 (1, 3-hexadiyne), C_3H_6 (propylene), H_2—constituted about 20% by weight of the total products, the rest 80% being liquid or solid (the solid was shown to have the same carbon-hydrogen ratio as in C_3H_4 within ~2%). Furthermore, the maximum C_3H_4 decomposition attained in the course of the experiment was estimated to be about 30% of the absorbed photons. These facts suggest that the polymetric formation worked quite efficiently through the excited molecular mechanism.

Some information on the primary decompositon processes has been made available by the experiment at 1470A due to Stief *et al* (1971), who obtained the result indicating the particular importance of hydrogen (atomic and molecular) elimination processes. They postulated the following decomposition scheme

$$CH_3C \equiv CH + h\nu \longrightarrow C_3H_3 \text{ (propargyl\dag)} + H \qquad \varPhi_1$$

$$C_3H + H_2 + H \qquad \varPhi_2$$

$$C_3H_2 + H_2 \qquad \varPhi_3$$

$$C_3 + 2H_2 \qquad \varPhi_4$$
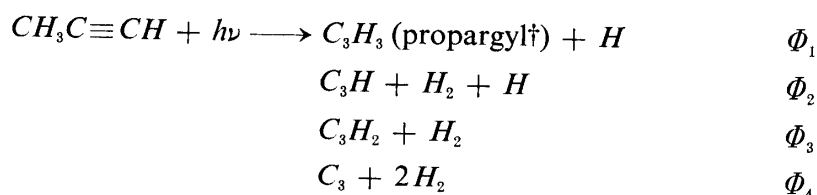
where, $\varPhi_1 + \varPhi_2 \geqslant 0.40$, $\varPhi_2 + \varPhi_3 + \varPhi_4 = 0.15$ and $\varPhi_1$ was estimated to be nearly twice as probable as $\varPhi_2$. The predominance of the process leading to the formation of this propargyl radical had been also found out in the mercury-photosensitized experiment (Kebarle, 1963) with such a high yield as 0.80

$$CH_3C \equiv CH + Hg^*({}^3P_1) \longrightarrow CH_2C \equiv CH + H + Hg({}^1S_0) .$$
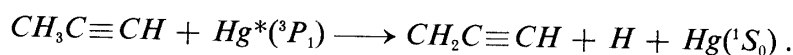
2.15 Allene (propadiene, $CH_2 = C = CH_2$)

Allene is the first member of alkadiene group. In spite of the importance in photochemistry and also of the importance as a fundamental in *diene* homologues, the least amount of attention has been paid to it.

Absorption

Generally speaking, the absorption is intensified in the longer wavelengths when the double bonds are adjacent, but it is still far less than that of a conjugated system. This is seen, *e.g.*, in the absorption spectrum of ethylallene $(CH_2 = C = CHC_2H_5)$, a derivative of allene (Burr & Miller, 1941). No data, however, appear to be available for the absorption of allene itself.

Photolysis

Probably we have no available photolytic data obtained with allene, which could give direct information of the primary photodecomposition processes. There, however, are a few experiments suggesting a probable mode of decomposition. This is the one that leads to the formation of propargyl radical $(CH_2C \equiv CH)$, *i.e.*,

$$C_3H_4 \longrightarrow C_3H_3 \text{ (propargyl)} + H .$$
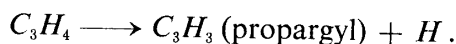
Collin & Lossing (1957) in the mercury-sensitized experiment proposed the following reaction

$$C_3H_4 \text{ (allene)} + Hg^*({}^3P_1) \longrightarrow C_3H_3 \text{ (propargyl)} + H + Hg({}^1S_0)$$
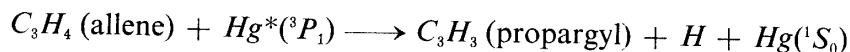
as the only one probable mode of decomposition, since no products responsible for *C–C* rupture were found (although a considerable amount of polymer was observed there). Such a decomposition was also inferred, one from the photolytic experiment (3450–2900A) by Ramsay & Thistlethwaite (1966) and the other from the radiolysis (2.8 MeV electrons) by Fessenden & Schuler (1963), both of which identified propargyl radical in the reaction systems by virtue of the *ESR* spectrum—convincing result for $C_3H_4 \longrightarrow C_3H_3 + H$.

\dag Photolysis of solid propyne at 77K confirmed the formation of propargyl radical $(CH_2C \equiv CH)$ which was identified by virtue of its *ESR* spectrum (Poole & Anderson, 1959).

2.16 *Cyclopropane* $\left(\begin{array}{c} CH_2 \\ \bigwedge \\ CH_2\!-\!CH_2 \end{array}\right)$

Absorption

Throughout the spectral region 5000 to 1950A, the spectrum of cyclopropane is quite transparent (Ashdown *et al*, 1936). There are three regions of continuous absorption with maxima at 1594, 1449 and 1202A (Wagner & Duncan, 1953) and very weak band system is found between 1800 and 1900A.

Photolysis

Currie *et al* (1963) photolyzed cyclopropane at 1470A and found that a large amount of ethylene was produced. From analysis of the deuterated material, they showed that the production is attributable to direct primary decomposition of $c\text{-}C_3H_6$ but not to the successive chemical reactions of its photofragments. Currie *et al* (1963) indicates the following primary processes in order of decreasing importance:

$$c\text{-}C_3H_6 \longrightarrow CH_2^{(++)} + C_2H_4, \qquad \longrightarrow C_3H_4 + H_2 \qquad \text{and} \longrightarrow C_3H_5 + H.$$

These results, however, appear to need modification on the ground of the more refined experiment performed by Scala & Ausloos (1968), in which they rejected the existence of molecular hydrogen and allyl radical (C_3H_5) as significant primary photofragments. Alternative, more sophisticated, routes were proposed as follows

$$c\text{-}C_3H_6 \longrightarrow CH_2CH_2CH_2 \text{ (trimethylene)} \longrightarrow CH_2 + C_2H_4$$

intermediate state

(propylene)*, very short lifetime

$$CH_3 + C_2H_3$$

$$CH_3 + C_2H_2 + H$$

and $c\text{-}C_3H_6 \longrightarrow C_3H_5^* + H \longrightarrow C_3H_4 + H + H.$

Their overall processes are:

			1470A	1236A
$c\text{-}C_3H_6 \longrightarrow C_2H_4 + CH_2$	Φ_1			0.44
$CH_3 + C_2H_2 + H$	Φ_2	$\left. \begin{array}{c} \\ \\ \end{array} \right\} \Phi_1/\Phi_2 \sim 4$		
$C_3H_4 + H + H$.				0.44

2.17 *Methylenecyclopropane* $\left(MCP,\ CH_2\!=\!C\!\!\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array}\right)$

Absorption

There appear to be no available data on absorption.

Photolysis

Direct (2537A) and mercury-sensitized photolysis for methylenecyclopropane were first carried out by Brinton (1968), who found acetylene and ethylene as major

[++] It was presumed by Dhingra & Koob (1971) that at 1236A the methylene radicals were mostly created in a singlet state.

products in nearly equal amounts and in addition small amount of allene. He postulated the primary processes as follows

$$MCP + 2537A \longrightarrow C_2H_2 + C_2H_4 \qquad \Phi_1$$
$$CH_2 + C_3H_4 \text{ (allene)} \qquad \Phi_2,$$

where Φ_1 was shown to occupy the fraction as much as 90% of the total decomposition.

The photolysis at the shorter wavelengths (1470 and 1236A) was performed later by Hill & Doepker (1972b). The primary processes and the yields obtained with MCP were as follows

	1470	1236A
$MCP + h\nu \longrightarrow C_4H_4$ (vinylacetylene) $+ H + H$	0.20	0.16
$CH_2 + C_3H_4$ (allene)	0.06	0.03
$C_2H_4 + C_2H_2$	0.37	0.27
$2C_2H_2 + H_2$	0.08	0.10
	$\Sigma = 0.71$	0.56[*]

Vinylacetylene is abundantly produced as has been observed in the photolyses for every other C_4H_6 compounds (1, 3-butadiene, 1, 2-butadiene, cyclobutene, 1-butyne and 2-butyne). That the process involves the elimination of two hydrogen atoms (not molecular hydrogen) was demonstrated by the fact that pressure stabilization effect was not found for the yield of vinylacetylene process; if $C_4H_6 \longrightarrow C_4H_4 + H_2$ should have happened, the resultant C_4H_4 molecules would possess enough energy to undergo further decompositions and, in consequence, the fragmentation and the pressure stabilization would have become two competing processes in determining the subsequent behavior of $C_4H_4^*$.

2.18 *Cyclobutene* $\begin{pmatrix} CH_2\text{—}CH \\ | \qquad || \\ CH_2\text{—}CH \end{pmatrix}$

There appear to be no available data on absorption.
Photolysis

It may be said that the gas-phase photolysis of cyclobutene was virtually initiated by Haller & Srinivasan (1966), although they actually executed the photolysis of 1, 3-butadiene, because they have shown that ethylene and acetylene—both of them were major products in the photolysis of 1, 3-C_4H_6—are most probably produced *via* an intermediate cyclobutene, that is,

$$1, 3\text{-}C_4H_6 \begin{pmatrix} CH_2 = CH \\ | \\ CH_2 = CH \end{pmatrix} \xrightarrow{h\nu} \begin{pmatrix} CH_2\text{—}\text{—}CH \\ | \qquad || \\ CH_2\text{—}\text{—}CH \end{pmatrix}^* \longrightarrow CH_2 = CH_2 + CH \equiv CH.$$
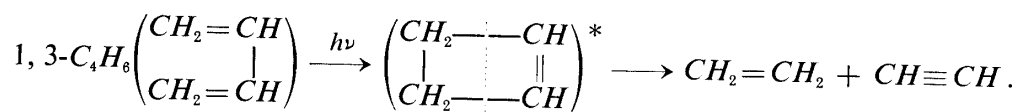
[*] The remaining portion which was not determined in the experiment could be attributable to a few radical processes that probably result in the production of the species as CH_3, C_2H_3 etc..

Direct photolysis for cyclobutene was first performed by DeLeon & Doepker (1971) in the various wavelength regions of 2600–2200, 1470, 1236 and 1067–1048A and the following decomposition processes were presented

$$cyclo\text{-}C_4H_6 \longrightarrow C_2H_2 + C_2H_4$$

$$C_4H_4 \text{ (vinylacetylene)} + 2H^{*)}$$

$$2C_2H_2 + H_2$$

$$C_2H_2 + C_2H_3 + H$$

$$C_2H_4 + C_2H \text{ (ethynyl)} + H$$
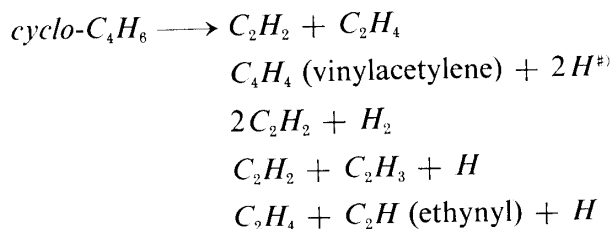
where the last three were considered to have minor contributions.

2.19 Methylcyclopropane $\left(\begin{array}{c} CH_3 \\ | \\ CH \\ CH_2 \triangle CH_2 \end{array} \right)$
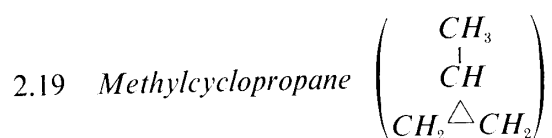
Absorption

It was only briefly reported that the spectrum for methylcyclopropane was photographed from 2400 to 1625A and that two narrow bands appeared at 2067 and 2022A superposed on a continuum absorption (Wagner & Duncan, 1953). Any other information (*e.g.*, quantitative values of the absorption strengths or graphic representation of the absorption feaure, or more simply λ_{max}, ε_{max} etc.) was not presented in it.

Photolysis

The sole experiment which has investigated photodecomposition processes for methylcyclopropane is the one by Doepker (1969) at 1470 and 1236A, in which he postulated the following three primary processes

$$\begin{array}{c} CH_3 \\ | \\ CH \\ CH_2 \triangle CH_2 \end{array} \longrightarrow \begin{cases} H_2 + C_4H_6^* \\ CH_4 + C_3H_4 \text{ (allene and/or propyne)} \\ [CH_3CH(CH_2)_2]^* . \end{cases}$$
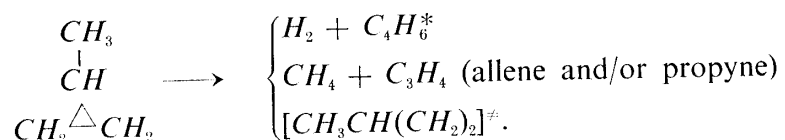
The first $C_4H_6^*$ was anticipated surely to decompose into the species like C_2H_2, C_2H_4 and C_3H_4. This process, together with the second, however, were considered as minor events. Nearly 90% of the photolytic products was suggested to originate in the fragmentation of a diradical intermediate, with the following modes presented as plausible.

$$[C_4H_8]^* \longrightarrow CH_2 + C_3H_6^*$$

$$CH_3 + C_3H_5^*$$

$$2H + 1,3\text{-}C_4H_6$$

$$C_2H_4 + C_2H_4^* .$$

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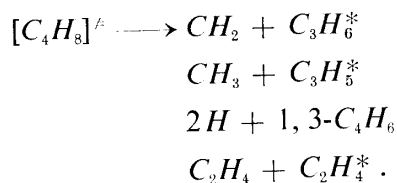
*) The decomposition is energetically forbidden in the 2600–2200A region. Alternatively, in such a low energy region, it was suspected that the substantial portion of the absorbed photons may contribute to isomerization (*e.g.*, to $1,3\text{-}C_4H_6$).

The species denoted by asterisk may or may not suffer a further decomposition and if it should happen, these would be

$$C_3H_6^* \longrightarrow H_2 + C_3H_4$$
$$CH_3 + C_2H_3$$
$$C_3H_5^* \longrightarrow H + C_3H_4$$
$$C_2H_4^* \longrightarrow C_2H_2 + H_2$$
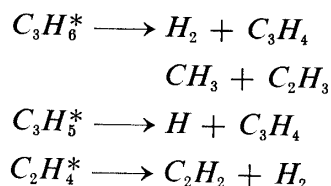
as is readily understood from the knowledge previously obtained with such compounds.

So far we have been describing the absorption features and the primary photo-decomposition processes for a number of familiar hydrocarbons with carbon atoms less than four. There are some other compounds like those of butatriene ($CH_2=C=C=CH_2$), cyclopropene $\left(\begin{array}{c} CH_2 \\ \triangle \\ CH \quad CH \end{array}\right)$, cyclobutadiene $\left(\begin{array}{c} CH—CH \\ \| \quad \| \\ CH—CH \end{array}\right)$, bicyclobutane $\left(CH_2 \diagdown \begin{array}{c} CH \\ | \\ CH \end{array} \diagup CH_2\right)$ and others whose existence is not inconceivable from stereo chemical reasons. These compounds, which, however, rarely appeared in the fore-going arguments on photolytic mechanisms, could be considered highly transient species having rather high heats of formation. The absorption features are far from certain.

Photodissociation of Radicals

Very often in the aeronomical problems relevant to planetary atmospheres, photo-dissociation of radical species, with or without the consciousness of its potential importance, was not taken into account. Indeed it is not always true that their lifetimes are much shorter for chemical reaction than for photodissociation. This is to be expected when radicals undergo UV dissociation in its comparatively long-ward wavelength region where the solar radiation rapidly increases in intensity, or when ambient atmospheric pressure is not high at the altitude level where the radical of our concern can be most abundantly found, or also when, even if the pressure is substantial, subsequent reaction of the radical with major atmospheric molecules is prohibited by some kinematic reasons.

Although the knowledge currently obtainable with radicals is very sparse and frag-mentary, we would like to briefly survey it by placing an emphasis on the photo-dissociation process. As is well known the band integrated absorption $\int k_\nu d\nu$ is equal to $\pi e^2/mc \cdot f$ where ν denotes the photon frequency, k_ν the absorption coefficient per unit frequency interval, f the oscillator strength of the band system responsible for specific transition, and the other symbols obey the conventional usage. Photo-dissociation rate β due to the solar UV is expressed as

$$\beta = \int I_\nu k_\nu d\nu$$

and if the solar radiation is not significantly changed in intensity over the frequency interval responsible for the absorption,

$$\beta = \langle I_\nu \rangle \cdot \pi e^2 / mc \cdot f$$

where $\langle I_\nu \rangle$ is the intensity of the solar UV around the center of the absorption. For successive convenience, we re-write the rate β in terms of the following specific units.

$$\beta(\text{sec}^{-1}) = 8.853 \times 10^{-21} \cdot f \cdot [\lambda(\text{Å})]^2 \cdot \langle I_\lambda \rangle$$

where, by $\langle I_\lambda \rangle$ is meant the average solar flux at the earth orbit, expressed in unit of photons/$(\text{cm}^2 \cdot \text{s} \cdot \text{Å})$.

2.20   CH

Three electronic transitions of CH are known in the near UV region: the $A^2\Delta \to X^2\Pi$, $B^2\Sigma^- \to X^2\Pi$, and $C^2\Sigma^+ \to X^2\Pi$ systems. These have band origins near 4315, 3850 and 3143A, respectively and the relative f numbers were found to be 1 : 0.62 : 1.26 by Linevsky (1967). Using the already known absolute f number of the first band system (Benett & Dalby, 1960), one can estimate the f number for $C^2\Sigma^+ \to X^2\Pi$ system to be 6.0×10^{-3}. Herzberg concluded from spectral studies that the upper state of this last transition was predissociated and succeeding studies (Hesser & Lutz, 1970, Elander & Hayden Smith, 1973) showed that the predissociation was nearly complete. Thus we can obtain the photodissociation rate by the solar UV at the earth's orbit as

$$\beta(CH \longrightarrow C + H) = 8.853 \times 10^{-21} \cdot 6.0 \times 10^{-3} \cdot 3143^2 \cdot 1.2 \times 10^{13}$$
$$= 6.3 \times 10^{-3} \quad \text{s}^{-1},$$

where the solar UV intensity data are taken from Donnelly & Pope (1973). The actual rate for CH dissociation could be slightly larger because all the higher states of CH are strongly predissociated (Herzberg & Johns, 1969) though their contributions to the totality would not be so large due to the greatly reducing intensities of the solar UV towards the shorter wavelengths.

2.21 CH_2

From the inspection of potential surfaces, Black et al (1975) states that "*there is no favorable channel for photodissociation until photon energies of about* 7.5 eV (1650A) *are reached.*" Herzberg (1961) first observed a diffuse band system around 1415A, tentatively assigning it to a transition $^3\Sigma_g^- \to {}^3\Sigma_u^-$, and suggested the rapid predissociation to occur, resulting in $CH + H$. Fortunately there is no significant fall in the solar emission lines in these wavelength region, which might otherwise have caused some difficulties in the actual evaluation process of photodissociation rate. These

facts, combined with the oscillator strength for the transition which was derived by Little & Pilling (1972/73), enable us to evaluate the rate as

$$\beta(CH_2 \longrightarrow CH + H) = 6.0 \times 10^{-8} \quad s^{-1} \quad at \; 1 AU.$$

The rate is quite small as is naturally expected from the high energy onset of photodissociation.

2.22 CH_3

Methyl radical is known to exhibit a strong but diffuse band absorption around 2160A which was identified as the first membeer (β_1) of a Rydberg series through the study of its far ultraviolet spectrum (Herzberg, 1961). Also it is known that this diffuseness stems from a predissociation to the repulsive state of $^1CH_2 + H$. The oscillator strength for this 2160A band $(\beta_1 \rightarrow X)$ was determined as 1.2×10^{-2} by Van den Bergh et al (1969). We can, in use of it, estimate the dissociation rate under the solar irradiation to be

$$\beta(CH_3 \longrightarrow {}^1CH_2 + H) = 2.88 \times 10^{-4} \quad s^{-1} \quad at \; 1 AU.$$

In a few articles on the molecular formation processes in interstellar region, a dissociation channel such as $CH_3 + h\nu \longrightarrow CH + H_2$ has been taken into account, although the theoretical grounds are uncertain.

2.23 C_2

C_2 has a rather high threshold energy (6.25 eV) for dissociation and *"it is quite reasonable to expect the photodissociation cross-section to be negligibly small below 10 eV* (Solomon & Klemperer, 1972)".

2.24 C_2H

Ethynyl is of importance for its intrinsic interest as an unusual σ-electron free radical. The threshold energy of its dissociation to $C_2 + H$ is 5.34 eV (2324A). Spin selection rule, however, constrains the first plausible mode of decomposition to $C_2H(X^2\Sigma) + h\nu \longrightarrow C_2(A^3\Pi) + H(1^2S)$ and, in consequence, the threshold should be practically higher. Experimentally, Graham et al (1974) reported that they were unable to find any absorption feature attributable to C_2H between 2500 and 1500A. Hence, the above dissociation, if it should happen, must be effective only at the wavelengths shortward of 1500A.

2.25 C_2H_3

The possible mode of photodecomposition of vinyl radical was briefly mentioned in the experimental work by Pacansky & Coufal (1979) which treated the dissociation of C_2H_5 radical encaged in Ar matrices. This is,

$$CH_2 = \dot{C}H + h\nu(\lambda < 2800A) \longrightarrow CH \equiv CH + H.$$

2.26 C_2H_5

Gaydon et al (1960) reported an absorption with the band maxima at 2220 and 2242A referring it to C_2H_5 radical. The result was, however, negatively accepted

by Wendt *et al* (1974), who observed no absorption feature attributable to C_2H_5 in these wavelength regions, but, instead, observed its possible absorption in the regions centered at 2260 and 2460A. The absorption spectra of ethyl radical were also studied at solute phase by Stevens *et al* (1972) and Hickel (1975) and the latter, from pulse radiolysis of C_2H_6 in water, obtained an absorption spectrum between 2700 and 2000A, monotonously increasing in intensity with increasing energy.

The dissociation process was recently studied by Pacansky & Coufal (1979) for the ethyl radical encaged in *Ar* matrices, suggesting molecular hydrogen elimination as the most probable process,

$$H_3C = \dot{C}H_2 + h\nu(\lambda < 2800\text{A}) \longrightarrow CH_2 = \dot{C}H + H_2 .$$

2.27 C_3

The 4050A bands of C_3 were first observed in comets (Swings, 1942) and first produced in the laboratory by a CH_4 discharge (Herzberg, 1942). These discrete bands have since been observed in a number of experimental sources: a story full of interest can be found in the book (Herzberg, 1975) as to the ultimate spectral identification to a linear triatomic molecule, C_3. As far as the photodissociation is concerned, the threshold is so high (~ 7.8 eV) that the practical importance to our purpose is greatly reduced.

2.28 C_3H_3

In flash photolyses of a series of compounds, $XCH_2C \equiv CH$ ($X = H$, Cl, Br, CH_3, C_2H_5, C_3H_7), Ramsay & Thistleswaite (1966) observed a new system of diffuse bands in the region of 3450 to 2900A, particularly intense between 3320 and 3120A. From its diffuseness, they interpreted the absorption to be a predissociation of the propargyl radical to $C_3H_2 + H$, *i.e.*,

$$\dot{C}H_2C \equiv CH \longrightarrow \ddot{C}HC \equiv CH + H$$
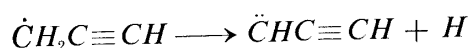
and set an upper limit for the dissociation energy as 3.73 eV.

2.29 C_3H_5

The new band system with the (0–0) band at 4083A was assigned to allyl radical ($CH_2 = CH\dot{C}H_2$) by the flash photolyses of nine allyl compounds and the predissociation into C_3H_4 (allene) + H was suggested (Currie & Ramsay, 1966). The absorption at the other wavelengths was reported in succession by Roginskii & Pshezheskii (1969) of the weak absorption at about 4500A and strong absorption at about 2320A. Of these wavelength regions, the oscillator strength for the last was investigated by Callear & Lee (1968) and Van den Bergh & Callear (1970) with the result being obtained as $f \sim 0.140$.

If we adopt as the average solar radiation intensity $\langle I_\lambda \rangle$, the value at 2250A—the wavelength position of maximum absorption of allyl—we can estimate β as

$$\beta_{C_3H_5(2250\text{A})} = 5.0 \times 10^{-3} \quad \text{s}^{-1} \quad \text{at 1 AU} .$$

It is, however, not certain into what fragments the excited allyl radical would dis-

socate. The safest assumption may be an elimination of hydrogen atom,

$$C_3H_5 \xrightarrow{2250A} H + C_3H_4^* \text{ (allene)}$$
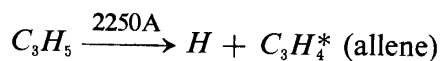
by analogy of the decomposition forms for most simple hydrocarbon radicals in this wavelength region and also by the photosensitized experiment due to Lossing *et al* (1956) in which a reaction

$$Hg(^3P_1) + C_3H_5 \text{ (allyl)} \longrightarrow Hg(^1S_0) + C_3H_4 \text{ (allene)} + H$$

$$(Hg(^3P_1 \longrightarrow {}^1S_0), \quad \Delta E = 2537A)$$
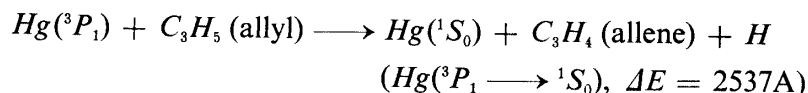
was claimed to be operative in order to account for the products.

The β-value as estimated above should, as a matter of fact, be regarded as giving a lower limit for photodissociation of allyl radical since absorptions at the longer wavelengths have not been taken into account in it. It would be premature in the present circumstances to speculate the net effect of the f value for those near-visible bands (probably very small) multiplied by the solar UV intensity (rapidly grows up with increasing wavelength).

2.30 C_3H_7

Pacansky & Coufal (1980) photolyzed diisobutyryl peroxide encaged in Ar matrices and suggested for a dissociation of i-C_3H_7

$$(CH_3)_2CH \xrightarrow{\lambda < 2800A} CH_3C \equiv CH \text{ (propyne)} + H + H_2 .$$
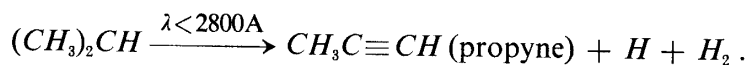
The absorption, compared with that belonging to ethyl radical which is centered at 2460A, is shifted to the slightly longer wavelengths.

2.31 C_4H_7

Spectra of α and β-methylallyl radical (higher homologues of allyl radical) were investigated by Callear & Lee (1968) and Van den Bergh & Callear (1970), both of which showed an absorption in the wavelength region centered at 2380A. It can be seen that the structure is essentially determined by its allylic structure, only with the methylation giving a shift slightly to the visible side.

Following the similar assumption adopted in Callear & Lee (1968) that the oscillator strength is the same as that for the 2250A band of allyl radical, the β-value will be estimated to be,

$$\beta_{\alpha-C_4H_7(2380)} = \beta_{\beta-C_4H_7(2380)} = 4.7 \times 10^{-3} \quad s^{-1} \quad \text{at } 1AU .$$

This 2380A band was also examined for β-C_4H_7 by Bayrakceken *et al* (1973) with the result being obtained as $\sigma(2380A) = 1.32 \, l/\text{mole} \cdot \text{cm} (= 5.05 \times 10^{-17} \text{cm}^2)$.

2.32 C_4H_9

Spectrum of t-butyl radical was taken by Parkes & Quinn (1975) between 2700 to 2200A. It was observed that a broad absorption band centered at 2300A (at the maximum, $\sigma = 5 \times 10^{-18} \text{cm}^2$) about 200A wide was superimposed on a weaker continuum that extends to 2700A.

Chapter III.   CHEMICAL REACTION PROCESSES

In this chapter we describe what kinds of chemical processes should effectively proceed in the upper atmospheres of the outer major planets and what kinds of simplifications in formulating chemical reaction models should be introduced thereby to make calculations feasible.

1.   Restrictions to chemical species

Even if the molecular species were limited to those within C_4-hydrocarbons, the number of the related molecules amounts to about 30 because of the various kinds of isomers, and the number, if it were extended to include quite short-lived free radicals, would be many times as increased as that (see, Tables 5 and 6). Therefore, it is evident that some policies are needed in order to make our calculation feasible.

We have escaped the difficulty by taking account of one molecular species alone for every group of the molecules that have a common chemical formula as $C_n H_m$. These 'representative' species have been chosen among the isomers as those that possess the lowest heat of formation (ΔH_f). Those representative species are usually the most popularly observed ones in the experiments under low temperature conditions (such species are marked by underlines in the Tables 5 and 6). And the data on photodissociation processes and chemical processes have been taken from the references dealing with such specified molecules, as far as possible. Only in these cases where no data exist, they have been substituted for by those of the other isomers. With respect to the above simplification, free radicals are not exceptional. On the contrary, available chemical data are much more fragmentary and quite frequently even the structural identifications of the radicals involved in reactions have not been made, with the chemical formulae alone indicated.

After all, current status of our knowledge on chemical reactions is almost to prohibit such calculations from being carried out, which incorporate every isomer separately as an independent member. Thus the results derived from the present calculations should be carefully interpreted with this underlying assumption being kept in mind, particularly for several large C_3- and C_4-compounds. For instance, by the species $C_3 H_6$ and $C_3 H_5$, if referred, are essentially meant propylene and allyl radical, respectively, since they appear the only reasonable products in the planetary environments alike, judging from the numerous laboratory experiments, although quite a small amount of other short-lived species are not necessarily excluded. Whereas by $C_4 H_8$, our calculations would be no more than indicating 'average' butene compound, because four butene isomers (1-, *cis* 2-, *trans* 2-, *iso*-butene), whch are, in ΔH_f, the heat of formation, not much different from each other, could all be observed with significant fractions under the actual experimental environments.

Anyway at the due place where each individual chemical reaction is to be described

Table 5. Structural formulae of hydrocarbons

	C_nH_{2n+2} alkane (paraffin)	C_nH_{2n} alkene (olefin)	C_nH_{2n} cycloalkane	C_nH_{2n-2} alkyne (acetylenic comp.)	C_nH_{2n-2} alkadiene (diolefinic comp.)	others
C_1	CH_4 methane -17.89(*)					
C_2	$CH_3 \cdot CH_3$ ethane -20.24	$CH_2{=}CH_2$ ethylene 12.50		$HC{\equiv}HC$ acetylene, ethyne 54.19		
C_3	$CH_3CH_2CH_3$ propane -24.82	$CH_3{-}CH{=}CH_2$ propylene propene 4.88	$CH_2 / H_2C\triangle CH_2$ cyclopropane 12.74	$CH_3C{\equiv}CH$ propyne methylacetylene allylene 44.32	$CH_2{=}C{=}CH_2$ allene propadiene 45.92	$CH_2 / CH\triangle CH$ cyclopropene (C_3H_4)
C_4	$CH_3CH_2CH_2CH_3$ n-butane -30.15; $CH_3CH(CH_3)CH_3$ isobutane 2-methylpropene -32.15	$CH_3{-}CH_2{-}CH{=}CH_2$ 1-butene (α-butylene) -0.03; $CH_3{-}CH{=}CH{-}CH_3$ cis 2-butene trans β-butylene $-1.67, -2.67$; $(CH_3)_2C{=}CH_2$ isobutene isobutylene 2-methylpropene γ-butylene -4.04	$H_2C{-}CH_2 / H_2C{-}CH_2$ cyclobutane 6.37; $CH_2 / H_2C\triangle CH{-}CH_3$ methylcyclopropane	$CH_3{-}CH_2{-}C{\equiv}CH$ 1-butyne ethylacetylene 39.48; $CH_3{-}C{\equiv}C{-}CH_3$ 2-butyne crotonylene dimethylacetylene 34.97	$CH_3{-}CH_2{-}C{=}CH_2$ 1,2-butadiene methylallene 38.77; $CH_2{=}CH{-}CH{=}CH_2$ 1,3-butadiene divinyl 26.33	$H{-}C{\equiv}C{-}C{\equiv}C{-}H$ diacetylene butadiyne biacetylene 113.0; $CH_2{=}CH{-}C{\equiv}CH$ (C_4H_4) vinylacetylene 1-buten-3-yne 72.80; $CH_2{=}C{=}C{=}CH_2$ (C_4H_4) butatriene; $HC{-}CH, HC{-}CH$ cyclobutadiene (C_4H_4); $CH_2{-}CH, CH_2{-}CH$ cyclobutene (C_4H_6) 31.00; $H_2C\langle\rangle CH_2$ CH bicyclobutane (C_4H_6); $CH_2{-}CH_2, CH_2{-}CH_2$ cyclobutane (C_4H_8); $H\rangle C{=}C\langle CH_2, CH_2$ methylenecyclo-propane (C_4H_6)

(*) ΔH_{f0}^0, standard-state heat of formation (kcal/mole)

Table 6. Structural formulae of hydrocarbons (radicals)

C_1

$C,$	$CH\equiv,$ methyne (methylidyne)	$CH_2=,$ methylene	$\underline{CH_3}$ methyl

C_2

$-C\equiv C-,$ (C_2) ethynylene	$CH\equiv C-$ (C_2H) ethynyl	$CH_2=C=,$ (C_2H_2) vinylidene (ethenylidene)	$-CH=CH-,$ (C_2H_2) vinylene (ethenylene)	$\underline{CH_2=CH-},$ (C_2H_3) vinyl (ethenyl)	$CH_3C\equiv$ (C_2H_3) ethylidyne	$CH_3 \cdot CH=$ (C_2H_4) ethylidene	$\underline{CH_3CH_2-}$ (C_2H_5) ethyl

C_3

$\left. \begin{array}{l} C_3,\ \underline{CH_3C\equiv C-},\ \text{1-propynyl} \\ \underline{CH\equiv CCH_2-},\ \text{2-propynyl (propargyl)} \end{array} \right\} (C_3H_3)$

$\left. \begin{array}{l} CH_2=CHCH=,\ \text{allylidene} \\ -CH_2CH=CH-,\ \text{propenylene} \\ -CH_2=C=CH_2,\ \text{allenyl} \end{array} \right\} (C_3H_4)$

$\left. \begin{array}{l} CH_2=C(CH_3)-,\ \text{isopropenyl} \\ CH_3CH_2C\equiv,\ \text{propylidyne} \\ CH_3-CH=CH-,\ \text{1-propenyl (propenyl)} \\ \underline{CH_2=CHCH_2-},\ \text{2-propenyl (allyl)} \\ \underset{H_2C-CH_2}{CH}\ \text{cyclopropyl} \end{array} \right\} (C_3H_5)$

$\left. \begin{array}{l} -CH_2CH_2CH_2-,\ \text{trimethylene} \\ (CH_3)_2C=,\ \text{isopropylidene} \\ CH_3CH_2CH=,\ \text{propylidene} \end{array} \right\} (C_3H_6)$

$\left. \begin{array}{l} CH_3CH_2CH_2-,\ n\text{-propyl} \\ \underline{(CH_3)_2CH-},\ \text{iso-propyl} \end{array} \right\} (C_3H_7)$

C_4

$\left. \begin{array}{l} CH_2=CHCH=CH- \\ \text{1,3-butadienyl} \\ \underline{CH_3CH=CHC\equiv} \\ \text{2-butenylidyne} \end{array} \right\} (C_4H_5)$

$\left. \begin{array}{l} CH_3CH=CHCH= \\ \text{2-butenylidene} \end{array} \right\} (C_4H_6)$

$\left. \begin{array}{l} (CH_3)_2C=CH-,\ \text{isobutenyl} \\ CH_2=C-CH_2-,\ \beta\text{-methylallyl} \\ \quad\ |\ CH_3 \quad (\text{methallyl}) \\ CH_3CH=CHCH_2-,\ \gamma\text{-methylallyl} \\ CH_3CHCH=CH_2,\ \alpha\text{-methylallyl} \\ CH_3CH=CHCH_2-,\ \text{2-butenyl (crotyl)} \\ CH_3CH_2CH=CH-,\ \text{1-butene-1 yl(1-butenyl)} \\ CH_2CH_2CH=CH_2,\ \text{1-butene-4 yl} \\ CH_3(CH_2)_2C\equiv,\ \text{butylidyne} \\ (CH_3)_2CHC\equiv,\ \text{isobutylidyne} \end{array} \right\} (C_4H_7)$

$\underset{H_2C}{\overset{H_2C}{\Big|}}{\overset{CH-}{\underset{CH_2}{\Big|}}},\ \text{c-butyl}$

$\left. \begin{array}{l} CH_3CH_2CH_2CH=,\ \text{butylidene} \\ CH_3CH_2C(CH_3)=,\ \text{sec-butylidene} \\ (CH_3)_2CHCH=,\ \text{isobutylidene} \end{array} \right\} (C_4H_8)$

$\left. \begin{array}{l} CH_3CH_2CH_2CH_2-,\ n\text{-butyl} \\ (CH_3)_2CHCH_2,\ \text{isobutyl} \\ C_2H_5CH(CH_3)-,\ \text{sec-butyl} \\ (CH_3)_3C,\ t\text{-butyl} \end{array} \right\} (C_4H_9)$

(Table 7 & its Remarks), the underlying working model and the bibliographic sources will be explicitly shown.

2. Atmospheric environments

The upper atmospheres to be discussed in the present work are well characterized by the quite *'chilly'* ($T \sim 150K$) and *'rarefied'* ($10^{-9} < p < 10^{-2}$ atm) conditions. This extremely low temperature constrains possible forms of reactions to those for which activation energies are hardly required. On the other hand, the broad coverage of the atmospheric pressure with altitude forces some of them to be described in terms of a transient expression that permits applications both in the high and low pressure limits.

In the following sections, we would like to enumerate the types of reactions which could possibly proceed under those severe atmospheric conditions.

3. Reactions to be expected in the upper atmospheres of the outer planets

i) *Reactions between radicals*

Extensive studies revealed such reactions to proceed with near-zero activation energies. Any other kind of reaction seems to require at least some amount of activation energy. Hence the occurrence of radical-radical reactions would be the most common and efficient step to the formation of the more complex molecules. They result in different products due to the different intermediate complexes depending upon the initial (energetical and stereochemical) conditions in reaction and also due to, from a stochastic viewpoint, the concentration of energies to a particular bond.

Shown below is the example of the various processes which are usually classified according to the form of the product species relative to the reactants,

$$C_2H_5 + C_3H_7 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_5H_{12}^* \overset{M}{\underset{k_\omega}{\longrightarrow}} C_5H_{12} \qquad \text{combination}$$

$$\longrightarrow C_2H_6 + C_3H_6 \qquad \text{disproportionation } (\Delta_1)$$

$$\longrightarrow C_2H_4 + C_3H_8 \qquad \text{disproportionation } (\Delta_2)$$

$$C_2H_5 + C_2H_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_4H_{10}^* \overset{M}{\underset{k_\omega}{\longrightarrow}} C_4H_{10} \qquad \text{combination}$$

$$\underset{k_d}{\longrightarrow} CH_3 + C_3H_7 \qquad \text{unimolecular decomposition}$$

$$\longrightarrow C_2H_6 + C_2H_4 \qquad \text{disproportionation}$$

$$H + C_3H_7 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_3H_8^* \overset{M}{\underset{k_\omega}{\longrightarrow}} C_3H_8 \qquad \text{combination}$$

$$\left. \begin{array}{l} \underset{k_d}{\longrightarrow} CH_3 + C_2H_5 \\ \underset{k_{d'}}{\longrightarrow} CH_4 + C_2H_4 \end{array} \right\} \text{unimolecular decomposition}$$

$$\longrightarrow H_2 + C_3H_6 \qquad \text{H-abstraction.}$$
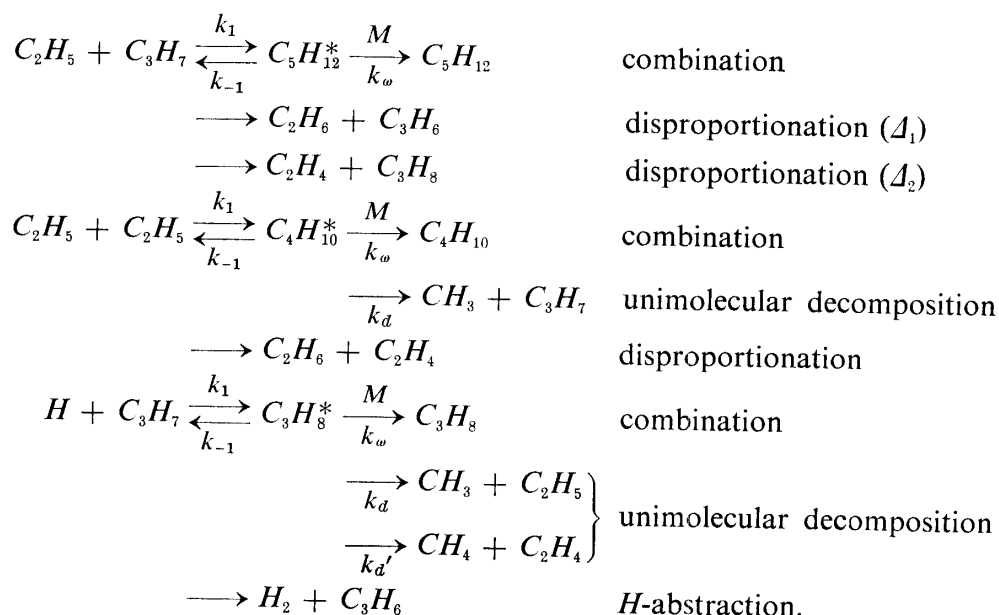
Here, by disproportionation is meant a reaction such as $R + R' \longrightarrow RH + R'(-H)$—this is usually distinguished in mechanism from an abstraction reaction which apparently resembles to the former. Indeed the actual rate coefficient for abstraction is much smaller than that for disproportionation. Redistribution of a pair of molecules by this disproportionation reaction is the most typical result obtained with radical reaction and would be frequently referred throughout this chapter. The ratio of the rate coefficient to that for combination is conventionally denoted by the symbol Δ. This value is known to be strongly influenced by the structure of radicals (such as 1-alkyl, 2-alkyl, 3-alkyl, allylic etc.) and influenced much less by temperatures (*e.g.*, Gibian & Corley, 1973). For example, mutual combination between two allylic radicals is more than 100 times as probable as mutual disproportionation (*i.e.*, $\Delta < 0.01$), while for combination between two alkyl radicals, Δ takes a value about ~ 0.14 for 1-alkyls, $0.6 \sim 0.8$ for 2-alkyls and $\geqslant 2$ for 3-alkyls.

Unimolecular decomposition here tentatively labeled is the process that works competitively to combination and its rate decreases with increase of the ambient pressure. The outcome is usually either returning back to the original reactant pair, or producing a pair of new radicals, or a pair of alkane and alkene. With increasing number of atoms constituting the reaction system, the decomposition rate into those new fragments would rapidly diminish due to the deconcentration of energy into a large number of vibrational modes, although the increase of the degrees of freedom may also produce a new decomposition channel. Simple estimates for these unimolecular rates are the purpose of the subsequent section. For such unimolecular rates and the combination rates, both of which depend on pressure, we have assumed the simplest form, *i.e.*, Lindemann's expression as is given below,

combination rate: $\quad k_1 \dfrac{k_\omega [M]}{k_d + k_\omega [M]}$, $\quad$ asymptotes $\begin{cases} k_1 \text{ as } [M] \to \infty \\ k_1 k_\omega / k_d \cdot [M] \text{ as } [M] \to 0 \end{cases}$

unimolecular
decomposition rate: $\quad k_1 \dfrac{k_d}{k_d + k_\omega [M]}$, $\quad$ asymptotes $\begin{cases} k_1 k_d / k_\omega [M] \text{ as } [M] \to \infty \\ k_1 \text{ as } [M] \to 0. \end{cases}$

It must be noted that our coverage of the pressure ranges under consideration is so large that there are not a few reaction systems to which the use of an expression in the high or low pressure limit alone is not pertinent. On the other hand, the adoption of a more accurate pressure-dependent formula based on more refined theories appears not compatible with the computational facilities available. This simplification may also be tolerated if one considers a variety of (implicit and explicit) assumptions included in the present research: assumptions of temperature profile and eddy diffusion profile *vs* altitude, and assumptions and/or simplifications introduced in the course of the modeling work of numerous elementary photo- and chemical reaction processes.

ii) *H addition reaction*

Addition of a free hydrogen is one of the processes which is likely to proceed under low temperature conditions as far as the partners are the unsaturates such as C_2H_4, C_2H_2, C_3H_6, C_4H_8 etc. (the first reaction, $H + C_2H_4 \longrightarrow C_2H_5$ is often used

as a standard when relative values of the rate constants are brought into absolute scale and has been extensively studied in the past: the experiments where particularly H_2 was used as the third-body can be found *e.g.*, in Girouard *et al* (1963), Baldwin *et al* (1966), Brown & Trush (1967), Cowfer *et al* (1971), and Teng & Jones (1972)).

Exceptionally small activation energies found for these systems, and abundances of the unsaturates, which were inferred from the earth-based infrared observations of the outer planets and Titan make the processes quite important. The importance is also obvious from that the radicals thus formed, such as C_2H_5 and C_2H_3, serve as a substantial source for the subsequent radical-radical reactions which eventually produce higher C_3- and C_4-hydrocarbons.

Some intermediates of these reactions decompose unimolecularly into a pair of products, provided that the ambient pressure is not so high that the stabilization of excited adduct is incomplete. For instance,

$$H + C_4H_8 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_4H_9^* \overset{k_\omega}{\underset{M}{\longrightarrow}} C_4H_9$$
$$k_d \searrow$$
$$CH_3 + C_3H_6 .$$
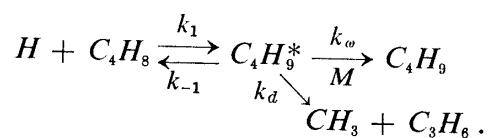
The products usually consist of a radical and an unsaturated stable molecule.

In the cases other than described above, the activation energies are rather high in general so that the inclusion of such reactions would be practically of no use. This is true for almost all the systems like H + saturated molecule (alkane), or free radical (other than atomic hydrogen) + stable molecule. There are, however, exceptions. This is the case if the reactant radical should happen to be a highly reactive one such as CH or C_2.

iii) *Reaction by excited state species*

The molecules excited to a metastable state usually have a considerable amount of energy, so that they often show high reactivity. This is true for CH_2^* and $C_2H_2^*$ of the molecules under our consideration.

It has long been known that singlet methylene inserts to the carbon-hydrogen bond or adds to the double bond of alkanes and alkenes (*e.g.*, see, DeMore & Benson, 1964). Such excited adducts would further undergo collisional stabilization, dissociation and isomerization. On the other hand, triplet methylene (the ground state of methylene) appears to be inactive to most of hydrocarbons. To be more correct, it is quite selective in reaction, as is seen from the fact that triplet (not singlet) methylene can be effectively removed by oxygen molecule from reaction vessels. This low reactivity of triplet methylene towards CH bonds was explained as due to the high activatian energies involved (Carr, 1972) and it was argued by Lee *et al* (1970) that the efficiency of the reaction with methane is not more than 10^{-9}. Furthermore, exceedingly small rates of reaction with H_2 were reported. The upper limit has been obtained to be 5×10^{-14} by Brown *et al* (1970) and 5×10^{-15} by Pilling & Robertson (1977). These are negligibly small values when compared with the known reactions for singlet methylene, all of which show the rates of the orders of $10^{-11} \sim 10^{-12}\,cm^3\,s^{-1}$.

Although the methylene's reactions were extensively studied in the past (DeMore & Benson, 1964), it was not until the 1970's that the absolute rate values were measured. The first important measurements were carried out by Braun *et al* (1970) about a series of the processes indispensable to the present study,

$$^3CH_2 + {}^3CH_2 \longrightarrow C_2H_2 + H_2 \qquad\qquad 5.3 \times 10^{-11}\, cm^3 s^{-1}$$

$$^1CH + H_2 \longrightarrow CH_3 + H \qquad\qquad 7.0 \times 10^{-12}$$

$$\longrightarrow {}^3CH_2 + H_2 \qquad\qquad < 1.5 \times 10^{-12}$$

$$^1CH_2 + CH_4 \longrightarrow C_2H_6^* \longrightarrow CH_3 + CH_3 \qquad 1.9 \times 10^{-12}$$

$$\longrightarrow {}^3CH_2 + CH_4 \qquad\qquad 1.6 \times 10^{-12}$$

$$^1CH_2 + He \longrightarrow {}^3CH_2 + He \qquad\qquad 3.0 \times 10^{-13}$$

$$^3CH_2 + H_2 \longrightarrow CH_3 + H \qquad\qquad 5.0 \times 10^{-14}$$

$$^3CH_2 + CH_4 \longrightarrow CH_3 + CH_3 \qquad\qquad 5.0 \times 10^{-14}.$$
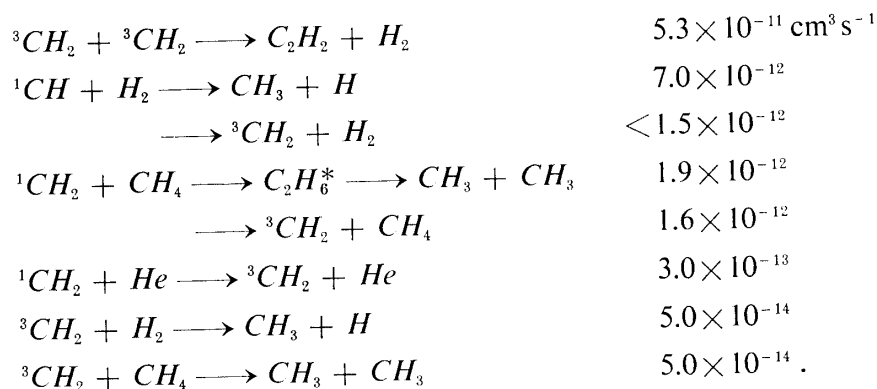
Since then, several studies of the reactions involving methylene radical have followed:

$$^3CH_2 + H_2 \longrightarrow CH_3 + H$$
Pilling & Robertson (1977)

$$^1CH_2 + C_3H_8 \longrightarrow \begin{cases} n\text{-} \\ i\text{-} \end{cases} C_4H_{10}^*$$
Bell (1971)
Halberstadt & Crump (1972/73)

$$^3CH_2 + CH_3 \longrightarrow C_2H_4 + H$$
Laufer & Bass (1975),
Diaz & Doepker (1977)

$$^3CH_2 + C_2H_2 \longrightarrow C_3H_4$$
Laufer & Bass (1974)
Pilling & Robertson (1977)

$$^1CH_2 + C_2H_6 \longrightarrow C_3H_8^*$$
Halberstadt & Crump (1972/73)

$$^1CH_2 + C_3H_6 \longrightarrow C_4H_8^*$$
Topor & Carr (1973)

$$^1CH_2 + \begin{cases} n\text{-} \\ i\text{-} \end{cases} C_4H_{10} \longrightarrow \begin{cases} n\text{-} \\ i\text{-}C_5H_{12} \\ neo\text{-} \end{cases}$$
Halberstadt & Crump (1972/73)

$$^1CH_2 + n\text{-}C_5H_{12} \longrightarrow C_6H_{14}$$
Topor & Carr (1973)

In the foregoing chapter it has been stated that acetylene will form a long-lived state in the upper atmospheres of the outer planets by *UV* irradiation. It is quite probable, from analogy of the mechanisms inferred in the laboratory experiments, that this excited species $C_2H_2^*$ may play an important role in forming higher hydro-carbons or polymeric products—vinylacetylene, benzene, cuprene. But the actual mechanism is still a matter of debate (see, Chap. II, 2.8).

Against those reactions of $C_2H_2^*$ with the unsaturates that result in higher mole-cular compounds, the reaction with hydrogen molecules, a predominant species in the atmosphere, serves to stabilize the excited acetylene

$$C_2H_2^* + H_2 \longrightarrow C_2H_2 + H_2.$$
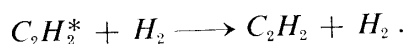
But the scheme, in reality, may not be correct since another possibility is also being suggested,

$$C_2H_2^* + H_2 \longrightarrow C_2H_3 + H.$$

Which branch would be more probable in this reaction is quite uncertain, only with the reaction rate being measured to be $8.3 \times 10^{-11} \text{cm}^3 \text{s}^{-1}$ (Becker *et al*, 1971). Another important route of $C_2H_2^*$ would be a radiative decay (fluorescence). Becker *et al* (1971) observed a fluorescence in the acetylene system irradiated by 1236A *UV* and estimated the lifetime of $C_2H_2^*$ to be $6.2 \times 10^{-6} \text{sec}$, arguing the emission for from $C_2H_2^*$ but against from C_2H^*.

Finally it must be born in mind that radiative processes are generally not important in our case (contrasted to the case of the interstellar molecular formations), except for the one particular case of ion-neutral reaction such as $H^+ + H_2 \longrightarrow H_3^+ + h\nu$. Significant alteration of the ion density profiles at the topside planetary ionospheres was confirmed to occur by the present and several previous researches with the change of this rate coefficient (see, Remark I in Table 8).

4. RRK Theory

Except for the types of reactions like disproportionation and abstraction, the reaction scheme may be written as follows

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB^* \overset{M}{\underset{k_\omega}{\longrightarrow}} AB$$
$$\overset{}{\underset{k_2}{\longrightarrow}} A' + B'$$
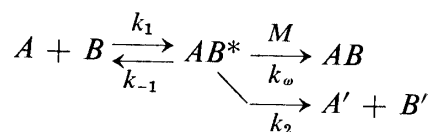
where A and B are the two colliding molecules, AB^* the activated complex, k_ω the rate coefficient of stabilization by molecule M and k_i the rate coefficient of the specific reaction designated by i.

Our primary concern in this section is a simple evaluation for the unimolecular rate k_{-1} or k_2 in such a form compatible to the Lindemann's expression as mentioned in the previous section. This may be partly attained if the falling off curve *vs* pressure or the rate coefficient in the low pressure limit was known experimentally. It, however, is not so in general. Only exceptions are some reactions involving two small molecules where the pressure conditions can produce a deviation of the combination rate from the limiting high pressure value. In the present problem

energy diagram

reaction coordinate
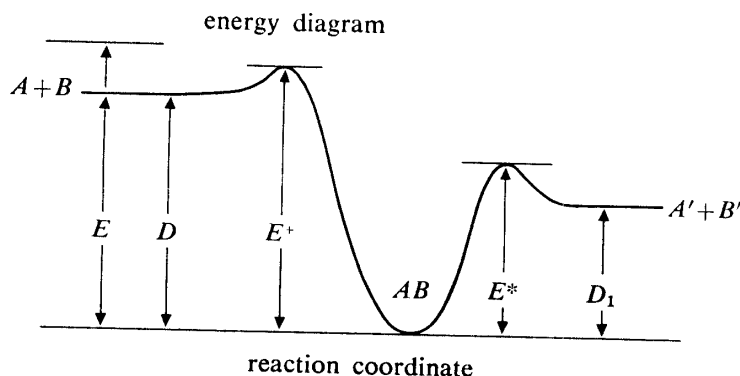
which covers extremely rarefied atmospheric levels such as $\sim 10^{-9}$ atm, even the excited adducts consisting of as much as $12 \sim 14$ atoms would not be fully stabilized, depending upon the *very* unimolecular processes involved.

The *RRK* theory (Rice & Ramsperger 1927, 1928, Rice, 1928, Kassel, 1928) of unimolecular decomposition relates the rate constant k_E to the internal energy content E of the molecule AB. This is given by

$$k_E = \nu \cdot \left(\frac{E - E^*}{E} \right)^{s-1},$$ (III–1)

where E^* represents the critical energy necessary for decomposition, s the number of effective oscillators in the conceptual model of *RRK*, and ν the frequency factor for the specific unimolecular fragmentation (roughly $\sim 10^{13}$ sec^{-1}). This is interpreted as the rate at which the total energy E possessed by the molecule with s oscillators is concentrated with a greater fraction than E^* to one particular bond (whose dissociation is characterized by E^*) and as a result the molecule dissociates.

The probability $f(\varepsilon)d\varepsilon$ that s oscillators have, in totality, energy in the range from ε to $\varepsilon + d\varepsilon$ is represented in the statistical equilibrium as

$$f(\varepsilon) = \frac{\varepsilon^{s-1}}{(s-1)!(kT)^s} e^{-\varepsilon/kT}.$$ (III–2)

Hence the average energy E_{av} of the molecule which can participate in reaction is given by

$$E_{av} = \int_{E^+}^{\infty} E \cdot f(E - D) k_E dE \Big/ \int_{E^+}^{\infty} f(E - D) k_E dE,$$ (III–3)

where E^+ is the energy of activation measured from the ground state of AB—for free radical reactions it is essentially equal to the dissociation energy D of the molecule AB.

Then the above integration reduces to a form

$$E_{av} = D + \frac{\displaystyle\int_0^{\infty} x^s ((x + D - E^*)/(x + D))^{s-1} e^{-x/kT} dx}{\displaystyle\int_0^{\infty} x^{s-1} ((x + D - E^*)/(x + D))^{s-1} e^{-x/kT} dx}.$$ (III–4)

Approximately this takes a value of $D + skT$, although the actual evaluation has been made more accurately based on a numerical integration. Inserting the expression again into eq. (III–1), one can obtain the average decomposition rate (k_2) of those molecules responsible for unimolecular reaction, *i.e.*,

$$k_2 = \nu \cdot \exp((s - 1)\ln(1 - E^*/E_{av})).$$ (III–5)

The modeling parameter s, which indicates the number of the active vibrational modes whose energies are available to decomposition, is empirically taken as a value from about two-thirds to half of the degrees of vibrational freedom for united

molecule. That is, $s=(1/2\sim2/3)\cdot(3N-6)$, where N is the number of atoms constituting the molecule. The values of s deduced from experiments reveal it to be a decreasing function with decreasing temperature. At the present calculations, s has been fixed at the value of $1/2\cdot(3N-6)$ for most of the reactions for which no experimental information on the parameter is obtainable.

The knowledge of the frequency factor ν and the energy E^* is often obtained from pyrolysis experiment for the stable molecule AB where the decomposition rate into the products $A'+B'$ is represented usually as $\nu=Ae^{-E^*/kT}$. Otherwise, a suitable value has been given to the frequency factor according to the compilations which had been arranged by inspecting a number of pyrolysis data beforehand. They are as follows,

a) $S \longrightarrow R + R$ $\qquad A \sim 10^{16.5} \quad s^{-1}$

b) $S \longrightarrow H + R$ $\qquad A \sim 10^{14.3}$

c) $S \longrightarrow S + S$ $\qquad A \sim 10^{14.6}$

d) $R \longrightarrow R + S$ $\qquad A \sim 10^{13.2}$

e) $R \longrightarrow H + S$ $\qquad A \sim 10^{13.5}$
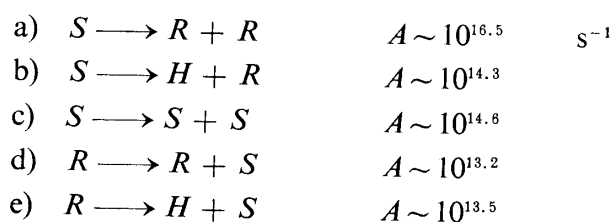
where A shows the representative frequency factor observed at the respective group concerned. Here, H denotes the free hydrogen, R the other radicals and S the other (stable) compounds—the estimated for the cases b) and c) may be less accurate than for the others due to the paucities of data.

For radical decompositions, the energy E^* (in case where no experimental information is available) does not cause any difficulty since it is essentially equal to dissociation energy, whereas for the decompositions belonging to other types, estimates of the activation energy are not necessarily straightforward. In some cases, however, it could be inferred from that for the reverse reaction $(A' + B' \longrightarrow A'B'^*)$.

The stabilization rate k_ω, has been estimated as $k_\omega=\varepsilon\cdot Z$, where Z is the collision number between the excited adducts and the dominant ambient molecules (H_2). The stabilizing efficiency ε, has been uniformly set to 0.1 for a variety of reaction systems except for those of which the information is experimentally available. And the collision number has been evaluated according to the expression given below

$$Z=7.89\times10^{-11}\frac{(R_A+R_B)^2}{\sqrt{\mu}} \qquad cm^3\cdot s^{-1} \qquad \text{(III–6)}$$

where, R_A and R_B are the molecular radii in Ångstrom and μ, the reduced mass of colliding system in atomic mass unit—this value has to be halved for a collision between identical particles.

5. Limiting High Pressure Value (k_1)

The two body reaction rate is the one that would be just obtained if the measurement has been carried out in the quite high pressure region. Accordingly the rate is unconditionally useful for our purpose as far as the reaction could be regarded

as belonging to its own high pressure region (though there are reaction systems of which the rates were reported by different experimenters with a difference of three to four orders of magnitude). This would be easily realized for those reactions where the system consists of a considerable number of atoms. In the case where the rate coefficient is not exactly known there may be several ways to guess it.

One is to assign a value identical to the known rate of the reaction system for which structural similarities are chemically expected. To such procedures a serious error is incidental since it has not been based on firm physical grounds.

Another method is to rely on the statistical theory which assumes an equilibrium between reactants and activated complex. Provided that, because of the low temperature, the energies are distributed only within the translational and rotational motions, the rate would be given as follows,

$$k_1 = \frac{kT}{h} \frac{Q_{tr}^{\neq}}{Q_{tr}^A Q_{tr}^B} \frac{Q_r^{\neq}}{Q_r^A Q_r^B} e^{-E_0/kT},$$

where, Q_{tr}, Q_r are the partition functions for translational and rotational motions, respectively, and superscript$^{\neq}$ designates tne activated complex. By using this formula, we have estimated the reaction rate k_1 for several reactions, assuming the intermediates to be '*rigid*' (*i.e.*, in estimating Q_r, use is made of the rotational constants pertaining to the ground state). It, however, must be born in mind that this simple way of evaluation may give rise to a too small rate coefficient for such reactions as between moderately large radicals, as is seen if a comparison is made with the corresponding data available by experiments.

As for the third method, there is a relation known as '*cross combination rule*' which states that the inter-radical combination rate is very nearly the geometric mean of the self-combination rates for these radical pairs (Kerr & Trotman-Dickenson, 1959, Bowles *et al*, 1962, Terry & Futrell, 1967); namely, when the self-combination rates are given as

$$R_1 + R_1 \xrightarrow{k'} R_1 R_1 \quad \text{and} \quad R_2 + R_2 \xrightarrow{k''} R_2 R_2$$
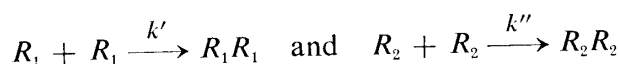
the rule predicts the combination rate for the inter-radical reaction

$$R_1 + R_2 \xrightarrow{k} R_1 R_2$$
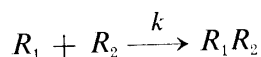
to be given by

$$k = 2\sqrt{k'k''} .$$

Although this relation is of an empirical nature, its approximate validity has been confirmed in a considerable number of reaction systems and it appears quite useful in the present study in assessing rate coefficients for the unknowns.

6. Ion-neutral Reactions

Radio occultation experiments performed by the planetary probes such as the Pioneers and the Voyagers are currently what is all, thereby to deduce any information about the extremely tenuous parts of the atmospheres (ionospheres). It is true that the published results (see the references in Table 4) contain some strange aspects which are not easily reconciled with the *common sense of aeronomy*. Nevertheless, calculations dealing with netural species alone may lose some valuable restricting conditions which might otherwise have imposed on the study of the upper atmospheres. Of course, the *UV* fluxes which are capable of ionizing the molecules of our interest are far less than those available for dissociation. It is, however, not to be claimed in our present CH_4 chemistry that their contributions would be of minor one and in consequence need not be incorporated into calculation, because the effects of ionization and subsequent ion-neutral reactions upon the eventual density profiles are quite selective on species as well as on altitude levels. This would be more thoroughly discussed in later chapters.

Ion-molecule reactions do not specifically cause such a difficulty as found in the neutral reactions, where rather a sophisticated procedure was required for describing the rate coefficient of combination process. This is due to the fact that ionization does not reach the deeper levels with higher pressures, even if transport process is incorporated, since ions react with neutrals or with electrons much faster than it being transported down to those altitudes. Hence the description in terms of a binary reaction rate will suffice for most of the reactions.—an exception is the reaction, $H^+ + H_2 + H_2 \longrightarrow H_3^+$, which could affect proton densities depending upon how CH_4 distributes with altitude, that is, upon how eddy diffusion profile is presumed with altitude. This is not the case if we should consider negative ion chemistry, which is likely to occur at deeper altitude levels, possibly initiated by three-body associations of electrons with neutrals from analogy of the terrestrial ionosphere.

There are several works that have treated ion chemistry in the Jovian upper atmosphere (see, Chap. I., § 2). A noticeable fact is that the prevaling hydrocarbon ions derived from those calculations often differ from each other. An ion does not stand out as a dominant one so far as it reacts with the surrounding abundant neutrals. Thus the different results of the ion densities obtained by different investigators are largely explained by the *very* reaction processes which were incorporated into calculations. In this respect, the present study tries to take into account all the reactions of ions not only with the usual major constituents (H_2, CH_4) but also with those neutrals expected to be abundant (C_2H_2, C_2H_4, C_2H_6). The ion-molecule reactions taken into calculation are listed in Table 8, which are from Huntress (1977), unless the explicit references are given.

One of the difficulties we have met in the course of the modeling procedure for hydrocarbon ions is the complete lack of knowledge on the product distributions which result from dissociative recombinations between an electron and those ions

with three or more carbon atoms (C_nH_m, $n \geqslant 3$). For such unknown branches, we have simply assumed that they will end up in the formation of atomic hydrogen and the rest (*i.e.*, $C_nH_m^+ + e \longrightarrow C_nH_{m-1} + H$, for $n \geqslant 3$). This may be partly justified if one considers several examples of the known reactions of this kind ($n \leqslant 2$). However, in the case where such a simplified assumption on the redistribution of atoms in recombination is not pertinent, the products obeying the other formats have been assumed—*e.g.*, $C_3H_{11}^+ + e \longrightarrow C_3H_8 + H + H_2$.

Table 7. Neutral reaction rate

	$k^{+)}$	k_{-1} (or k_d)	k_ω	Remarks & References
1)* $H + H + H \longrightarrow H_2 + H$	$8.1(-31)/T^{0.5}$			Kondrat'ev (1967)
2)* $H + H + H_2 \longrightarrow H_2 + H_2$	$2.5(-31)/T^{0.6}$			Trainor *et al* (1973)
3) $H + C \longrightarrow CH + h\nu$	$8.5(-22)/T^{1.2}$			Klemperer (1971)
4) $H + CH \longrightarrow C + H_2$	$1.0(-14)$			Solomon &
				Klemperer (1972)
5)* $H + CH_3 + M \longrightarrow CH_4$	$1.2(-22)/T^2$			*I*, Troe (1977)
6) $H + C_2H_2 \longrightarrow C_2H_3^*$	$9.2(-12)e^{-1210/T}$			*II*
7) $\longrightarrow H_2 + C_2H$	$1.3(-12)e^{-1800/T}$			Panfilov (1964)
8) $H + C_2H_3 \longrightarrow H_2 + C_2H_2$	$2.5(-11)$			*III*, Keil *et al* (1976)
9) $H + C_2H_4 + M \longrightarrow C_2H_5$	$9.1(-13)$	$10^{7.2}$	$7.7(-11)$	*IV*
10) $H + C_2H_5 + M \longrightarrow C_2H_6$	$6.0(-11)$		$7.8(-11)$	*V*
11) $\longrightarrow CH_3 + CH_3$		$10^{9.4}$		*V*
12) $\longrightarrow H_2 + C_2H_4$	$3.0(-12)$			*V*
13) $H + C_3H_3 + M \longrightarrow C_3H_4$	$1.0(-11)$	$10^{5.1}$	$9.1(-11)$	*VI*
14) $H + C_3H_4 + M \longrightarrow C_3H_5$	$1.1(-11)e^{-1000/T}$		$9.1(-11)$	*VII*
15) $\longrightarrow CH_3 + C_2H_2$		$10^{5.6}$		*VII*
16) $H + C_3H_5 \longrightarrow C_3H_6$	$2.0(-11)$			*VIII*
17) $\longrightarrow CH_3 + C_2H_3$	0			*VIII*
18) $\longrightarrow H_2 + C_3H_4$	$1.4(-11)$			*VIII*
19) $H + C_3H_6 + M \longrightarrow C_3H_7$	$9.0(-12)e^{-630/T}$	10^5	$9.0(-11)$	*IX*
20) $\longrightarrow H_2 + C_3H_5$	$2.9(-12)e^{-1260/T}$			Panfilov (1964)
21) $H + C_3H_7 + M \longrightarrow C_3H_8$	$2.0(-11)$		$8.3(-12)$	*X*
22) $\longrightarrow CH_3 + C_2H_5$		$10^{5.5}$		*X*
23) $\longrightarrow CH_4 + C_2H_4$		$10^{5.3}$		*X*
24) $\longrightarrow H_2 + C_3H_6$	$9.0(-12)$			*X*
25) $H + C_4H_2 + M \longrightarrow C_4H_3$	$2.2(-13)$	$10^{5.3}$	$1.0(-10)$	*XI*
26) $H + C_4H_3 + M \longrightarrow C_4H_4$	$2.0(-10)$		$1.0(-10)$	*XII*
27) $\longrightarrow C_2H_2 + C_2H_2$		10^7		*XII*
28) $\longrightarrow H_2 + C_4H_2$	$2.5(-11)$			*XII*
29) $H + C_4H_4 + M \longrightarrow C_4H_5$	$3.3(-12)$		$1.0(-10)$	*XIII*
30) $\longrightarrow C_2H_3 + C_2H_2$		$10^{6.1}$		*XIII*
31) $H + C_4H_5 + M \longrightarrow C_4H_6$	$2.0(-10)$		$1.0(-10)$	*XIV*
32) $\longrightarrow C_2H_2 + C_2H_4$		$10^{8.4}$		*XIV*
33) $\longrightarrow H_2 + C_4H_4$	$2.5(-11)$			*XIV*
34) $H + C_4H_6 + M \longrightarrow C_4H_7$	$2.3(-12)$		$1.0(-10)$	*XV*
35) $\longrightarrow C_2H_3 + C_2H_4$		$10^{5.7}$		*XV*
36) $\longrightarrow CH_3 + C_3H_4$	0			*XV*
37) $H + C_4H_7 + (M) \longrightarrow C_4H_8$	$2.0(-10)$		$(1.0(-10))$	*XVI*
38) $\longrightarrow CH_3 + C_3H_5$	0	$(<10^3)$		*XVI*
39) $\longrightarrow H_2 + C_4H_6$	$6.0(-11)$			*XVI*
40) $H + C_4H_8 + M \longrightarrow C_4H_9$	$3.4(-12)$	$10^{3.5}$	$6.5(-12)$	*XVII*
41) $\longrightarrow CH_3 + C_3H_6$	$4.8(-15)$			*XVII*

$^{+)}k$: in most reactions, the unit is cm^3s^{-1}. It shows the rate at which the particular activated complex is formed in reaction. The asterisks on the reaction numbers indicate combination rates, in units of cm^6s^{-1}, in the low pressure limit. For the few (radiative or nonradiative) self-decay processes of excited species, the unit is sec^{-1}.

$k_{-1}(k_d)$: the rate at which the excited adduct formed in reaction decomposes unimolecularly into initial reactants or into a pair of new fragments. The unit is sec^{-1}.

k: the stabilization rate in units of cm^3s^{-1}.

Table 7. *Continued*

	k	k_{-1} (or k_d)	k_ω	Remarks & References
42) $H + C_4H_9 + M \longrightarrow C_4H_{10}$	2.0(-10)	$10^{4.2}$	8.3(-11)	XVIII
43) $\longrightarrow CH_3 + C_3H_7$		$10^{4.0}$		XVIII
44) $\longrightarrow CH_4 + C_3H_6$		$10^{3.8}$		XVIII
45) $\longrightarrow H_2 + C_4H_8$	5.5(-10)			XVIII
46) $C + C \longrightarrow C_2 + h\nu$	1.0(-16)			Watson (1975)
47) $C + CH \longrightarrow C_2 + H$	4.0(-11)			Klemperer (1971)
48)* $C + H_2 + M \longrightarrow CH_2$	6.9(-32)			Husain & Young (1975)
49) $C + CH_3 \longrightarrow C_2H_2 + H$	1.5(-10)			XIX
50)* $C + CH_4 + M \longrightarrow C_2H_4$	1.5(-30)			XX
51) $\longrightarrow C_2H_2 + H_2$	9.1(-12)			XX
52)* $CH + H_2 + M \longrightarrow CH_3$	4.9(-31)			XXI
53) $CH + CH + M \longrightarrow C_2H_2$	2.3(-11)	10^6	7.3(-11)	XXII
54) $CH + CH_4 \longrightarrow C_2H_4 + H$	3.0(-10)			XXIII, Butler *et al* (1979)
55) $CH + C_2H_4 \longrightarrow C_3H_4 + H$	1.1(-10)			XXIV, Bosnali & Perner (1971)
56) $CH + C_3H \longrightarrow C_3 + CH_2$				XXV
57) $CH_2 + H_2 + M \longrightarrow CH_4$	1.0(-40)			XXVI
58) $\longrightarrow CH_3 + H$	1.0(-20)			XXVI
59) $CH_2 + CH_2 + M \longrightarrow C_2H_4$	0			XXVII
60) $\longrightarrow C_2H_2 + H_2$	5.3(-11)			XXVII
61) $CH_2 + CH_3 \longrightarrow C_2H_4 + H$	5.0(-11)			Pilling & Robertson (1975)
62) $CH_2 + C_2H_2 + M \longrightarrow C_3H_4$	4.0(-12)		8.5(-11)	XXVIII
63) $\longrightarrow C_3H_3 + H$		10^6		XXVIII
64) $CH_2 + C_2H_3 \longrightarrow C_3H_4 + H$	2.4(-10)			XXIX
65) $CH_2 + C_2H_5 \longrightarrow CH_3 + C_2H_4$	3.7(-11)			XXX
66) $^1CH_2 + He \longrightarrow CH_2 + He$	3.0(-13)			Braun *et al* (1970)
67) $^1CH_2 + H_2 \longrightarrow CH_2 + H_2$	1.5(-12)			Braun *et al* (1970)
68) $\longrightarrow CH_3 + H$	7.0(-11)			Braun *et al* (1970)
69) $^1CH_2 + CH_4 \longrightarrow CH_2 + CH_4$	1.6(-12)			Bell (1971)
70)* $^1CH_2 + CH_4 + M \longrightarrow C_2H_6$	1.2(-31)			XXXI, Braun *et al* (1970)
71) $\longrightarrow CH_3 + CH_3$	1.9(-12)			Halberstadt & Crump (1972/73)
72) $^1CH_2 + CH_4 \longrightarrow C_2H_2 + 2H_2$	0			XXXII
73)* $^1CH_2 + C_2H_4 + M \longrightarrow C_3H_6$	2.5(-29)			XXXIII
74) $\longrightarrow CH_3 + C_2H_3$	1.2(-10)			XXXIII
75)* $^1CH_2 + C_2H_6 + M \longrightarrow C_3H_8$	1.8(-30)			XXXIV
76) $\longrightarrow CH_3 + C_2H_5$	4.8(-12)			XXXIV
77) $^1CH_2 + C_3H_6 + M \longrightarrow C_4H_8$				XXXV
78) $\longrightarrow CH_3 + C_3H_5$	4.8(-11)			XXXV
79) $^1CH_2 + C_3H_8 + M \longrightarrow C_4H_{10}$		$10^{7.9}$	1.9(-10)	XXXVI
80) $\longrightarrow CH_3 + C_3H_7$	6.3(-12)			XXXVI
81) $CH_3 + CH_3 + M \longrightarrow C_2H_6$	5.2(-11)	$10^{3.9}$	2.6(-10)	XXXVII
82) $CH_3 + C_2H_3 + M \longrightarrow C_3H_6$	1.7(-11)	$10^{4.2}$	1.1(-10)	XXXVIII
83) $\longrightarrow CH_4 + C_2H_2$	1.7(-12)			XXXVIII
84) $CH_3 + C_2H_5 + M \longrightarrow C_3H_8$	3.7(-11)	$10^{1.8}$	9.6(-11)	XXXIX

Table 7. *Continued*

	k	k_{-1} (or k_d)	k_ω	Remarks & References
85) $\longrightarrow CH_4 + C_2H_4$	1.4(-12)			*XXXIX*
86) $CH_3 + C_3H_3 + M \longrightarrow C_4H_6$	1.0(-11)	$10^{3.4}$	1.0(-11)	*XL*
87) $CH_3 + C_3H_5 + M \longrightarrow C_4H_8$	2.3(-11)	$10^{2.4}$	9.5(-11)	*XLI*
88) $\longrightarrow CH_4 + C_3H_4$	5.3(-13)			*XLI*
89) $CH_3 + C_3H_7 \longrightarrow C_4H_{10}$	1.2(-11)			*XLII*
90) $\longrightarrow CH_4 + C_3H_6$	2.0(-12)			*XLII*
91) $CH_3 + C_4H_3 \longrightarrow C_5H_6$	1.0(-11)			*XLIII*
92) $\longrightarrow CH_4 + C_4H_2$	1.0(-12)			*XLIII*
93) $CH_3 + C_4H_5 \longrightarrow C_5H_8$	1.0(-11)			*XLIII*
94) $\longrightarrow CH_4 + C_4H_4$	1.0(-12)			*XLIII*
95) $CH_3 + C_4H_7 \longrightarrow C_5H_{10}$	9.5(-11)			*XLIV*
96) $\longrightarrow CH_4 + C_4H_6$	2.2(-12)			*XLIV*
97) $CH_3 + C_4H_9 \longrightarrow C_5H_{12}$	2.1(-11)			*XLV*
98) $\longrightarrow CH_4 + C_4H_8$	6.3(-12)			*XLV*
99) $C_2 + H_2 \longrightarrow C_2H + H$	1.38(-12)			*XLVI*, Pasternack & McDonald (1979)
100) $C_2 + CH_4 \longrightarrow C_2H + CH_3$	1.9(-11)			*XLVI*
101) $C_2 + C_2H_4 \longrightarrow 2C_2H_2$	3.26(-10)			*XLVI*
102) $C_2 + C_2H_6 \longrightarrow C_2H + C_2H_5$	1.6(-10)			*XLVI*
103) $C_2H + H_2 \longrightarrow C_2H_2 + H$	1.5(-13)			Laufer & Bass (1979)
104) $C_2H + CH_4 \longrightarrow C_2H_2 + CH_3$	0			*XLVII*
105) $C_2H + C_2H_2 \longrightarrow C_4H_2 + H$	3.1(-11)			Laufer & Bass (1979)
106) $C_2H + C_2H_6 \longrightarrow C_2H_2 + C_2H_5$	1.4(-16)			*XLVIII*
107) $C_2H + C_3H_4 \longrightarrow C_2H_2 + C_3H_3$	0			*XLIX*
108) $C_2H_2^* \longrightarrow C_2H_2 + h\nu$	1.6(5)			*L*
109) $\longrightarrow C_2H + H$	1.6(4)			*L*
110) $C_2H_2^* + H_2 \longrightarrow C_2H_3 + H$	8.3(-11)			*LI*
111) $C_2H_2^* + CH_4 \longrightarrow C_2H_2 + CH_3 + H$	3.1(-13)			*LII*
112) $C_2H_2^* + C_2H_2 \longrightarrow C_4H_2 + H + H$	3.1(-11)			*LIII*
113) $C_2H_2^* + C_2H_2 (+M) \longrightarrow C_4H_4$	0			*LIV*
114) $C_2H_3 + C_2H_2 + M \longrightarrow C_4H_5$	3.3(-13)	$10^{5.3}$	1.0(-10)	*LV*
115) $\longrightarrow C_4H_4 + H$	0			*LV*
116) $C_2H_3 + C_2H_3 \longrightarrow C_4H_6$	2.7(-10)			*LVI*
117) $\longrightarrow C_2H_2 + C_2H_4$	5.3(-12)			*LVI*
118) $C_2H_3 + C_2H_5 + M \longrightarrow C_4H_8$	8.4(-11)		9.5(-11)	*LVII*
119) $\longrightarrow CH_3 + C_3H_5$		$10^{6.8}$		*LVII*
120) $\longrightarrow C_2H_2 + C_2H_6$	3.1(-11)			*LVII*
121) $\longrightarrow 2C_2H_4$	5.7(-11)			*LVII*
122) $C_2H_3 + C_4H_3 \longrightarrow C_6H_6$	1.0(-11)			*XLIII*
123) $\longrightarrow C_2H_4 + C_4H_2$	1.0(-12)			*XLIII*
124) $\longrightarrow C_2H_2 + C_4H_4$	1.0(-12)			*XLIII*
125) $C_2H_3 + C_4H_5 \longrightarrow C_6H_8$	1.0(-11)			*LVIII*
126) $\longrightarrow C_2H_4 + C_4H_4$	1.0(-12)			*LVIII*
127) $C_2H_3^* \longrightarrow C_2H_2 + H$	1.0(6)			*LIX*
128) $C_2H_3^* + H_2 \longrightarrow C_2H_3 + H_2$	2.2(-11)			*LX*
129) $\longrightarrow C_2H_4 + H$	5.3(-12)			*LXI*
130) $C_2H_5 + C_2H_5 \longrightarrow C_4H_{10}$	6.6(-12)			*LXII*
131) $\longrightarrow C_2H_6 + C_2H_4$	8.6(-13)			*LXII*
132) $C_2H_5 + C_3H_5 \longrightarrow C_5H_{10}$	1.9(-11)			*LXIII*

Table 7. *Continued*

		k	k_{-1} (or k_d)	k_ω	Remarks & References
133)	$\longrightarrow C_2H_6 + C_3H_4$	7.6(-13)			LXIII
134)	$\longrightarrow C_2H_4 + C_3H_6$	2.1(-12)			LXIII
135)	$C_2H_5 + C_3H_7 \longrightarrow C_5H_{12}$	1.0(-11)			LXIV
136)	$\longrightarrow C_2H_6 + C_3H_6$	1.8(-12)			LXIV
137)	$\longrightarrow C_2H_4 + C_3H_8$	1.2(-12)			LXIV
138)	$C_2H_5 + C_4H_3 \longrightarrow C_6H_8$	1.0(-11)			XLIII
139)	$\longrightarrow C_2H_6 + C_4H_2$	1.0(-12)			XLIII
140)	$\longrightarrow C_2H_4 + C_4H_4$	1.0(-12)			XLIII
141)	$C_2H_5 + C_4H_5 \longrightarrow C_6H_{10}$	1.0(-11)			XLIII
142)	$\longrightarrow C_2H_6 + C_4H_4$	1.0(-12)			XLIII
143)	$\longrightarrow C_2H_4 + C_4H_6$	1.0(-12)			XLIII
144)	$C_2H_5 + C_4H_9 \longrightarrow C_6H_{14}$	7.3(-12)			LXV
145)	$\longrightarrow C_2H_6 + C_4H_8$	3.8(-12)			LXV
146)	$\longrightarrow C_2H_4 + C_4H_{10}$	2.3(-12)			LXV
147)	$C_3H_5 + C_3H_5 \longrightarrow C_6H_{10}$	1.4(-11)			LXVI
148)	$\longrightarrow C_3H_6 + C_3H_4$	1.4(-13)			LXVI
149)	$C_3H_5 + C_4H_7 \longrightarrow C_7H_{12}$	4.9(-11)			LXVII
150)	$\longrightarrow C_3H_6 + C_4H_6$	4.9(-13)			LXVII
151)	$\longrightarrow C_3H_4 + C_4H_8$	4.9(-13)			LXVII
152)	$C_3H_5 + C_4H_9 \longrightarrow C_7H_{14}$	1.1(-11)			LXVIII
153)	$\longrightarrow C_3H_6 + C_4H_8$	1.2(-12)			LXVIII
154)	$\longrightarrow C_3H_4 + C_4H_{10}$	4.4(-13)			LXVIII
155)	$C_3H_7 + C_3H_7 \longrightarrow C_6H_{14}$	4.0(-12)			LXIX
156)	$\longrightarrow C_3H_8 + C_3H_6$	2.6(-12)			LXIX
157)	$C_3H_7 + C_4H_9 \longrightarrow C_7H_{16}$	5.7(-12)			LXX
158)	$\longrightarrow C_3H_8 + C_4H_8$	4.0(-12)			LXX
159)	$\longrightarrow C_3H_6 + C_4H_{10}$	3.8(-12)			LXX
160)	$C_4H_3 + C_4H_3 \longrightarrow C_8H_6$	1.0(-11)			XLIII
161)	$\longrightarrow C_4H_2 + C_4H_4$	1.0(-12)			XLIII
162)	$C_4H_3 + C_4H_5 \longrightarrow C_8H_8$	1.0(-11)			XLIII
163)	$\longrightarrow C_4H_2 + C_4H_6$	1.0(-12)			XLIII
164)	$\longrightarrow C_4H_4 + C_4H_4$	1.0(-12)			XLIII
165)	$C_4H_5 + C_4H_5 \longrightarrow C_8H_{10}$	1.0(-11)			XLIII
166)	$\longrightarrow C_4H_4 + C_4H_6$	1.0(-12)			XLIII
167)	$C_4H_7 + C_4H_7 \longrightarrow C_8H_{14}$	4.3(-11)			LXXI
168)	$\longrightarrow C_4H_8 + C_4H_6$	0			LXXI
169)	$C_4H_7 + C_4H_9 \longrightarrow C_8H_{16}$	1.9(-11)			LXXII
170)	$\longrightarrow C_4H_8 + C_4H_8$	2.1(-12)			LXXII
171)	$\longrightarrow C_4H_6 + C_4H_{10}$	7.6(-13)			LXXII
172)	$C_4H_9 + C_4H_9 \longrightarrow C_8H_{18}$	2.0(-12)			LXXIII
173)	$\longrightarrow C_4H_{10} + C_4H_8$	5.6(-12)			LXXIII

Remarks in Table 7

$$I. \qquad H + CH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CH_4^* \xrightarrow{\ M\ }_{k_\omega} CH_4$$
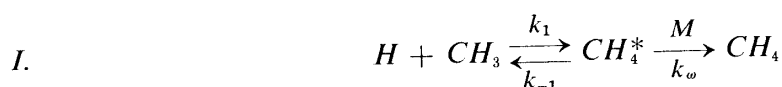
Overall agreements exist on the rate constants measured in the high pressure

regions (which are indicated by k_1).

Unimolecular decomposition rate k_{-1} was calculated to be $6.3 \times 10^9 \text{ s}^{-1}$ by Rabinovitch & Setser (1964) and $1.5 \times 10^9 \text{ s}^{-1}$ by Cheng & Yeh (1977) at 35°C. Hence under the atmospheric pressure conditions relevant to our problem ($p < 0.01$ atm), $k_{-1} \gg k_\omega [M]$ is sufficiently fulfilled, which enables us to use for the reaction rate the expression in the low pressure limit (third-order rate coefficient). This relation holds even at the lower temperatures of the order of 150K, where in general the rate k_{-1} would be much smaller. The listed value is adopted from the theoretical calculation by Troe (1977), although it is about 20 times as large as the rate estimated by Cheng & Yeh (1977) and also about 100 times as large as that given by Pratt & Veltman (1974)—the discrepancies may be partly ascribed to the uses of different third-bodies. This reaction system has a decisive importance, together with the reaction $CH_3 + CH_3 + M \longrightarrow C_2H_6$, in our present problem, which will be described in detail in a later chapter.

II. This is the first part of the reaction scheme shown below

$$H + C_2H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_2H_3^* \xrightarrow[k_\omega]{M} C_2H_3$$
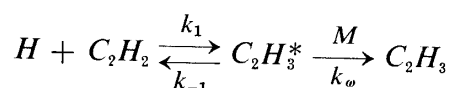
The value k_1 is of vital importance in determining the density distributions of acetylene itself and those molecules (C_2H, C_2H_3, C_4H_2, C_4H_4 etc.) which are closely connected chemically with the former. There are several recent experiments available for this reaction (Volpi & Zocchi 1966, Hoyermann *et al.*, 1968, Jones *et al*, 1973, Payne & Stief, 1976) and the listed value is taken from the last literature. See also *LIX* and *LX*.

III. Other available data are $6.6 \times 10^{-12} \text{ cm}^3 \cdot \text{s}^{-1}$ (Benson & Haugen, 1967b) and $3.3 \times 10^{-11} \text{ cm}^3 \cdot \text{s}^{-1}$ (Skinner *et al*, 1971).

IV.
$$H + C_2H_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_2H_5^* \xrightarrow[k_\omega]{M} C_2H_5$$
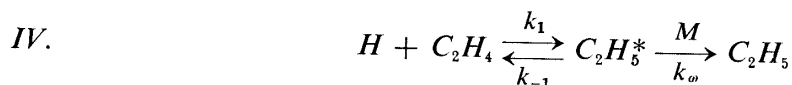
As for the rate k_1, an extensive number of literature is now available as mentioned in the text (Chap. III, § 3). The data in the high pressure limit, however, appear somewhat scattered (within a factor ~ 10) and among them we have, rather arbitrarily, chosen an 'average' data of $9.1 \times 10^{-13} \text{ cm}^3 \cdot \text{s}^{-1}$ by Eyre *et al* (1970). For the rate k_{-1}, Rabinovitch & Setser (1964) calculated it to be $1.4 \times 10^7 \text{ s}^{-1}$ and $7.8 \times 10^6 \text{ s}^{-1}$, respectively, in the high and low pressure limits, and Michael & Weston (1966) estimated it to be $1.6 \times 10^7 \text{ s}^{-1}$ in the high pressure limit. Since it appears that k_1 and k_{-1} are little influenced by change of temperature (Westenberg & DeHaas, 1969) these quantities have been treated here as independent of temperature. Utilizing the third-order combination rate of $4.4 \times 10^{-30} \text{ cm}^6 \cdot \text{s}^{-1}$ (at 296K) by Dodonov *et al* (1969), stabilization rate k_ω has been simply estimated to be $7.7 \times 10^{-11} \text{ cm}^3 \cdot \text{s}^{-1}$.

$V.$

$$H + C_2H_5 \xrightleftharpoons[k_{-1}]{k_1} C_2H_6^* \xrightarrow[M]{k_\omega} C_2H_6$$
$$\searrow^{k_d}$$
$$\dot{C}H_3 + CH_3$$

$$H + C_2H_5 \xrightarrow{k_2} H_2 + C_2H_4$$
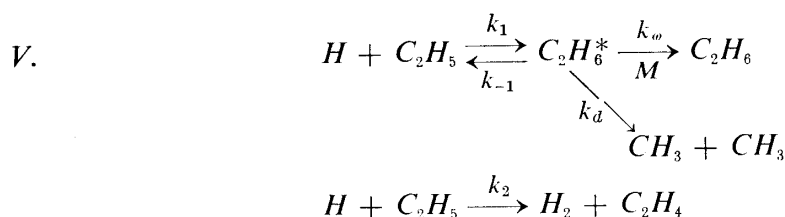
It is a well-known fact that the unimolecular decomposition resulting in central carbon splitting is much faster than that into the initial reactants ($k_d \gg k_{-1}$). This rate k_d was calculated to be $2.8 \times 10^9 \, \text{s}^{-1}$ by Rabinovitch & Setser (1964). For k_1, $6.0 \times 10^{-11} \, \text{cm}^3 \cdot \text{s}^{-1}$ is taken from Kurylo *et al* (1970) and for k_ω, it has been estimated to be $7.8 \times 10^{-11} \, \text{cm}^3 \cdot \text{s}^{-1}$ according to the assumption made in the text (Chap. III, § 4).

On the other hand, the rate k_2 has been determined from the conclusion that $\Delta(\equiv k_2/k_1) \simeq 0.05$ (Camilleri *et al*, 1974).

$VI.$

$$H + C_3H_3 \xrightleftharpoons[k_{-1}]{k_1} C_3H_4^* \xrightarrow[k_\omega]{M} C_3H_4$$
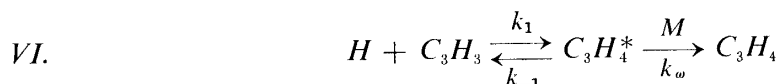
The reaction path is considered probable but the rates themselves are not known. Here, the rate k_1 has been simply evaluated by the statistical theory of reaction ($\sim 1.0 \times 10^{-11} \, \text{cm}^3 \cdot \text{s}^{-1}$) and the unimolecular rate k_{-1} evaluated to be $10^{5.1} \, \text{s}^{-1}$ at 150K by the procedures explained in chap. III, § 4, where the utilized values are: $D = D_1 = 3.67$, $s = 8$, and $A = 10^{14.3}$—of the last, see the text.

$VII.$

$$H + C_3H_4 \xrightleftharpoons[k_{-1}]{k_1} C_3H_5 \xrightarrow{M} C_3H_5$$
$$\searrow^{k_d}$$
$$CH_3 + C_2H_2 .$$
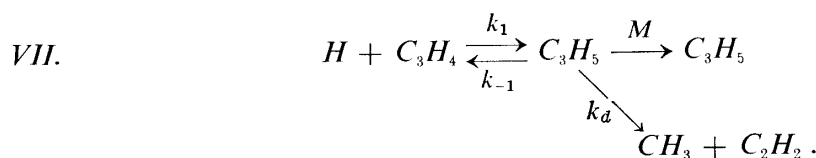
By C_3H_4, it is usually meant propyne and/or allene and their heats of formation are not so different from each other (1.923 and 1.992 eV, respectively). When either of them is produced in a certain chemical reaction, very frequently the other is also found to have non-negligible amounts. For both cases of propyne and allene, the detailed schemes in reaction were investigated by Wagner & Zellner (1972b, c). We have simplified the subsequent modeling procedures by assuming C_3H_4 to be propyne (see, Chap. III, § 1). For the case of H + allene, the unimolecular decompositions into $CH_3 + C_2H_2$ and/or into original reactants are greatly reduced and most excited adducts tend to be stabilized, competing with the sole possibility of the decomposition into H + propyne.

Wagner & Zellner (1972b) postulated the following two different intermediates,

$$H + C_3H_4 \text{(propyne)} \xrightarrow{k_1'} CH_3 - \dot{C} = CH_2^* \qquad (1 - C_3H_5^*)$$

$$\xrightarrow{k_1''} CH_3 - CH = CH^* \qquad (2 - C_3H_5^*)$$
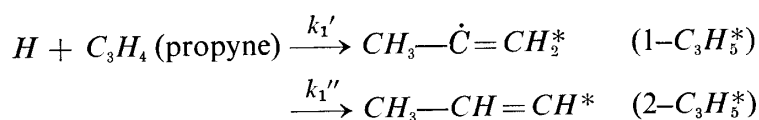
and obtained the rate coefficients as

$$k_1' = 1.1 \times 10^{-11} e^{-1000/T} \quad cm^3 \cdot s^{-1}$$

$$k_1'' = 9.6 \times 10^{-12} e^{-1570/T} \quad cm^3 \cdot s^{-1}.$$

(Therefore, the latter process is relatively unimportant owing to the higher activation energy.)

With this 1-methylvinyl radcal ($1\text{-}C_3H_5^*$), three possible routes were suggested: the recurrence to the original reactants (k_{-1}), the decomposition into $CH_3 + C_2H_2$ (k_d) and the stabilization to $1\text{-}C_3H_5$ (decomposition into H + allene is energetically not favorable under our low temperature conditions). We have equated $k_d = k_{-1}$ from the implications of the above experiment ($k_d \leq k_{-1}$) and estimated k_{-1} with the parameters: $D = D_1 = 1.91$, $s = 9$ and $A = 10^{13.5}$. The value listed at the middle column is thus twice the one of k_{-1} at 150K.

If the atmospheric temperature should be changed, the unimolecular rate is to be re-evaluated according to the relation given at Chap. III, § 4. Hereafter, such a modification would be applied to all those cases where unimolecular rate values at 150K are explicitly shown in the table.

VIII.

$$H + C_3H_5 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_3H_6^* \overset{M}{\longrightarrow} C_3H_6$$

$$\overset{k_2}{\longrightarrow} H_2 + C_3H_4 \text{ (propyne and allene)}$$
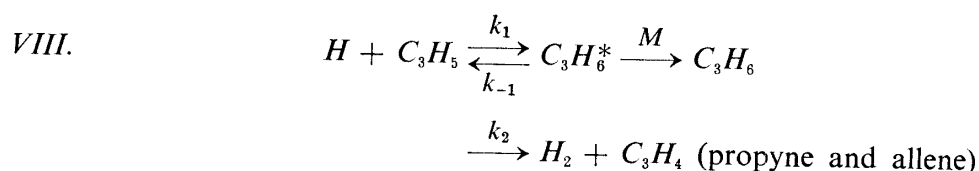
For allyl radicals, a decomposition into $CH_3 + C_2H_3$ is not energetically possible, dissimilar to the case of methylvinyl radicals. If one estimated the order of magnitude for the rate k_{-1} by the *RRK* theory, one could confirm that it has fairly small decomposition rate and that the system can be well treated essentially as a two-body reaction process.

At present, there appear to be no available data on k_1 and we have adopted the value of $2.0 \times 10^{-10} cm^3 \cdot s^{-1}$ from the work by Allara & Shaw (1975) that simulated chemical reactions occurring in pyrolytic system wherein the value just above was uniformly assumed for all the unknown rates of the systems of H + free radicals. The ratio k_1/k_2 has been taken as 0.7, the value observed for the reaction, H + 1-methylvinyl radical (Wagner & Zellner, 1972b, c).

IX.

$$H + C_3H_6 \text{ (propylene)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} i\text{-}C_3H_7^* \overset{M}{\longrightarrow} i\text{-}C_3H_7$$
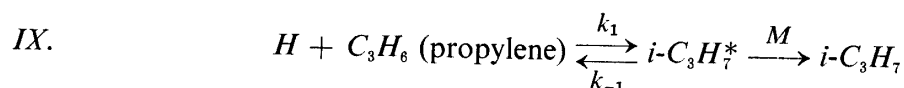
At the extremely low temperatures, the excited adducts are almost all formed at isopropyl structure and will go back to the initial reactants unless it should be collisionally stabilized. In fact, Wagner & Zeller (1972a) derived distinctly different rates between *n-* and *iso*-propyl radical formation, as follows,

$$H + C_3H_6 \overset{k_1'}{\longrightarrow} i\text{-}C_3H_7 \text{ (H addition to terminal olefinic position)}$$

$$\overset{k_1''}{\longrightarrow} n\text{-}C_3H_7^* \text{ (H addition to non-terminal position)}$$

with $k_1'=9.0\times10^{-12}\,e^{-630/T}\,\mathrm{cm^3\cdot s^{-1}}$ and $k_1''=7.3\times10^{-12}\,e^{-1380/T}\,\mathrm{cm^3\cdot s^{-1}}$. The latter process has not been, here, taken into account owing to the higher activation energy, although $n\text{-}C_3H_7^*$ has an intrinsic decomposition path into $CH_3 + C_2H_4$, of which the rate is much larger than that of $i\text{-}C_3H_7^* \longrightarrow H + C_3H_6$ (Rabinovitch & Setser, 1964). Here the rate k_{-1} has been taken as $10^5\,\mathrm{s^{-1}}$, an average of the somewhat different unimolecular rates belonging, respectively, to the high and low pressure limits (Ravinovitch & Setser, 1964). On the other hand, the first rate k_1 has been simply equated to k_1'.

X.

$$H + i\text{-}C_3H_7 \xrightarrow{k_1} C_3H_8^* \xrightarrow[k_\omega]{M} C_3H_8$$

$$k' \searrow$$
$$CH_3 + C_2H_5$$
$$k'' \searrow$$
$$CH_4 + C_2H_4$$

$$H + i\text{-}C_3H_7 \xrightarrow{k_2} H_2 + C_3H_6$$

Wagner & Zellner (1972a) estimated the following quantities by assuming $k_\omega \sim 5 \times 10^{12}\,\mathrm{cm^3\cdot mole^{-1}\cdot s^{-1}}$ $(8.3\times10^{-12}\,\mathrm{cm^3\cdot s^{-1}})$,

$$k_2/k_1 = 0.47$$
$$k' = 3.5\times10^5\,\mathrm{s^{-1}}$$
$$k'' = 2\times10^5\,\mathrm{s^{-1}}.$$

It can be expected that these unimolecular rates do not differ greatly from those of room temperature from the energetic consideration between reactant and product states (This would be valid if $D-(D_1+a)\gg skT$ is satisfied).

As for k_1, we have simply followed Allara & Shaw (1975), who used the value $2.0\times10^{-10}\,\mathrm{cm^3\cdot s^{-1}}$.

XI.

$$H + C_4H_2\,(\text{diacetylene}) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_4H_3^* \xrightarrow{M} C_4H_3$$

The first rate k_1 was measured, $2.2\times10^{-12}\,\mathrm{cm^3\cdot s^{-1}}$ by Schwaneback and Warnetz (1975). The rate k_{-1} has been estimated to be $10^{5.3}\,\mathrm{s^{-1}}$ at 150K with the parameters: $D=D_1=2.65$, $s=8$, and $A=10^{13.5}$.

XII.

$$H + C_4H_3 \xrightarrow{k_1} C_4H_4^* \xrightarrow{M} C_4H_4\,(\text{vinylacetylene})$$

$$k_d \searrow$$
$$C_2H_2 + C_2H_2$$

$$\xrightarrow{k_2} H_2 + C_4H_2$$

The reaction scheme was discussed by Schwaneback & Warnetz (1975) and the lifetime of the vibrationally excited vinylacetylene $C_4H_4^*$ was assessed to be about $10^{-7}\,\mathrm{s}$ at room temperature. Although the activation energy (x) for the decomposition into acetylenes is not yet available it may be estimated to be around 1.5 to

2.0 eV from the simple *RRK* theory using the above rate, $k_d = 10^7\,\mathrm{s}^{-1}$. The temperature dependence of the decomposition rate (k_d) would be significant if the activation energy should lie near 2.0 eV, or else, it would predict a moderate variation of k_d with temperature. In the absence to the contrary, we have simply adopted the latter case (*cf.* it is known that the system $C_2H_4 + C_2H_4 \longrightarrow C_4H_8$ has an activation energy of about 1.5 eV).

To the rate k_1, the value of $2.0 \times 10^{-10}\,\mathrm{cm}^3 \cdot \mathrm{s}^{-1}$ has been assigned—this is the method we have always adopted for such a reaction system as H + free radicals, whenever the actual rate is not known. Note that an estimate according to a simple statistical theory may sometimes result in too small values for these kinds of reactions. For the rate k_2, it is assumed to be the same as for $H + C_2H_3 \longrightarrow H_2 + C_2H_2$.

XIII.
$$H + C_4H_4 \xrightarrow{k_1} C_4H_5^* \xrightarrow{M} C_4H_5$$
$$\xrightarrow{k_d} C_2H_3 + C_2H_2$$

The first rate k_1 was measured by Schwaneback & Warnetz (1975) who derived the value of $3.3 \times 10^{-12}\,\mathrm{cm}^3 \cdot \mathrm{s}^{-1}$. The reaction scheme, however, was examined in more detail by Benson & Haugen (1967a)
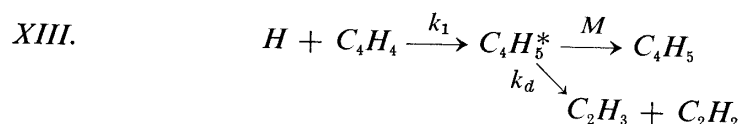
$$H + C_4H_4 \xrightarrow{k_1'} \dot{C}H = CHCH = CH_2 \xrightarrow{M} C_4H_5$$
$$\xrightarrow{k_d'} C_2H_3 + C_2H_2$$

$$\underset{k_{-1}''}{\overset{k_1''}{\rightleftharpoons}} CH_2 = \dot{C}CH = CH_? \xrightarrow{M} C_4H_5$$

with the result of $k_1'/k_1'' \sim 1/1.8$ being obtained. In the above simplified reaction scheme (our working model), the value k_d has been taken from the position by k_d' with the value being adjusted by a factor $1.0/(1.0+1.8)$—the rate k_d' has been estimated based on the parameters: $D = 1.98$, $D_1 = 1.74$, $s = 11$ and $A = 10^{13.7}$. The activation energy of this process was suggested *exceedingly small* (Benson & Haugen, 1967a) and the value of k_1 above mentioned has been simply applied at 150K.

XIV.
$$H + C_4H_5 \xrightarrow{k_1} C_4H_6^* \xrightarrow{M} C_4H_6$$
$$\searrow{k_d}$$
$$C_2H_2 + C_2H_4$$
$$\searrow$$
$$CH_2 + C_3H_4$$
$$\xrightarrow{k_2} H_2 + C_4H_4$$

There appear to be no quantitative studies available for this process. Only the decompositions into $C_2H_2 + C_2H_4$ and $CH_2 + C_3H_4$ were qualitatively inferred (Schwaneback & Warnetz, 1975), although the latter may not be favorable in our problems from an energetic viewpoint. Furthermore, if the excited intermediate should (intially or *via* isomerization) happen to be 1-$C_4H_6^*$, the decomposition into $CH_3 + C_3H_3$ would be also not impossible. Here we have incorporated only the process leading to $C_2H_2 + C_2H_4$. Assuming 1, 2-C_4H_6 structure for the excited adduct, the rate k_d has been roughly estimated as $10^{8.4}\,\text{s}^{-1}$ with $D = 3.46$, $D_1 = 2.69$ and $A = 10^{14.6}$. For the first part of the reaction, $k_1 = 2.0 \times 10^{-10}\,\text{cm}^3 \cdot \text{s}^{-1}$ has been assigned (see, *VIII*) and k_2 is assumed to be the same as for $H + C_2H_3 \longrightarrow H_2 + C_2H_2$.
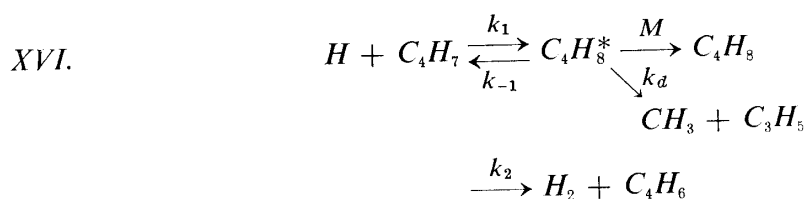
XV. The existence of the four kinds of C_4H_6 compounds makes the process of constructing a simplified but realistic model of reaction quite difficult. Several unimolecular processes are known to occur such as

$$H + 1, 3\text{-}C_4H_6 \longrightarrow C_2H_3 + C_2H_4$$

$$H + 1, 2\text{-}C_4H_6 \longrightarrow CH_3 + C_3H_4 \text{ (propyne/allene)}$$

$$H + 1\text{-butyne} \longrightarrow CH_3 + C_3H_4 \text{ (propyne/allene)}$$

$$H + 2\text{-butyne} \longrightarrow \qquad ?$$

and also do the mutual isomerizations among these excited intermediates.
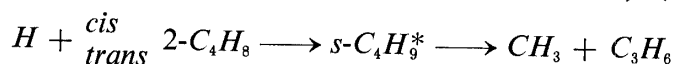
We postulate the model by taking account of 1, 3-C_4H_6 only, since the heat of formation is smallest with it as compared with those belonging to the others (1.142, 1.682, 1.517 and 1.713 eV, respectively, for 1, 3-C_4H_6, 1, 2-C_4H_6, 1-butyne and 2-butyne).

$$H + 1, 3\text{-}C_4H_6 \xrightarrow{k_1} C_4H_7^* \longrightarrow C_4H_7 \text{ (mainly } trans\text{-1-methylallyl,}$$
$$\qquad\qquad\qquad {}_{k_d}\searrow \qquad\qquad \text{Benett \& Mile, 1973)}$$
$$\qquad\qquad\qquad C_2H_3 + C_2H_4$$

The rate k_1 relative to that for $H + C_2H_4$ was reported by Cvetanovic & Doyl (1969), $k_1/k\,(H + C_2H_4 \longrightarrow C_2H_5) = 7.5$ at 25°C and later the absolute value was assessed to be $(1.8 \sim 2.8) \times 10^{-12}\,\text{cm}^3 \cdot \text{s}^{-1}$ by Koda & Hikita (1971). Here in our calculations, the value of $2.5 \times 10^{-12}\,\text{cm}^3 \cdot \text{s}^{-1}$ has been thus employed. As to the unimolecular rate k_d, it has been calculated to be about $10^{5.7}\,\text{s}^{-1}$ at 150K with the parameters: $D = 1.67$, $D_1 = 1.38$, $s = 14$ and $A = 10^{13.2}$.
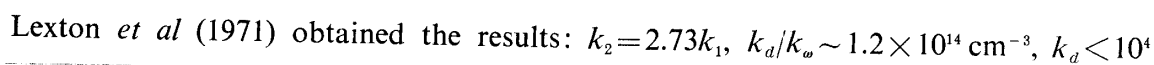
Finally, the reaction *36* has been simply equated to zero, because a reactant is possibly required to be 1, 2-butadiene in order for the dissociation to be effective.

XVI.
$$H + C_4H_7 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_4H_8^* \xrightarrow{M} C_4H_8$$
$$\qquad\qquad\qquad\qquad \searrow^{k_d}$$
$$\qquad\qquad\qquad CH_3 + C_3H_5$$

$$\xrightarrow{k_2} H_2 + C_4H_6$$

For k_1 and k_2 we have followed Allara & Shaw (1975) ($k_1 = 2.0 \times 10^{-10}$ cm$^3 \cdot$s^{-1} and $k_2 = 0.3 \cdot k_1$). The usual products observed at the above system are *iso-* or 2-C_4H_8, whereas the decomposition into $CH_3 + C_3H_5$ would be expected only in the case where the intermediate is of normal structure. Even n-$C_4H_8^*$ is allowed for the intermediate, the rate k_d, however, seems not to exceed about 10^3 s^{-1}. Moreover, it is known from energetic consideration that the rate k_{-1}, which describes a recurrence to the original reactants, is much more reduced. All these would justify the reaction being described in terms essentially of a two-body reaction process.

XVII. The heat of formation among four butene isomers is not very different from each other (-0.00130, -0.0724, -0.116 and -0.175 eV, respectively, for 1-, *cis* 2-, *trans* 2-, and *iso*-C_4H_8) and their likely unimolecular processes are:

$$H + 1\text{-}C_4H_8 \longrightarrow n\text{-}C_4H_9^* \longrightarrow C_2H_4 + C_2H_5 \;\left.\right\} \;\text{mainly,}\; n\text{-}C_4H_9^*$$
$$\longrightarrow s\text{-}C_4H_9^* \longrightarrow CH_3 + C_3H_6 \;\left.\right\} \;\text{(Collin, 1973)}$$

$$H + \begin{matrix} cis \\ trans \end{matrix} \; 2\text{-}C_4H_8 \longrightarrow s\text{-}C_4H_9^* \longrightarrow CH_3 + C_3H_6$$

$$H + i\text{-}C_4H_8 \rightleftarrows t\text{-}C_4H_9^*$$
$$\longrightarrow i\text{-}C_4H_9^* \longrightarrow CH_3 + C_3H_6$$

According to the prescription described in the text, a working model for this process has been proposed on isobutene as follows,

$$H + i\text{-}C_4H_8 \;\underset{k_{-1}}{\overset{k_1}{\rightleftarrows}}\; t\text{-}C_4H_9^* \;\overset{M}{\underset{k_\omega}{\longrightarrow}}\; t\text{-}C_4H_9$$
$$\underset{k_2}{\longrightarrow}\; i\text{-}C_4H_9^* \;\underset{k_d}{\longrightarrow}\; CH_3 + C_3H_6.^{[*]}$$

The rate k_1 has been taken from Cowfer *et al* (1971), while the ratio k_2/k_1 and the stabilization coefficient k_ω is estimated to be, respectively, 0.0014 and 6.5×10^{-12} cm$^3 \cdot$ s^{-1} by Lexton *et al* (1971). Here for the rate k_{-1}, it has been given a value of $10^{3.5}$ based on parameters: $D = D_1 = 1.86$, $A = 10^{15.5}$.

XVIII. The reaction scheme may be postulated, supposing that C_4H_9 is *tert*-butyl radical, as follows

$$H + t\text{-}C_4H_9 \;\overset{k_1}{\longrightarrow}\; i\text{-}C_4H_{10}^* \;\overset{M}{\underset{k_\omega}{\longrightarrow}}\; i\text{-}C_4H_{10}$$
$$\overset{k_d}{\searrow} \; CH_3 + i\text{-}C_3H_7$$
$$\overset{k_{d'}}{\searrow} \; CH_4 + C_3H_6$$
$$\overset{k_2}{\longrightarrow}\; H_2 + i\text{-}C_4H_8.$$

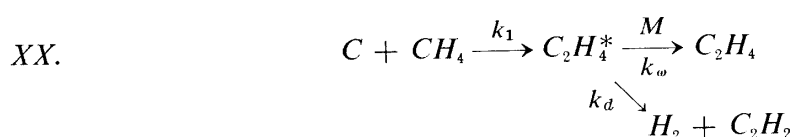Lexton *et al* (1971) obtained the results: $k_2 = 2.73k_1$, $k_d/k_\omega \sim 1.2 \times 10^{14}$ cm^{-3}, $k_d < 10^4$

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[*] Lexton *et al* (1971), in the experiment under the pressures of 4~12 torr, states that the stabilization of i-$C_4H_9^*$ is not a significant reaction compared with the decomposition. Note that our calculations are to be made at the pressures lower than that.

and $k_{d'} < k_d$. An estimate of k_d based on the simple *RRK* theory appears to bring about a value too small to be reconciled with the existing experimental results and hence we have utilized the above data, equating k_d to 10^4. The stabilization rate k_ω, which can be derived by virtue of the k_d/k_ω relation, falls inside its quite reasonable range. On the other hand, with the second decomposition, there has been no information obtained other than $k_{d'} < k_d$. Presently, we have introduced for the ratio $k_d/k_{d'}$ a similar relation as that found at the reaction system of $H + i$-C_3H_7. As to k_1, see *XII*.

XIX. The reaction would be written as follows

$$C + CH_3 \xrightarrow{k_1} C_2H_3^* \xrightarrow[k_\omega]{M} C_2H_3$$
$$\qquad\qquad k_d \searrow$$
$$\qquad\qquad\qquad C_2H_2 + H$$
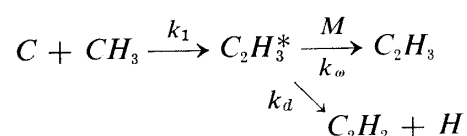
However, owing to the very large energy separation between the reactant and product states, stabilization is unlikely to have any importance compared with decomposition even at our highest pressures (*i.e.* $k_d \gg k_\omega[M]$) and the above reaction could be treated in terms essentially of a second-order reaction. The rate k_1 has been estimated to be $1.5 \times 10^{-11} \mathrm{cm^3 \cdot s^{-1}}$ at 150K on the basis of the statistical reaction theory.

XX. $\qquad\qquad\qquad C + CH_4 \xrightarrow{k_1} C_2H_4^* \xrightarrow[k_\omega]{M} C_2H_4$
$$\qquad\qquad\qquad\qquad k_d \searrow$$
$$\qquad\qquad\qquad\qquad\qquad H_2 + C_2H_2$$

The rate k_1 has been estimated to be $9.1 \times 10^{-12} \mathrm{cm^3 \cdot s^{-1}}$ as in *XIX*. Braun *et al* (1967) showed the ratio of decomposition of the excited $C_2H_4^*$ to stabilization (by H_2) to be about $k_d/k_\omega[M] = 180$ torr, i.e., $k_d/k_\omega = 6.4 \times 10^{18} \mathrm{cm^{-3}}$. As any plausible range of the stabilizing efficiency seems enough to satisfy $k_d \gg k_\omega[M]$ under the pressures of our interest, both processes would be securely described in terms of the expression in the low pressure limit, that is, combination rate $= k_1 \cdot k_\omega/k_d = 1.5 \times 10^{-30}$ the $\mathrm{cm^6 \cdot s^{-1}}$ and decomposition rate $= k_1$.

XXI. $\qquad\qquad\qquad CH + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CH_3^* \xrightarrow[k_\omega]{M} CH_3$
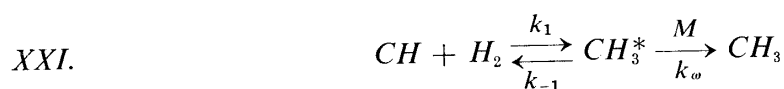
Here, the data of k_1 has been taken from the recent work done by Butler *et al* (1979)—the other values can be found in literature like 1.74×10^{-11} and 1.0×10^{-12} $\mathrm{cm^3 \cdot s^{-1}}$ (Bosnali & Perner, 1971 and Braun *et al*, 1967, respectively). Utilizing the reverse rate k_{-1} which is obtained with $D = D_1 = 4.65$ and $A = 10^{13.2}$, the expression for combination in the low pressure limit ($k_1 \cdot k_\omega/k_{-1}$) has been applied to this system.

XXII. $\qquad\qquad\qquad CH + CH \xrightarrow{k_1} C_2H_2^* \xrightarrow{M} C_2H_2$
$$\qquad\qquad\qquad k_d \text{ (or } k_{-1}) \searrow$$
$$\qquad\qquad\qquad\qquad\qquad \text{decompose}$$
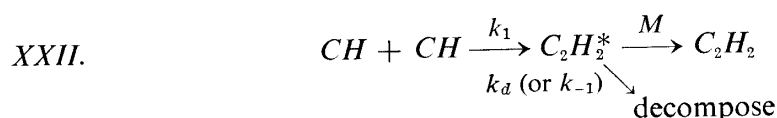
Despite the comparatively simple reaction system consisting of a few atoms, the third-body requirement for association is satisfied even at rather low pressures. This would be easily realized by virtue of the existence of the long-lived state in acetylene that was described in the foregoing chapter. Braun *et al* (1967) derived the experimental results indicating $k_1 = 2.0 \times 10^{-11}$ cm$^3 \cdot$ s^{-1} and k_d (or k_{-1}) = 10^6 s^{-1}.

XXIII. It would be more accurate to write the reaction as

$$CH + CH_4 \xrightarrow{\ k_1\ } C_2H_5^* \xrightarrow{\ M\ } C_2H_5$$
$$\searrow\ C_2H_4 + H$$
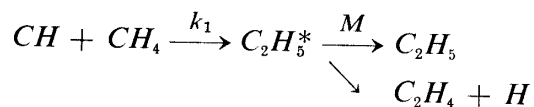
Experiments, however, show the reaction to be entirely of second-order even at the pressure of 100 mmHg (Braun *et al*, 1967). This may be readily understood if one considers the large energy separation lying between the both (reactant and product) states.

XXIV.
$$CH + C_2H_4 \longrightarrow C_3H_5^* \xrightarrow{\ M\ } C_3H_5 \text{ (allyl)}$$
$$\searrow\ C_3H_4 \text{ (allene)} + H$$
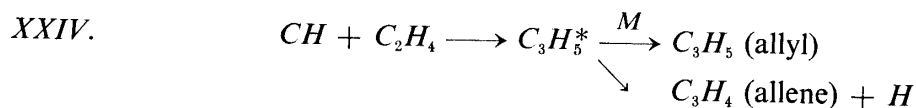
The situation is quite similar to *XXIII*.

XXV. This is the reaction introduced by Callomon & Ramsay (1957) in elucidating 4050A absorption of C_3 observed in flash photolysis of diacetylene ($C_4H_2 \xrightarrow{\ UV\ } C_3H \xrightarrow{\ CH\ } C_3$). The actual rate, however, is not known. At any rate, as our calculations do not take into account the molecules like C_3 and C_3H, the relevant position in the table is left unfilled.

XXVI.
$$^3CH_2 + H_2 \longrightarrow CH_4^* \xrightarrow{\ M\ } CH_4$$
$$\searrow\ CH_3 + H$$
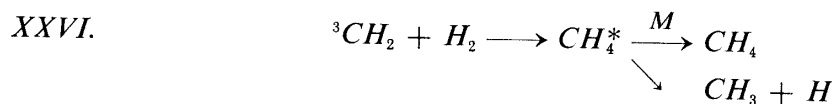
A number of experiments show that triplet methylene is nearly incapable of inserting into a *H-H* bond (*e.g.*, Haller & Srinivasan, 1964, MacKay *et al*, 1967, Braun *et al*, 1970, Pilling & Robertson, 1977). Should the reaction, however, proceed even with an exceedingly small rate, the influence over our present calculation would be rather serious. For instance, a complete removal of the above reaction results in intolerably large amounts of acetylene and acetylenic compounds, when compared with those inferred from the *IR* observations. This is owed to the relatively more enhanced role performed by the mutual interactions between triplet methylenes (*XXVII*).

Anyway the actual rate values are completely unknown and we have tentatively changed them to see the effects on the obtained results (see Chap. V), finally adopting the listed values as those in our nominal calculation.

XXVII.
$$^3CH_2 + {}^3CH_2 \xrightarrow{\ k_1\ } C_2H_4^* \xrightarrow{\ M\ } C_2H_4$$
$$\searrow\ C_2H_2 + H_2$$
$$\searrow\ CH + CH_3 \text{ (unimportant)}$$

Braun *et al* (1970) studied this reaction and observed that acetylene yield is independent of total pressure up to as high as one atmosphere, a result indicating that pressure considerably in excess of this is required to stabilize the excited ethylene. This may be rather natural, considering the high heat of formation possessed by methylene radical. The process leading to association product, ethylene is thus completely negligible. Braun *et al* (1970) derived the rate coefficient for production of acetylene to be $5.3 \times 10^{-11}\,cm^3 \cdot s^{-1}$,

$$XXVIII. \qquad {}^3CH_2 + C_2H_2 \xrightarrow{k_1} C_3H_4^* \xrightarrow[k_\omega]{M} C_3H_4 \;(\text{propyne/allene} \simeq 1/2)$$
$$k_d \searrow\; C_3H_3 + H$$

The unimolecular process is that inferred from pyrolyses of allene and/or propyne. The experiment by Laufer & Bass (1974), however, implied that such an association reaction proceeds bimolecularly at the low pressures of 20 torr (i.e., $k_\omega[M] \gg k_d$). Even the choice of the optimum parameters in determining k_d (and the changes of k_ω within its reasonable ranges) appears not to be easily reconciled with the above relation. We have rather arbitrarily assigned the value $\sim 10^6\,s^{-1}$ to this decomposition. The first rate k_1 was obtained $4.0 \times 10^{-12}\,cm^3 \cdot s^{-1}$ by Pilling & Robertson (1977).

$$XXIX. \qquad CH_2 + C_2H_3\;(\text{vinyl}) \xrightarrow{k_1} \underset{(\text{allyl})}{C_3H_5^*} \xrightarrow[k_\omega]{M} C_3H_5$$
$$k_d \searrow\; C_3H_4 \;(\text{allene and/or propyne}) + H$$

For this system, $k_d \gg k_\omega[M]$ is confirmed to hold with little problem. The rate k_1 is estimated according to the cross combination rule (*CCR*) which has already been mentioned at the relevant part of the text.

$$XXX. \qquad CH_2 + C_2H_5 \xrightarrow{k_1} n\text{-}C_3H_7^* \xrightarrow[k_\omega]{M} n\text{-}C_3H_7$$
$$k_d \searrow\; CH_3 + C_2H_4$$

Even at the pressure of one atmosphere, $k_d \gg k_\omega[M]$ is sufficiently fulfilled, similar to the reaction just before. Applying the *CCR* for $CH_2 + CH_2 \longrightarrow C_2H_4^*$ and $C_2H_5 + C_2H_5 \longrightarrow C_4H_{10}^*$, the unknown rate k_1 has been estimated to be $3.7 \times 10^{-11}\,cm^3 \cdot s^{-1}$.

$$XXXI. \qquad {}^1CH_2 + CH_4 \xrightarrow{k_1} C_2H_6^* \xrightarrow[k_\omega]{M} C_2H_6$$
$$k_d \searrow\; 2CH_3$$

The excited ethane formed in this reaction has a much longer lifetime than the excited methane formed in ${}^1CH_2 + H_2 \longrightarrow CH_4^* \longrightarrow CH_3 + H$ and yet experimental behavior of the variation of the products *vs* pressure suggests that about the same

contributions to decomposition and stabilization are attained at the high densities around $10^{18} \sim 10^{19}$ cm^{-3} (Bell & Kristiakowsky, 1962, Braun *et al*, 1970). The listed value for combination in the low pressure limit ($k_1 \cdot k_\omega / k_d$) has been thus obtained from the former reference by applying $k_\omega \approx 7.8 \times 10^{-11}$ cm$^3 \cdot$ s^{-1}.

XXXII. The reaction was suggested by Mahan & Mandal (1962) but there appears to be no firm evidence of the occurrence. Hence we have not taken the process into account. If the reaction were incorporated into our calculation, substantial changes of the results could be expected under certain conditions.

XXXIII. More detailed reaction scheme will be written as

$$^1CH_2 + C_2H_4 \xrightarrow{k_1} c\text{-}C_3H_6^* \xrightarrow{M} c\text{-}C_3H_6$$

$$\downarrow \text{isomerization}$$

$$C_3H_6^* \text{ (propylene)} \xrightarrow{M} C_3H_6$$

$$k_d \searrow$$

$$CH_3 + C_2H_3$$

$$k_d' \searrow$$

$$C_3H_5 + H \text{ (unimportant)}$$
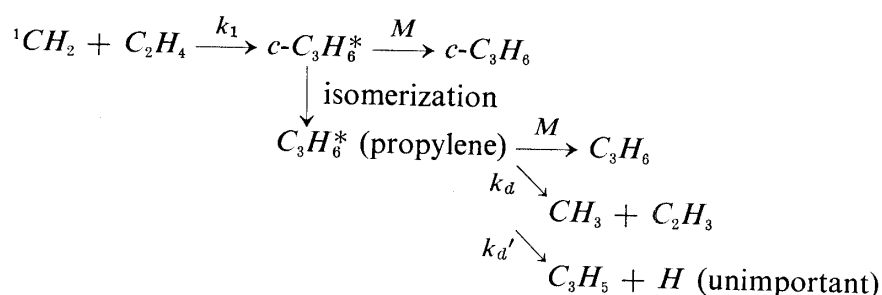
Firstly, the excited intermediate is formed mostly at cyclopropane except for the rare case where methylene radical attacks CH bond of ethylene. This excited cyclopropane, in the pressure ranges of our interest, isomerizes to propylene faster than it being stabilized—isomerization of cyclopropane is one of the most extensively studied topics because of the typical unimolecular process. The rate k_d for radical decomposition has been estimated to be $10^{8.6}$ s^{-1} with the parameters: $D = 4.75$, $D_1 = 3.72$, $s = 13$ and $A = 10^{16.1}$.

Although there appear to be no available data obtained with this reaction, *"the reaction of methylene with olefins is very fast"* (DeMore & Benson, 1964). For example, Frey (1959) showed that methylene reacts with $t\text{-}C_4H_8$ at a rate 2.4 times slower than with CH_2N_2 (it is believed that the rate of reaction of CH_2 with CH_2N_2 is comparable to the collision rate). Hence we have assigned the same value as that of $^1CH_2 +$ *trans* $2\text{-}C_4H_8$ to the present rate k_1, thereby a third-order association rate is to be calculated.

XXXIV.

$$^1CH_2 + C_2H_6 \xrightarrow{k_1} C_3H_8^* \xrightarrow[k_\omega]{M} C_3H_8$$

$$k_d \searrow$$

$$CH_3 + C_2H_5$$
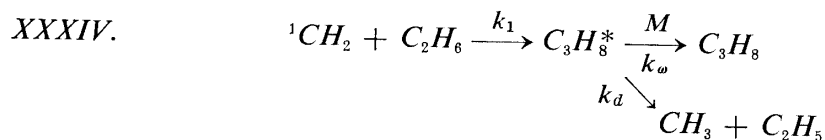
The rate k_1 was measured to be 4.8×10^{-12} cm$^3 \cdot$ s^{-1} by Halberstadt & Crump (1972/73). The rate k_d is here estimated to be $10^{8.4}$ s^{-1} by the use of the parameters: $D = 4.62$, $D_1 = 3.72$ and $A = 10^{17.2}$. The listed value shows the resultant three-body association rate at the low pressure limit ($k_1 \cdot k_\omega / k_d$).

XXXV. The first excited intermediate is formed mainly at methylcyclopropane and this *MCP*, unless stabilized, isomerizes to various butenes which may undergo further

decompositions. However, based on the similar argument made at *XXXIII*, the part relevant to *MCP* need not be taken into consideration.
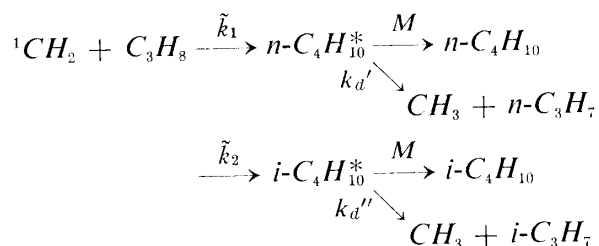
Isomerization to excited 1-butene occupies a fraction as much as 40% (Topor & Carr, 1973), which can decompose into $CH_3 + C_3H_5$ (allyl). The decompositions belonging to other isomeric butenes than $1\text{-}C_4H_8$, such as $C_4H_7 + H$ are negligible. Thus the reaction scheme may be simplified as follows

$$^1CH_2 + C_3H_6 \text{ (propylene)} \xrightarrow{k_1} 1\text{-}C_4H_8^* \xrightarrow[k_\omega]{M} C_4H_8$$
$$\searrow^{k_d} CH_3 + C_3H_5$$
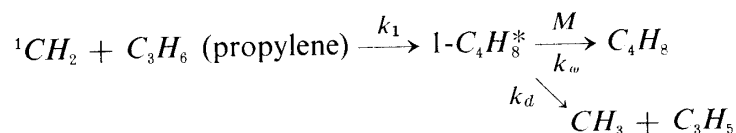
where k_1 is taken two fifths of the rate for $^1CH_2 + C_3H_6 \longrightarrow MCP^*$, of which it is here assumed to be the same as in *XXXIII*.

The rate k_d has been estimated $10^{9.3}\,s^{-1}$ with the parameters: $D=4.63$, $D_1=3.28$ and $A=10^{16.4}$. These would, if all combined, enable us to express the association rate as $0.6k_1[^1CH_2][C_3H_6]+0.4k_1\,k_\omega/k_d\cdot[^1CH_2][C_3H_6][M]$, i.e., $k_1[^1CH_2][C_3H_6][M]\{0.6/[M]+0.4k_\omega/k_d\}$, and for the rate of radical productions, as $0.4k_1$.

XXXVI. Insertion reaction of singlet methylene in propane yields *normal-* and *iso-*butane, depending upon whether it attacks a primary or secondary $C\text{-}H$ bond.

$$^1CH_2 + C_3H_8 \xrightarrow{\tilde{k}_1} n\text{-}C_4H_{10}^* \xrightarrow{M} n\text{-}C_4H_{10}$$
$$\searrow^{k_{d'}} CH_3 + n\text{-}C_3H_7$$

$$\xrightarrow{\tilde{k}_2} i\text{-}C_4H_{10}^* \xrightarrow{M} i\text{-}C_4H_{10}$$
$$\searrow^{k_{d''}} CH_3 + i\text{-}C_3H_7$$

The rates at which the excited adducts are formed were given by Bell (1971), 4.4×10^{-12} and $1.9\times10^{-12}\,cm^3\cdot s^{-1}$, respectively, for *normal* and *iso*-species, and the rates into decomposition, respectively, 6.6×10^7 and $1.3\times10^8\,s^{-1}$ by Koob (1972). In our models, the reaction has been simplified:

$$^1CH_2 + C_3H_8 \xrightarrow{k_1} C_4H_{10} \xrightarrow{M} C_4H_{10}$$
$$\searrow^{k_d} CH_3 + C_3H_7$$
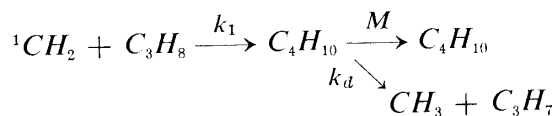
and their rates are modified as $k=\tilde{k}_1+\tilde{k}_2=6.3\times10^{-12}\,cm^3\cdot s^{-1}$ and $k_d=10/14\cdot k_{d'}+4/14\cdot k_{d''}=10^{7.9}\,s^{-1}$.

XXXVII. $$CH_3 + CH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_2H_6^* \xrightarrow{M}_{k_\omega} C_2H_6$$
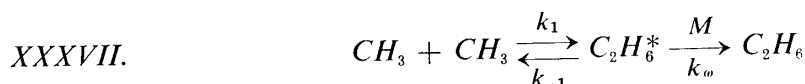
The reaction is of crucial importance as a bottle-neck reaction to the eventual formation of various higher hydrocarbon species in the present calculations. An extensive collection of literature on this system is available—historical summary can be found in Waage & Rabinovitch (1971)—and the rate for association in the high
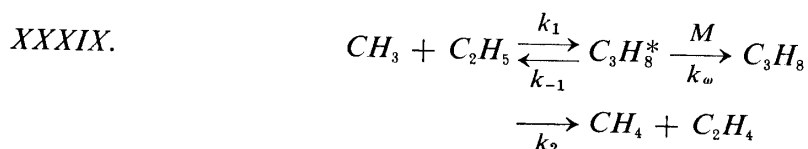
pressure regions seems to have been well established. We have adopted the value of 5.2×10^{-11} cm$^3 \cdot$s^{-1} for k_1, the best recommended value by Gibian & Corley (1973). The combination rate at the low pressures, however, reveals strong negative temperature dependence and the data are exceedingly scattered experiment by experiment. Not only the Kassel parameter s (the number of *effective* oscillators) which is obtainable in experiment from the falling off curves *vs* pressure distributes between 3 to 12, but also it often differs with the s value which is obtainable from the Slater's expression $(P_1/P_2)_{1/2} = (T_1/T_2)^{s-1/2}$, the one inferable from the shift of the falling off curve with temperature.

The third-order rate constants (in the low pressure limit) appear to be currently available only through theoretical calculations (Van den Bergh, 1976, Troe, 1977). Their strong collision rates—perfect stabilization by a single collision of third body —were determined to be $3.8 \sim 4.4 \times 10^{-25}$ cm$^6 \cdot$s^{-1} at 300K. However, in the present state of things, the direct application of such a low pressure expression is far from being justified. Here, at our expression for association, $k = k_1 k_\omega[M]/(k_{-1} + k_\omega[M])$, the information has been utilized so as the rate, if k_{-1} and k_ω properly chosen, asymptotes to the above third-order rate with decreasing densities of third body.

The strong collision third-order rates, k^{sc} due to Troe (1977) have been extrapolated towards lower temperatures than room temperature, in spite of the striking dependence on it in this system. On the other hand, for the stabilization rate k_ω, it has been assumed to be the collision number Z multiplied by stabilization efficiency: this efficiency, in *He* gas, was assessed, by Van den Berg (1976) as 0.094, 0.18 and 0.25, respectively, at 900, 450 and 300K. These values, though the dependence on temperature is weak, have been also extrapolated to the lower temperature regions (*e.g.* 0.33 at 150K).
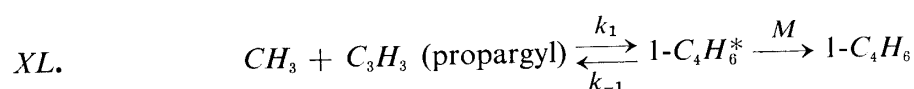
XXXVIII.
$$CH_3 + C_2H_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_3H_6^* \overset{M}{\longrightarrow} C_3H_6 \text{ (propylene)}$$
$$\overset{k_2}{\longrightarrow} CH_4 + C_2H_2$$
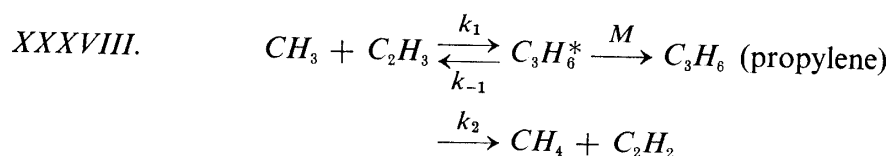
For the rate k_1, we have used 1.7×10^{-11} cm$^3 \cdot$s^{-1}, the value introduced at the pyrolytic study of propylene by Chappell & Shaw (1968)—the cross combination rule, in our case, gives 3.4×10^{-11} cm$^3 \cdot$s^{-1}. We have not adopted the more recent data by Figuera *et al* (1974), which are as much smaller, as $6.0 \times 10^{-14} \sim 1.7 \times 10^{-13}$ cm$^3 \cdot$s^{-1} at 298K. The reverse reaction rate k_{-1} has been estimated to be $10^{4.2}$ s^{-1} with the parameters: $D = D_1 = 3.72$, $s = 11$ and $A = 10^{16.1}$. The rate k_2 is taken from Lee & Yeh (1979).

XXXIX.
$$CH_3 + C_2H_5 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_3H_8^* \overset{M}{\underset{k_\omega}{\longrightarrow}} C_3H_8$$
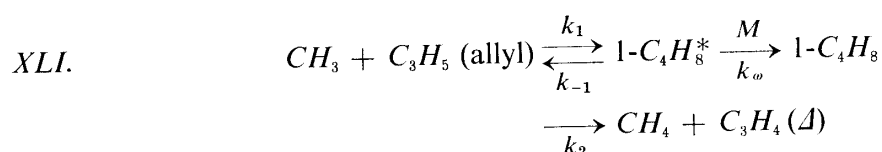$$\underset{k_2}{\longrightarrow} CH_4 + C_2H_4$$

From the respective self-combination rates of methyl and ethyl radicals, one can, in use of *CCR*, estimate the rate k_1 to be 3.7×10^{-11} cm$^3 \cdot$s^{-1}. As to the reverse rate

k_{-1}, it was calculated by Rabinovitch & Setser (1964) as $2.3 \times 10^5 \, \text{s}^{-1}$ at 25°C. If we are going to obtain the value within the framework of our simplified treatment of the *RRK* theory, it is necessary, under the conditions of $D = D_1 = 3.72$ and $A = 10^{17.2}$, to adopt for the Kassel parameters s, a value about 16 to 17. The use of this s-value at the other temperatures results in, *e.g.*, $k_{-1} = 10^{1.8} \, \text{s}^{-1}$ at 150K. Although the actual value of s may be expected to be somewhat smaller than that (in consequence, faster decomposition), the rate of such orders of magnitudes means the above combination process to be essentially of a two-body reaction process in the altitude ranges of any importance.

Disproportionation to combination ratio $\Delta (\equiv k_2/k_1)$ is taken to be 0.039 from Cheng *et al* (1977).

$$XL. \qquad CH_3 + C_3H_3 \ (\text{propargyl}) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 1\text{-}C_4H_6^* \xrightarrow{M} 1\text{-}C_4H_6$$

The rate is not known experimentally while the rate estimated from the statistical theory appears too small when compared with those commonly observed for these kinds of reactions. Here the value k_1 has been rather arbitrarily taken as 1.0×10^{-11} $\text{cm}^3 \cdot \text{s}^{-1}$ (the rate of the typical orders of magnitude for radical reactions). As for the unimolecular rate k_{-1}, it has been estimated to be $10^{3.4} \, \text{s}^{-1}$ with the parameters: $D = D_1 = 3.24$, $s = 12$ and $A = 10^{15.4}$.

$$XLI. \qquad CH_3 + C_3H_5 \ (\text{allyl}) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 1\text{-}C_4H_8^* \xrightarrow[k_\omega]{M} 1\text{-}C_4H_8$$
$$\xrightarrow{k_2} CH_4 + C_3H_4 \, (\Delta)$$

The limiting high pressure rate of combination, k_1 was derived by Throssell (1972) to be $2.3 \times 10^{-11} \, \text{cm}^3 \cdot \text{s}^{-1}$ and $\Delta = 0.023$ by James and Troughton (1966). For the unimolecular rate k_{-1} which has been estimated to be $10^{2.4} \, \text{s}^{-1}$, a similar argument as made at *XXXIX* is valid in this case owing to the increased molecules in dimension.

$$XLII. \qquad CH_3 + i\text{-}C_3H_7 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} i\text{-}C_4H_{10}^* \xrightarrow{M} i\text{-}C_4H_{10}$$
$$\xrightarrow{} CH_4 + C_3H_6 \, (\Delta)$$
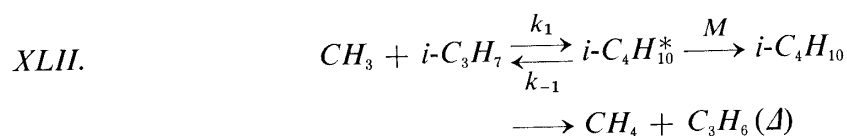
It would be no problem for the present combination reaction to be treated as a second-order reaction, as is readily seen from the simple evaluation for k_{-1}. The combination rate $(1.2 \times 10^{-11} \, \text{cm}^3 \cdot \text{s}^{-1})$ and the ratio $(\Delta = 0.163)$ has been taken, respectively, from Hiatt & Benson (1972a) and Terry & Futrell (1967).

$$XLIII. \qquad CH_3 + C_4H_3 \xrightarrow{k_1} C_5H_6$$
$$\xrightarrow{} CH_4 + C_4H_2 \, (\Delta)$$
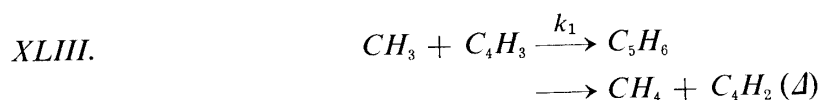
In the course of the modeling work for the chemical reactions initiated at acetylene, it has soon become clear that for the radicals like C_4H_3 and C_4H_5, reactions

with some abundant radicals other than a free hydrogen—for instance, CH_3, C_2H_5—must be taken into account.

The above and the following reactions (*93*, *94*, *134~139*) have been introduced for this purpose in our present calculations. They are, in nature, of combination and disproportionation, typical patterns expected between inter-radical reactions. The combination rate k_1 and the disproportionation ratio Δ have been rather arbitrarily set, respectively, to 1.0×10^{-11} cm$^3 \cdot$ s^{-1} and 0.1 for all the reactions of *91~94* and *134~139*.

XLIV. From the self-combination rates for methyls $(5.3 \times 10^{-11}$ cm$^3 \cdot$ s$^{-1})$ and β-methylallyls $(4.3 \times 10^{-11}$ cm$^3 \cdot$ s$^{-1})$, the combination rate has been estimated to be 9.5 $\times 10^{-11}$ cm$^3 \cdot$ s^{-1} *(CCR)*. For Δ, there appears to be no available information at present. It is assumed to be the same as that for $CH_3 + C_3H_5$ (allyl), *i.e.*, $\Delta = 0.023$ (James & Troughton, 1966).

XLV. From the self-combination rates for methyls and *t*-butyls $(2.0 \times 10^{-12}$ cm$^3 \cdot$ s$^{-1})$, the combination rate has been estimated to be 2.1×10^{-11} cm$^3 \cdot$ s^{-1} *(CCR)*, while for disproportionation, $\Delta = 0.3$ is used, a value known for the system of $CH_3 + s\text{-}C_4H_9$ (Wieckowski & Collin, 1977).

XLVI. C_2 has a triplet state $(a^3\Pi_u)$ at the position narrowly separated from the ground $(X^1\Sigma_g^+)$—$\Delta E = 0.076$ eV. It is well known that this forbidden state, famous as the lower level of the Swan band systems, had once been mistaken as the ground state of C_2 before the 1960's. State-selective experiments are now available (Donnelly & Pasternack, 1979, Pasternack & McDonald, 1979) and the values tabulated for the present and subsequent three reactions of C_2 (*99~102*) are of those belonging to the ground state. Although the reaction involving $C_2(a^3\Pi_u)$ could be safely ignored under our extremely low temperature conditions, it will be no longer justified at room temperature condition, since the results obtained for the same reaction partners are often quite different to these two states of C_2 (*e.g.* for $C_2(a^3\Pi) + CH_4$ $\xrightarrow{k} C_2(a^3\Pi)$ disappearance, $k < 10^{-16}$ cm$^3 \cdot$ s^{-1}, Donnelly & Pasternack, 1979).

XLVII. For all the abundance of methane, a fairly large activation energy found in this system $(E \sim 2500K$, Cullis *et al*, 1973) makes the process unimportant. Hence the reaction rate has been simply set equal to zero.

XLVIII. The activation energy of this system is believed to be of about $E \sim 1000K$ and the listed rate value is due to $k = k^{\text{statis}} \cdot e^{-1000/150}$.

XLIX. This is a channel with the lowest activation energy of the three processes postulated below by Cullis *et al* (1973),

$$C_2H + C_3H_4 \text{ (propyne)} \xrightarrow{k_1} C_2H_2 + C_3H_3$$

$$\xrightarrow{k_2} C_4H_2 + CH_3$$

$$\xrightarrow{k_3} C_5H_4 + H,$$
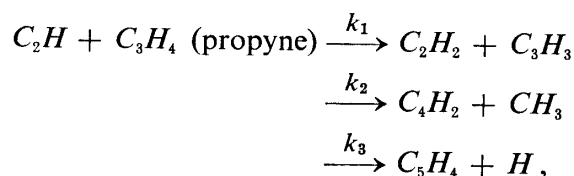
where they report $k_1 : k_2 : k_3 = 25 : 10 : 1$ at 298K. The probable value ($\sim 1000K$) of the activation energy required for the first and the abundance expected from the density calculation for those molecules which are closely related to this reaction would justify the process to be ignored at 150K.

L. Here, the decay of $C_2H_2^*$, unless stabilized, has been assumed to be mostly due to radiative fluorescence and the lifetime taken to be 6.2×10^{-6} s from Becker *et al* (1971). The dissociation into a radical pair of $C_2H + H$ has been included with the yield of 0.1 from Payne & Stief (1976) in our present calculations, although it is still a matter of controversy whether such a decomposition is likely to occur with a significant yield—for the detail, see the part relevant to acetylene in Chapter II.

LI. The listed value is taken from Becker *et al* (1971), which was presented as the quenching rate of a fluorescence possibly ascribed to $C_2H_2^*$. No indications, however, were given there of whether it resulted in $C_2H_2^* + H_2 \longrightarrow C_2H_2 + H_2$, or $\longrightarrow C_2H_3 + H$. Here the latter path has been formulated in the present calculations similar to the way adopted by Prasad *et al* (1975)—for the possibility, *e.g.*, see, Takita *et al* (1969). An alternative selection of the branching is, at any rate, unlikely to have a significant effect on the final results, since the reaction of $C_2H_3 + H \longrightarrow C_2H_2 + H_2$ would rapidly recycle the vinyl radical back to acetylene.

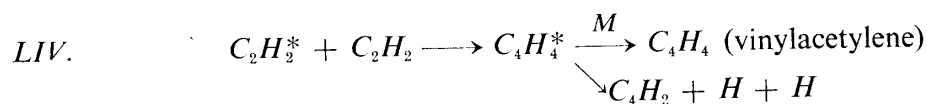*LII.* $\qquad\qquad\qquad C_2H_2^* + CH_4 \longrightarrow C_2H_2 + CH_3 + H$
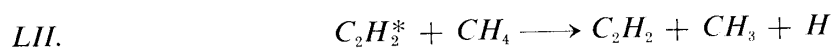
The reaction rate relative to $C_2H_2^* + C_2H_2 \longrightarrow C_4H_2 + H + H$ was estimated by Takita *et al* (1968) with the ratio of about 0.01 being presented. See also *LIII.*

LIII. $\qquad\qquad\qquad C_2H_2^* + C_2H_2 \longrightarrow C_4H_2 + H + H$
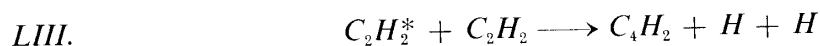
The above reaction, together with the previous reaction *105*, were suggested by Takita *et al* (1968), where the present path utilizing excited acetylene was, in diacetylene formation, preferred to $C_2H + C_2H_2 \longrightarrow C_4H_2 + H$, whereas the conclusion attained by Laufer & Bass (1979) is rather contrary to it.

Here, the same value as that taken at the reaction *105* has been tentatively assigned for this reaction whence the value just above mentioned (*LII*) is determinable.

LIV. $\qquad\qquad C_2H_2^* + C_2H_2 \longrightarrow C_4H_4^* \xrightarrow{\ M\ } C_4H_4$ (vinylacetylene)

$\qquad\qquad\qquad\qquad\qquad\qquad \searrow C_4H_2 + H + H$
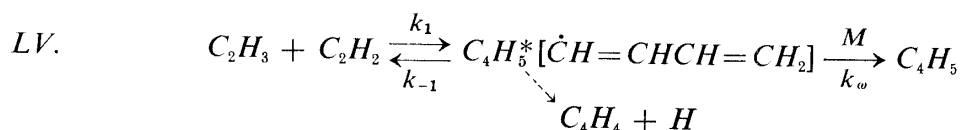
It is often seen in old literature that vinylacetylene (C_4H_4) would be formed through the collisional stabilization of the excited acetylene's dimer (*e.g.* Stief *et al*, 1965). The process has, however, not been incorporated into our calculations because the yield was not observed to increase with increasing total pressure in the acetylene system or in the acetylene/methane system (Takita *et al*, 1968)—where formation of the vinylacetylene was explained by disproportionation reaction,

$$C_2H_3 + C_4H_5 \longrightarrow C_2H_4 + C_4H_4 \ .$$
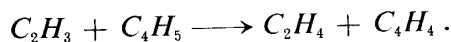
Although much higher pressures may be able to stabilize the excited dimer, such conditions are nothing to do with the present problem. These situations are rather different from the case of benzene (C_6H_6) formation which is thought to be due to the process,
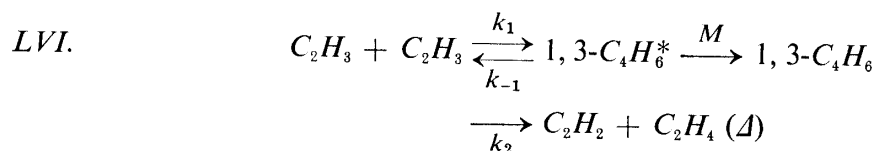
$$C_4H_4^* + C_2H_2 \longrightarrow C_6H_6^* \xrightarrow[\text{stabilize}]{} \text{benzene}.$$
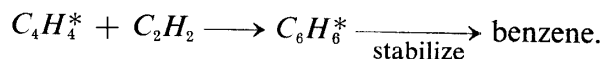
Presently, the last and those reactions that follow it are not taken into account since the inclusion appears to exceed the limit of our present calculations.

LV.
$$C_2H_3 + C_2H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_4H_5^*[\dot{C}H=CHCH=CH_2] \xrightarrow{M}{k_\omega} C_4H_5$$
$$\searrow C_4H_4 + H$$

For this system, Benson & Haugen (1967a) assigns the rate constant of 3.3×10^{-13} $\text{cm}^3 \cdot \text{s}^{-1}$, a consequence of the values reported for the addition of allyl radicals to conjugated diens, stating that *"although these systems have an activation energy of about 6 kcal/mole, a considerably smaller value is expected for the addition of vinyl radical to an unsaturated system"*. Here the same value was applied to the above reaction under our lower temperature conditions.

Prasad *et al* (1975) considers the reaction, $C_2H_3 + C_2H_2 \longrightarrow C_4H_4 + H$ in their calculations. But we have not taken into account the process, since, at the excited intermediate $C_4H_5^*$ thus formed, such a unimolecular decomposition appears to be energetically unfavorable (endothermic). The rate, k_{-1} for the reverse reaction has been estimated to be $10^{5.3}\,\text{s}^{-1}$ at 150K with the parameters: $D = D_1 = 1.98$ and $A = 10^{14.7}$.

LVI.
$$C_2H_3 + C_2H_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 1,3\text{-}C_4H_6^* \xrightarrow{M} 1,3\text{-}C_4H_6$$
$$\xrightarrow{k_2} C_2H_2 + C_2H_4 \ (\Delta)$$

$\Delta = 0.02$ was determined by Sherwood & Gunning (1965b) and the disproportionation rate, $5.3 \times 10^{-12}\,\text{cm}^3 \cdot \text{s}^{-1}$ by MacFadden & Currie (1973). The combination would be securely treated as a two-body reaction process even in our low pressure conditions, so far as no unimolecular processes other than simple restoration of the initial reactants are operative (at room temperature, the situation seems to be somewhat marginal). We note, however, that the combination rate under such conditions might be greatly reduced if some other efficient decompositions should occur *e.g.*, *via* isomerizations of the excited adducts.

LVII.
$$C_2H_3 + C_2H_5 \xrightarrow{k_1} 1\text{-}C_4H_8^* \xrightarrow{M} 1\text{-}C_4H_8$$
$$\overset{k_d}{\searrow} CH_3 + C_3H_5$$
$$\longrightarrow C_2H_2 + C_2H_6 \ (\Delta_1)$$
$$\longrightarrow C_2H_4 + C_2H_4 \ (\Delta_2)$$
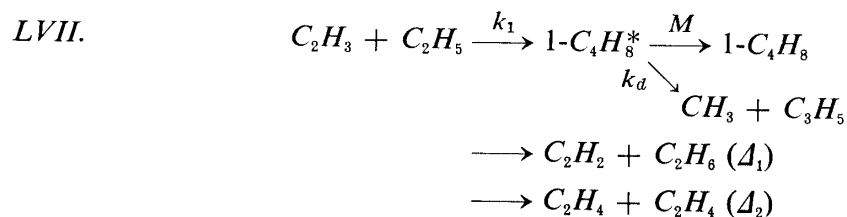
Currently available data for Δ are quite scattered. We have, among them, chosen rather moderate vaues due to Ibuki & Takezaki (1975) where $\Delta_1 = 0.37$ and $\Delta_2 = 0.68$ were obtained. The combination rate k_1 has, in use of the *CCR*, been estimated to be 8.4×10^{-11} cm$^3 \cdot$ s^{-1} and the unimolecular rate k_d, $10^{6.8}$ s^{-1} with the parameters: $D = 3.96$, $D_1 = 3.28$ and $A = 10^{16.4}$.

LVIII. Neither rate is known and the similar assumptions made at *XLIII* have been brought into use. Another possible form of disproportionation, $C_2H_3 + C_4H_5 \longrightarrow C_2H_2 + C_4H_6$ was shown to be unimportant (Takita *et al*, 1968).

LIX.
$$C_2H_3^* \xrightarrow{k_{-1}} H + C_2H_2$$

The lifetime of the excited vinyl radical into decomposition, which was formed at the hydrogen addition to acetylene (reaction 6), was estimated to be about 10^{-7} s at 313K by Volpi & Zocchi (1966). Inspection of those falling off curves *vs* pressure obtained at the lower temperatures suggests a considerable decrease of the decomposition rate k_{-1} with temperature (Hoyermann *et al*, 1968 (463 ~ 243K), Payne & Stief, 1976 (400 ~ 193K)—yet their coverage of the pressure and temperature ranges is not sufficient for the rate k_{-1} to be quantitatively determined under the circumstances relevant to the present calculations. Considering also the fact that the above lifetime of 10^{-7} s has been actually deduced with the stabilization supposed to occur at every collision, we give it rather a moderate value of 10^6 s^{-1} at 150K (though much smaller value may be not unlikely).

LX. The stabilization rate k_ω is given so that the third-body rate coefficient obtained in use of the reaction rate 6 and the lifetime of $C_2H_3^*$ (*LIX*) would, at room temperature, coincide with the expression derived by Hoyermann *et al* (1968), $1.2 \times 10^{-30} e^{-350/T}$ cm$^6 \cdot$ s^{-1}.

LXI.
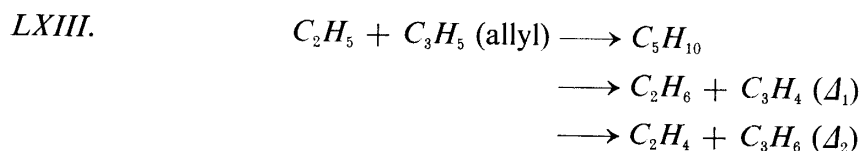$$C_2H_3^* + H_2 \longrightarrow C_2H_4 + H$$

From the remarkable increase of ethylene yield with increasing pressure of hydrogen, Takita *et al* (1969) suggested that the reaction $C_2H_3^* + H_2 \longrightarrow C_2H_4 + H$ might be important in addition to a thermal reaction $C_2H_3 + H_2 \longrightarrow C_2H_4 + H$ (where the rate for the latter had been estimated to be $5.3 \times 10^{-12} e^{-3200/T}$ cm$^3 \cdot$ s^{-1}). Although thermal reaction with such a high activation energy is not important for our purpose, the rate value in the high temperature limit has been utilized for the present unknown reaction coefficient.

LXII.
$$C_2H_5 + C_2H_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} n\text{-}C_4H_{10}^* \xrightarrow[k_\omega]{M} n\text{-}C_4H_{10}$$
$$\overset{k_d}{\searrow} CH_3 + C_3H_7$$
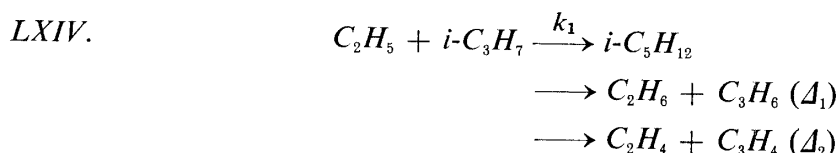$$\xrightarrow{k_2} C_2H_6 + C_2H_4 \ (\Delta)$$
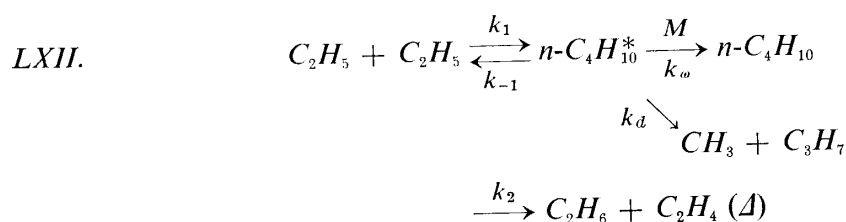
There are a number of available experiments about ethyl recombination but the

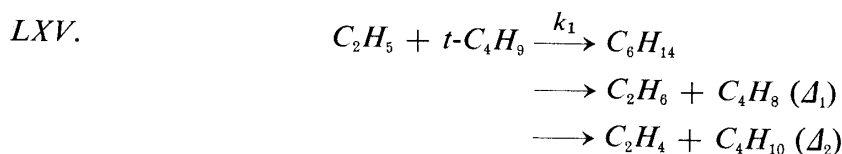data on the absolute value and the temperature dependence are rather scattered. Here we have adopted the rate of 6.6×10^{-12} cm$^3 \cdot$s^{-1} by Hiatt & Benson (1972a), the recommended value in the review article by Gibian & Corley (1973). The situation is more satisfactory for the ratio of disproportionation to combination and almost all the reported values of $\varDelta$ lie between $0.12 \sim 0.14$. The reaction scheme shown above indicates that the excited n-C_4H_{10}, unless it isomerizes to i-$C_4H_{10}^*$, would be recurrent to a pair of initial reactants or collisionally stabilized. Although the pyrolysis experiment for n-C_4H_{10} (Hughes *et al*, 1974) reveals that $k_{-1}/k_d \simeq 3$, such a unimolecular process itself would probably be not so important in our calculations. For Rabinovitch & Setser (1964) calculated the decomposition rate k_{-1} to be $4.7 \times 10^4 \sim 1.2 \times 10^3$ s^{-1} at 25°C depending upon the pressures of ambient gas. It can be shown that our simple estimate gives rise to a much smaller rate value ($k_{-1} < 10^2$ s^{-1}) at those low temperatures of our interest. Hence it would be possibly justified for the present combination reaction to be treated as a two-body process.

LXIII.
$$C_2H_5 + C_3H_5 \text{ (allyl)} \longrightarrow C_5H_{10}$$
$$\longrightarrow C_2H_6 + C_3H_4 \ (\varDelta_1)$$
$$\longrightarrow C_2H_4 + C_3H_6 \ (\varDelta_2)$$

From the self-combination rates of ethyls and allyls, the rate of 1.9×10^{-11} cm$^3 \cdot$s^{-1} has, in use of the *CCR*, been given to the above combination. On the other hand, $\varDelta_1$ and $\varDelta_2$ have been taken, respectively, as 0.04 and 0.11 from James & Troughton (1966).

LXIV.
$$C_2H_5 + i\text{-}C_3H_7 \xrightarrow{k_1} i\text{-}C_5H_{12}$$
$$\longrightarrow C_2H_6 + C_3H_6 \ (\varDelta_1)$$
$$\longrightarrow C_2H_4 + C_3H_4 \ (\varDelta_2)$$

Again, use is made of the *CCR* in determining the rate k_1. $\varDelta_1 = 0.18$ and $\varDelta_2 = 0.12$ have been taken from Terry & Futrell (1967)—disproportionation ratios with n-C_3H_7 are about twice as small as those with i-C_3H_7 (Grotewold & Kerr, 1963).

LXV.
$$C_2H_5 + t\text{-}C_4H_9 \xrightarrow{k_1} C_6H_{14}$$
$$\longrightarrow C_2H_6 + C_4H_8 \ (\varDelta_1)$$
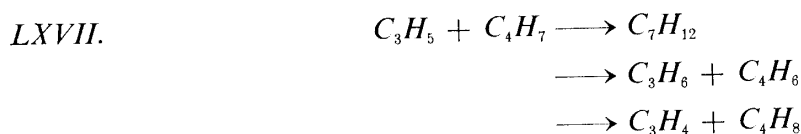$$\longrightarrow C_2H_4 + C_4H_{10} \ (\varDelta_2)$$

$k_1 = 7.3 \times 10^{-12}$ cm$^3 \cdot$s^{-1} has, in use of the *CCR*, been estimated from the self-combination rates for ethyls and t-butyls. And $\varDelta_1 = 0.52$ and $\varDelta_2 = 0.32$ have been taken from Gibian & Corley (1973).
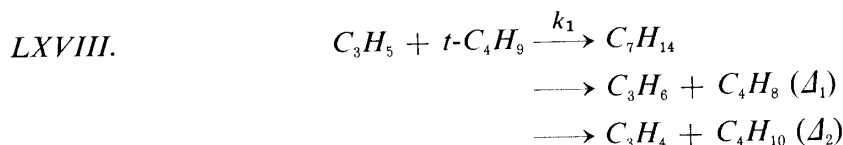
For all the butyl isomers (n-, s-, t-, i-) as a reaction partner of the ethyl, disproportionation to combination ratios are now available and it must be born in mind that they are greatly changed with the isomeric identities, for instance, with i-C_4H_9, $\varDelta_1 = \varDelta_2 = 0.04$ (Larson *et al*, 1967 and Terry & Futrell, 1968)—it is a general trend that the more substituted radicals become to abstract rather than to combine.

LXVI. $C_3H_5 + C_3H_5 \longrightarrow C_6H_{10}$ (diallyl)

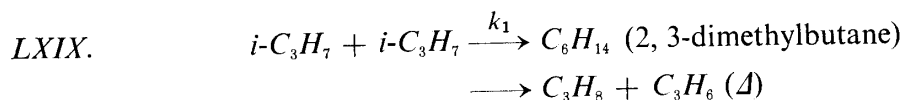 $\longrightarrow C_3H_6 + C_3H_4$ (allene) (Δ)
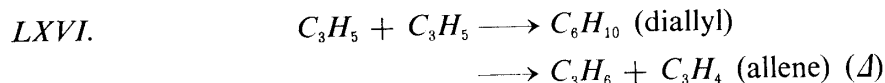
The adopted combination rate is due to Van den Bergh & Callear (1970). It is a well known fact that the reactions between two allylic radicals (allyl, methylallyl etc.) end up almost in combination. James & Troughton (1966) anticipates that *"when two allyl radicals interact, mutual combination is more than* 100 *times as probable as mutual disproportionation"*. Perhaps the disproportionation to combination ratio has never been actually measured up to the present time. Apart from allyl radicals, it could, however, with all the same chemical formulae, be quite different from the above situation for some C_3H_5 radical, as is seen in the case of 1-methylvinyl where quite a large value of $\Delta \simeq 14$ was suggested (Wagner & Zellner, 1972b). Here, $\Delta = 0.01$ has, though rather arbitrary, been used for disproportionation.
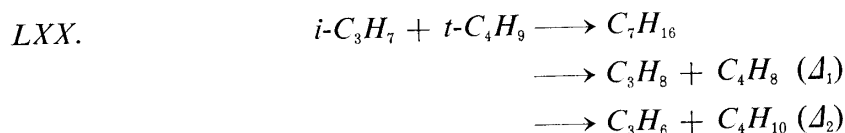
LXVII. $C_3H_5 + C_4H_7 \longrightarrow C_7H_{12}$

                                $\longrightarrow C_3H_6 + C_4H_6$

                                $\longrightarrow C_3H_4 + C_4H_8$

The *CCR* has been applied, supposing C_4H_7 to be β-methylallyl. On disproportionation, we have adopted the same assumptions as given at *LXVI*.

LXVIII. $C_3H_5 + t\text{-}C_4H_9 \xrightarrow{k_1} C_7H_{14}$

                                $\longrightarrow C_3H_6 + C_4H_8$ (Δ_1)

                                $\longrightarrow C_3H_4 + C_4H_{10}$ (Δ_2)

The *CCR* has been used in estimating combination rate k_1 from those of allyls and t-butyls. The same values of Δ as given at *LXIII* have been employed for the present purpose due to the structural similarities existing between the both reaction systems.

LXIX. $i\text{-}C_3H_7 + i\text{-}C_3H_7 \xrightarrow{k_1} C_6H_{14}$ (2, 3-dimethylbutane)

                                $\longrightarrow C_3H_8 + C_3H_6$ (Δ)

The combination rate k_1 and the ratio Δ have been taken, respectively, from Parkes & Quinn (1975) and Thynne (1962).

LXX. $i\text{-}C_3H_7 + t\text{-}C_4H_9 \longrightarrow C_7H_{16}$

                                $\longrightarrow C_3H_8 + C_4H_8$ (Δ_1)

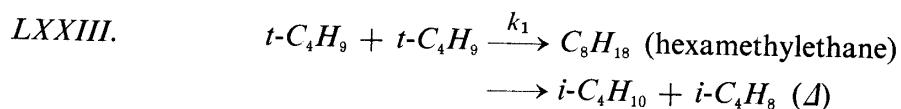 $\longrightarrow C_3H_6 + C_4H_{10}$ (Δ_2)

Disproportionation ratios were obtained by Dominquez *et al* (1962). The combination rate is here determined, in use of the *CCR*, in terms of the self-combination rates of the respective reactant radicals.

LXXI. $C_4H_7 + C_4H_7 \longrightarrow C_8H_{14}$

                                $\longrightarrow C_4H_8 + C_4H_6$ (Δ)
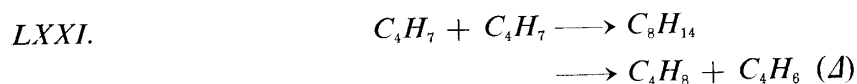
The combination rate for β-methylallyl radicals was measured to be 4.3×10^{-11} $cm^3 \cdot s^{-1}$ by Bayrakceken *et al* (1973). On the other hand, the rate for disproportionation has been taken equal to zero, because it is generally believed that almost all the reactions between allylic radicals end up in combination.

LXXII. The *CCR* has been used in estimating the combination rate from those of β-methylallyls and *t*-butyls. On disproportionation the same assumption as made at *LXVIII* is applied.

LXXIII.

$$t\text{-}C_4H_9 + t\text{-}C_4H_9 \xrightarrow{\ k_1\ } C_8H_{18} \text{ (hexamethylethane)}$$
$$\longrightarrow i\text{-}C_4H_{10} + i\text{-}C_4H_8 \ (\varDelta)$$

Although the data on k_1 and $\varDelta$ have been taken from those for *t*-butyls by Parkes & Quinn (1975), we note that all the existing butyl isomers behave, in disproportionation, quite differently from each other—$\varDelta = 0.14$, 0.77, 2.3 and 0.076 for *n*-, *s*-, *t*-, and *i*-C_4H_9, see, Gibian & Corley (1973).

Table 8. Ion-molecule reaction rates

	$k^{+)}$	Remarks and References
1) $H_2^+ + H_2 \longrightarrow (H_3^+)^* + H$	2.08(-9)	Huntress (1974)
2) $H_2^+ + He \longrightarrow HeH^+ + H$	1.3(-10)	,,
3) $H_2^+ + H \longrightarrow H^+ + H_2$	5.8(-10)	Herbst & Klemperer (1973)
4) $H^+ + H_2 \longrightarrow H_3^+ + h\nu$	1.0(-19)	*I*
5) $H^+ + He \longrightarrow HeH^+ + h\nu$	1.0(-19)	*II*
6) $H^+ + H \longrightarrow H_2^+ + h\nu$	1.0(-19)	*II*
7) $He^+ + H_2 \longrightarrow H_2^+ + He$	8.0(-14)	*III*
8) $\longrightarrow HeH^+ + H$	1.0(-14)	*III*
9) $\longrightarrow H^+ + H + He$	1.0(-14)	*III*
10) $He^+ + H_2 \longrightarrow HeH_2^+ + h\nu$	1.0(-19)	*II*
11) $He^+ + He \longrightarrow He_2^+ + h\nu$	1.0(-19)	*II*
12) $He^+ + H \longrightarrow HeH^+ + h\nu$	1.3(-15)	Sando *et al* (1971)
13) $\longrightarrow H^+ + He + h\nu$	7.0(-16)	,,
14) $HeH^+ + H_2 \longrightarrow H_3^+ + He$	1.83(-9)	Theard & Huntress (1974)
15) $HeH^+ + H \longrightarrow H_2^+ + He$	9.0(-10)	Rutherford & Vroom (1973)
16) $He_2^+ + H_2 \longrightarrow He_2H^+ + H$	5.3(-10)	Adams *et al* (1970)
17) $He_2^+ + H \longrightarrow H^+ + 2He$		*IV*
$\longrightarrow HeH^+ + He$		*IV*
18) $He_2H^+ + H_2 \longrightarrow H_3^+ + 2He$	1.8(-9)	theor, expected Huntress (1974)
19) $He_2H^+ + H \longrightarrow H_2^+ + 2He$		
$\longrightarrow HeH_2^+ + He$		
20) $HeH_2^+ + H_2 \longrightarrow H_3^+ + H + He$	1.88(-9)	theor, expected Huntress (1974)
21) $HeH_2^+ + H \longrightarrow H_3^+ + He$		
22) $H^+ + H_2 + H_2 \longrightarrow H_3^+ + H_2$	3.1(-29)	Johnson & Biondi (1974)
23) $He^+ + He + He \longrightarrow He_2^+ + He$	3.19(-29)/T	Niels & Robertson (1965)
24) $H_3^+ + H_2 + H_2 \longrightarrow H_5^+ + H_2$	3.1(-30)	*V*
25) $H^+ + H_2 + He \longrightarrow H_3^+ + He$		
$\longrightarrow HeH^+ + H_2$		
26) $H^+ + He + He \longrightarrow HeH^+ + He$		
27) $He^+ + H_2 + H_2 \longrightarrow H_3^+ + H + He$		
$\longrightarrow H_2^+ + H_2 + He$		
$\longrightarrow H^+ + H + H_2 + He$		
$\longrightarrow HeH_2^+ + H_2$		
$\longrightarrow HeH^+ + H + H_2$		
28) $He^+ + H_2 + He \longrightarrow H_2^+ + 2He$		
$\longrightarrow H^+ + H + 2He$		
$\longrightarrow HeH_2^+ + He$		
$\longrightarrow HeH^+ + H + He$		
$\longrightarrow He_2H^+ + H$		
$\longrightarrow He_2^+ + H_2$		
29) $He^+ + CH_4 \longrightarrow CH_2^+ + H_2 + He$	9.3(-10)	Huntress *et al* (1974)
30) $\longrightarrow CH^+ + H_2 + H + He$	2.4(-10)	,,
31) $\longrightarrow CH_3^+ + H + He$	6.0(-11)	,,
32) $\longrightarrow CH_4^+ + He$	4.0(-11)	,,
33) $H^+ + CH_4 \longrightarrow CH_4^+ + H$	1.5(-9)	Huntress (1975)
34) $\longrightarrow CH_3^+ + H_2$	2.3(-9)	,,
35) $H_3^+ + CH_4 \longrightarrow CH_5^+ + H_2$	2.4(-9)	Huntress *et al* (1974)
36) $CH_4^+ + H_2 \longrightarrow CH_5^+ + H$	3.3(-11)	Smith & Adams (1977)

$+)$ Units are $cm^3 \cdot s^{-1}$ or $cm^6 \cdot s^{-1}$, respectively, denendent on *second* or *third* order reactions.

Table 8. *Continued*

			k	Remarks and References
37)	$CH_4^+ + H$	$\longrightarrow CH_3^+ + H_2$	1.0(-11)	used in Prasad & Tan (1974)
38)	$CH_4^+ + CH_4$	$\longrightarrow CH_5^+ + CH_3$	1.5(-9)	Smith & Adams (1977)
39)	$CH_3^+ + CH_4$	$\longrightarrow C_2H_5^+ + H_2$	1.2(-9)	,,
40)	$CH_2^+ + H_2$	$\longrightarrow CH_3^+ + H$	1.6(-9)	,,
41)	$CH_2^+ + CH_4$	$\longrightarrow C_2H_5^+ + H$	2.5(-10)	Huntress *et al* (1974)
42)		$\longrightarrow C_2H_4^+ + H_2$	4.7(-10)	,,
43)		$\longrightarrow C_2H_3^+ + H + H_2$	2.4(-10)	,,
44)		$\longrightarrow C_2H_2^+ + 2H_2$	1.4(-10)	,,
45)	$CH^+ + H_2$	$\longrightarrow CH_2^+ + H$	1.01(-9)	Kim *et al* (1975)
46)	$CH^+ + CH_4$	$\longrightarrow C_2H_4^+ + H$	7.0(-11)	Huntress *et al* (1974)
47)		$\longrightarrow C_2H_3^+ + H_2$	9.8(-10)	,,
48)		$\longrightarrow C_2H_2^+ + H_2 + H$	1.4(-10)	,,
49)	$CH_5^+ + H$	$\longrightarrow CH_4^+ + H_2$	1.0(-10)	used in Capone *et al* (1976)
50)	$C_2H_5^+ + H$	$\longrightarrow C_2H_4^+ + H_2$	1.0(-10)	,,
51)	$He^+ + C_2H_2$	$\longrightarrow C_2H_2^+ + He$	2.5(-10)	*VI* (for this and following
52)		$\longrightarrow C_2H^+ + H + He$	8.8(-10)	reactions)
53)		$\longrightarrow C_2^+ + H_2 + He$	1.6(-9)	
54)		$\longrightarrow CH^+ + CH + He$	8.0(-10)	
55)	$He^+ + C_2H_4$	$\longrightarrow C_2H_4^+ + He$	2.4(-10)	
56)		$\longrightarrow C_2H_3^+ + H + He$	1.7(-10)	
57)		$\longrightarrow C_2H_2^+ + H_2 + He$	2.2(-9)	
58)		$\longrightarrow C_2H^+ + H + H_2 + He$	4.4(-10)	
59)		$\longrightarrow CH_2^+ + CH_2 + He$	4.1(-10)	
60)	$He^+ + C_2H_6$	$\longrightarrow C_2H_4^+ + H_2 + He$	4.2(-10)	
61)		$\longrightarrow C_2H_3^+ + H + H_2 + He$	1.7(-9)	
62)		$\longrightarrow C_2H_2^+ + 2H_2 + He$	8.4(-10)	
63)	$H_2^+ + CH_4$	$\longrightarrow CH_5^+ + H$	1.1(-10)	
64)		$\longrightarrow CH_4^+ + H_2$	1.4(-9)	
65)		$\longrightarrow CH_3^+ + H + H_2$	2.3(-9)	
66)	$H_2^+ + C_2H_2$	$\longrightarrow C_2H_3^+ + H$	4.8(-10)	
67)		$\longrightarrow C_2H_2^+ + H_2$	4.8(-9)	
68)	$H_2^+ + C_2H_4$	$\longrightarrow C_2H_4^+ + H_2$	2.2(-9)	
69)		$\longrightarrow C_2H_3^+ + H + H_2$	1.8(-9)	
70)		$\longrightarrow C_2H_2^+ + 2H_2$	8.8(-10)	
71)	$H_2^+ + C_2H_6$	$\longrightarrow C_2H_6^+ + H_2$	2.9(-10)	
72)		$\longrightarrow C_2H_5^+ + H + H_2$	1.4(-9)	
73)		$\longrightarrow C_2H_4^+ + 2H_2$	2.4(-9)	
74)		$\longrightarrow C_2H_3^+ + H + 2H_2$	6.9(-10)	
75)		$\longrightarrow C_2H_2^+ + 3H_2$	2.0(-10)	
76)	$H_3^+ + C_2H_2$	$\longrightarrow C_2H_3^+ + H_2$	3.5(-9)	
77)	$H_3^+ + C_2H_4$	$\longrightarrow C_2H_5^+ + H_2$	1.4(-9)	
78)		$\longrightarrow C_2H_3^+ + 2H_2$	2.2(-9)	
79)	$H_3^+ + C_2H_6$	$\longrightarrow C_2H_5^+ + 2H_2$	3.4(-9)	
80)	$(H_3^+)^* + CH_4$	$\longrightarrow CH_5^+ + H_2$	1.0(-9)	*VII*
81)		$\longrightarrow CH_3^+ + 2H_2$	1.4(-9)	*VII*
82)	$(H_3^+)^* + C_2H_2$	$\longrightarrow C_2H_3^+ + H_2$	3.5(-9)	*VII*
83)	$(H_3^+)^* + C_2H_4$	$\longrightarrow C_2H_5^+ + H_2$	3.6(-10)	*VII*
84)		$\longrightarrow C_2H_4^+ + H_2 + H$	8.0(-10)	*VII*
85)		$\longrightarrow C_2H_3^+ + 2H_2$	2.8(-9)	*VII*
86)	$(H_3^+)^* + C_2H_6$	$\longrightarrow C_2H_5^+ + 2H_2$	3.4(-9)	*VII*

Table 8. *Continued*

			k	Remarks and References
87)	$(H_3^+)^* + H_2$	$\longrightarrow H_3^+ + H_2$	3.0(-10)	Kim *et al* (1974)
88)	$H_5^+ + CH_4$	$\longrightarrow CH_5^+ + 2H_2$	2.0(-9)	used in Capone *et al* (1976)
89)	$C_2^+ + H_2$	$\longrightarrow C_2H^+ + H$	1.4(-9)	Adams & Smith (1977)
90)	$C_2H^+ + H_2$	$\longrightarrow C_2H_2^+ + H$	1.7(-9)	,,
91)	$CH_3^+ + C_2H_2$	$\longrightarrow C_3H_3^+ + H_2$	1.15(-9)	
92)	$CH_3^+ + C_2H_4$	$\longrightarrow C_2H_3^+ + CH_4$	3.5(-10)	
93)		$\longrightarrow C_3H_3^+ + 2H_2$	5.0(-11)	
94)		$\longrightarrow C_3H_5^+ + H_2$	5.2(-10)	
95)	$CH_3^+ + C_2H_6$	$\longrightarrow C_2H_5^+ + CH_4$	1.5(-9)	
96)		$\longrightarrow C_3H_5^+ + 2H_2$	1.6(-10)	
97)		$\longrightarrow C_3H_7^+ + H_2$	1.0(-10)	
98)	$CH_3^+ + H_2 + M$	$\longrightarrow CH_3^+ \cdot H_2 + M$	1.3(-28)	Smith & Adams (1978)
99)	$CH_4^+ + C_2H_2$	$\longrightarrow C_2H_2^+ + CH_4$	1.1(-9)	
100)		$\longrightarrow C_2H_3^+ + CH_3$	1.2(-9)	
101)		$\longrightarrow C_3H_3^+ + H_2 + H$	1.5(-10)	
102)	$CH_4^+ + C_2H_4$	$\longrightarrow C_2H_4^+ + CH_4$	1.4(-9)	
103)		$\longrightarrow C_2H_5^+ + CH_3$	4.2(-10)	
104)		$\longrightarrow C_3H_5^+ + H_2 + H$	6.0(-11)	
105)	$CH_4^+ + C_2H_6$	$\longrightarrow C_2H_4^+ + CH_4 + H_2$	1.91(-9)	
106)	$C_2H_2^+ + CH_4$	$\longrightarrow C_3H_4^+ + H_2$	1.8(-10)	
107)		$\longrightarrow C_3H_5^+ + H$	6.6(-10)	
108)	$C_2H_2^+ + C_2H_2$	$\longrightarrow C_4H_2^+ + H_2$	5.2(-10)	
109)		$\longrightarrow C_4H_3^+ + H$	8.9(-10)	
110)	$C_2H_2^+ + C_2H_4$	$\longrightarrow C_2H_4^+ + C_2H_2$	4.0(-10)	
111)		$\longrightarrow C_3H_3^+ + CH_3$	5.1(-10)	
112)		$\longrightarrow C_4H_5^+ + H$	2.7(-10)	
113)	$C_2H_2^+ + C_2H_6$	$\longrightarrow C_2H_4^+ + C_2H_4$	2.6(-10)	
114)		$\longrightarrow C_2H_5^+ + C_2H_3$	1.3(-10)	
115)		$\longrightarrow C_3H_3^+ + CH_3 + H_2$	9.0(-11)	
116)		$\longrightarrow C_3H_5^+ + CH_3$	7.9(-10)	
117)		$\longrightarrow C_4H_5^+ + H_2 + H$	7.0(-11)	
118)		$\longrightarrow C_4H_7^+ + H$	1.3(-10)	
119)	$C_2H_3^+ + CH_4$	$\longrightarrow C_3H_5^+ + H_2$	2.2(-10)	Adams & Smith (1977)
120)	$C_2H_3^+ + C_2H_2$	$\longrightarrow C_4H_3^+ + H_2$	2.5(-10)	
121)	$C_2H_3^+ + C_2H_4$	$\longrightarrow C_2H_5^+ + C_2H_2$	9.3(-10)	
122)	$C_2H_3^+ + C_2H_6$	$\longrightarrow C_2H_5^+ + C_2H_4$	2.9(-10)	
123)		$\longrightarrow C_3H_5^+ + CH_4$	2.5(-10)	
124)		$\longrightarrow C_4H_7^+ + H_2$	8.0(-11)	
125)	$C_2H_4^+ + C_2H_2$	$\longrightarrow C_3H_3^+ + CH_3$	6.3(-10)	
126)		$\longrightarrow C_4H_5^+ + H$	1.6(-10)	
127)	$C_2H_4^+ + C_2H_4$	$\longrightarrow C_3H_5^+ + CH_3$	7.3(-10)	
128)		$\longrightarrow C_4H_7^+ + H$	7.0(-11)	
129)	$C_2H_4^+ + C_2H_6$	$\longrightarrow C_3H_6^+ + CH_4$	3.7(-13)	
130)		$\longrightarrow C_3H_7^+ + CH_3$	4.9(-12)	
131)	$C_2H_5^+ + C_2H_2$	$\longrightarrow C_3H_3^+ + CH_4$	6.8(-11)	
132)		$\longrightarrow C_4H_5^+ + H_2$	1.2(-10)	
133)	$C_2H_5^+ + C_2H_2 + H_2$	$\longrightarrow C_2H_5^+ \cdot C_2H_2 + H_2$	1.34(-25)	Burt *et al* (1970)
134)	$C_2H_5^+ + C_2H_4$	$\longrightarrow C_3H_5^+ + CH_4$	3.9(-10)	
135)	$C_2H_5^+ + C_2H_6$	$\longrightarrow C_4H_9^+ + H_2$	9.0(-12)	Burt *et al* (1970)
136)		$\longrightarrow C_2H_7^+ + C_2H_4$	0	,,

Table 8. *Continued*

|		k	Remarks and References
137)	$\longrightarrow C_3H_7^+ + CH_4$	1.4(-12)	Burt *et al* (1970)
138)	$C_2H_6^+ + C_2H_2 \longrightarrow C_2H_5^+ + C_2H_3$	2.2(-10)	
139)	$\longrightarrow C_3H_5^+ + CH_3$	8.2(-10)	
140)	$\longrightarrow C_4H_7^+ + H$	1.3(-10)	
141)	$C_2H_6^+ + C_2H_4 \longrightarrow C_2H_4^+ + C_2H_6$	1.15(-9)	
142)	$C_2H_6^+ + C_2H_6 \longrightarrow C_3H_8^+ + CH_4$	8.0(-12)	
143)	$\longrightarrow C_3H_9^+ + CH_3$	1.1(-11)	
144)	$C^+ + H_2 \longrightarrow$ products		
145)	$C^+ + CH \longrightarrow C_2^+ + H$	2.0(-9)	Herbst & Klemperer (1973)
146)	$C^+ + CH_2 \longrightarrow C_2H^+ + H$	2.0(-9)	,,
147)	$C^+ + C_2H \longrightarrow C_3^+ + H$	1.0(-9)	used in Giguere & Huebner (1978)
148)	$C^+ + CH_4 \longrightarrow C_2H_3^+ + H$	8.0(-10)	Adams & Smith (1977)
149)	$\longrightarrow C_2H_2^+ + H_2$	4.0(-10)	,,
150)	$C^+ + H \longrightarrow CH^+ + h\nu$	1.7(-17)·300/T	Klemperer (1971)
151)	$C^+ + H_2 + M \longrightarrow CH_2^+ + M$	2.1(-29)	Fehsenfeld *et al* (1974)
152)	$CH_3^+ + C \longrightarrow C_2H^+ + H_2$	1.0(-9)	Klemperer (1971)
153)	$CH_5^+ + CH_3 \longrightarrow C_2H_6^+ + H_2$	5.0(-10)	used in Capone *et al* (1976)
154)	$CH_5^+ + C_2H_6 \longrightarrow C_2H_7^+ + CH_4$	1.5(-9)	,,
155)	$CH_5^+ + CH_4 + M \longrightarrow C_2H_9^+ + M$	1.0(-29)	,,
156)	$CH_5^+ + C_2H_2 \longrightarrow C_2H_3^+ + CH_4$	1.56(-9)	MacKay *et al* (1977)
157)	$C_2H_2^+ + H_2 \longrightarrow C_2H_3^+ + H$	1.0(-11)	Adams & Smith (1977)
158)	$C_2H_2^+ + H_2 + M \longrightarrow C_2H_4^+ + M$	1.0(-29)	used in Capone *et al* (1976)
159)	$C_2H_3^+ + H_2 + H_2 \longrightarrow C_2H_5^+ + H_2$	1.49(-29)	Burt *et al* (1970)
160)	$C_2H_3^+ + H_2 + He \longrightarrow C_2H_5^+ + He$	2.0(-29)	Adams & Smith (1977)
161)	$C_2H_4^+ + H \longrightarrow C_2H_3^+ + H_2$	1.0(-10)	used in Capone *et al* (1976)
162)	$C_2H_4^+ + CH_3 \longrightarrow CH_3^+ + C_2H_4$	1.0(-9)	,,
163)	$C_2H_4^+ + CH_4 + M \longrightarrow C_3H_8^+ + M$	1.0(-29)	,,
164)	$C_2H_4^+ + H_2 + M \longrightarrow C_2H_6^+ + M$	1.0(-29)	,,
165)	$C_2H_5^+ + CH_3 \longrightarrow C_2H_4^+ + CH_4$	5.0(-10)	,,
166)	$C_2H_5^+ + H_2 \longrightarrow$ products		
167)	$C_2H_5^+ + CH_4 + M \longrightarrow C_3H_9^+ + M$	1.0(-29)	used in Capone *et al* (1976)
168)	$C_2H_5^+ + H_2 + M \longrightarrow C_2H_7^+ + M$	1.0(-29)	,,
169)	$C_2H_6^+ + H \longrightarrow C_2H_5^+ + H_2$	1.0(-10)	,,
170)	$C_2H_6^+ + CH_3 \longrightarrow CH_3^+ + C_2H_6$	1.0(-9)	,,
171)	$C_2H_6^+ + CH_4 + M \longrightarrow C_3H_{10}^+ + M$	1.0(-29)	,,
172)	$C_2H_7^+ + H \longrightarrow C_2H_6^+ + H_2$	1.0(-10)	,,
173)	$C_2H_7^+ + CH_3 \longrightarrow C_2H_6^+ + CH_4$	5.0(-10)	,,
174)	$C_2H_7^+ + CH_4 + M \longrightarrow C_3H_{11}^+ + M$	1.0(-29)	,,
175)	$C_3^+ + H_2 \longrightarrow C_3H^+ + H$	1.0(-9)	Johnson & Biondi (1974)
176)	$C_2^+ + CH_4 \longrightarrow C_2H^+ + CH_3$	2.4(-10)	Adams & Smith (1977)
177)	$\longrightarrow C_2H_2^+ + CH_2$	1.8(-10)	,,
178)	$\longrightarrow C_3H^+ + H + H_2$	2.0(-10)	,,
179)	$\longrightarrow C_3H_2^+ + H_2$	5.8(-10)	,,
180)	$\longrightarrow C_3H_3^+ + H$	2.1(-10)	,,
181)	$C_2H^+ + CH_4 \longrightarrow C_2H_2^+ + CH_3$	3.7(-10)	,,
182)	$\longrightarrow C_3H_3^+ + H_2$	3.7(-10)	,,
183)	$\longrightarrow C_3H_4^+ + H$	1.3(-10)	,,
184)	$\longrightarrow C_3H_5^+$	2.2(-10)	,,
185)	$C_2H_3^+ + C_2H_2 + H_2 \longrightarrow C_2H_3^+ \cdot C_2H_2 + H_2$	2.98(-25)	Burt *et al* (1970)

Table 8. *Continued*

	k	Remarks and References
186) $C_3H_5^+ + C_2H_4 + H_2 \longrightarrow C_5H_9^+ + H_2$	5.4(-26)	Burt *et al* (1970)
187) $C_4H_9^+ + C_2H_4 \longrightarrow C_6H_9^+ + 2H_2$	4.0(-10)	"
188) $H^+ + e \longrightarrow H + h\nu$	6.25(-12)	estimated by Hunten (1969)
189) $He^+ + e \longrightarrow He + h\nu$	6.25(-12)	"
190) $H_2^+ + e \longrightarrow H + H$	3.4(-7)	Leu *et al* (1973)
191) $H_3^+ + e \longrightarrow H_2 + H$	4.16(-6)/$T^{0.5}$	Johnson & Biondi (1974)
192) $H_5^+ + e \longrightarrow H_2 + H_2 + H$	1.7(-7)/$T^{0.5}$	"
193) $He_2^+ + e \longrightarrow He + He$	1.0(-7)	assumed
194) $HeH^+ + e \longrightarrow He + H$	1.0(-7)	used in Prasad & Tan (1974)
195) $HeH_2^+ + e \longrightarrow He + H_2$	4.0(-7)	"
196) $He_2H^+ + e \longrightarrow He + He + H$	1.0(-7)	assumed
197) $C^+ + e \longrightarrow C + h\nu$	1.9(-10)/$T^{0.7}$	used in Giguere & Huebner (1978)
198) $CH^+ + e \longrightarrow C + H$	1.7(-6)/$T^{0.5}$	Krauss & Julienne (1973)
199) $\longrightarrow CH + h\nu$	5.7(-9)/$T^{0.7}$	"
200) $CH_2^+ + e \longrightarrow CH + H$	4.3(-6)/$T^{0.5}$	used in Giguere & Huebner (1978)
201) $\longrightarrow C + H_2$	4.3(-6)/$T^{0.5}$	"
202) $CH_3^+ + e \longrightarrow CH_2 + H$	2.9(-6)/$T^{0.5}$	"
203) $\longrightarrow CH + H_2$	2.9(-6)/$T^{0.5}$	"
204) $\longrightarrow CH + H + H$	2.9(-6)/$T^{0.5}$	"
205) $CH_5^+ + e \longrightarrow CH_4 + H$	3.3(-5)/$T^{0.5}$	Rebbert *et al* (1973)
206) $CH_4^+ + e \longrightarrow CH_3 + H$	1.7(-6)/$T^{0.5}$	used in Giguere & Huebner (1978)
207) $\longrightarrow CH_2 + H_2$	1.7(-6)/$T^{0.5}$	"
208) $\longrightarrow CH_2 + H + H$	1.7(-6)/$T^{0.5}$	"
209) $\longrightarrow CH + H_2 + H$	1.7(-6)/$T^{0.5}$	"
210) $\longrightarrow CH + H + H + H$	1.7(-6)/$T^{0.5}$	"
211) $C_2^+ + e \longrightarrow C + C$	8.7(-6)/$T^{0.5}$	"
212) $C_2H^+ + e \longrightarrow C_2 + H$	3.3(-5)/$T^{0.5}$	"
213) $C_2H_2^+ + e \longrightarrow C_2H + H$	1.7(-5)/$T^{0.5}$	"
214) $\longrightarrow C_2 + H + H$	1.7(-5)/$T^{0.5}$	used in Capone *et al* (1976)
215) $C_2H_3^+ + e \longrightarrow C_2H_2 + H$	3.3(-5)/$T^{0.5}$	"
216) $C_2H_4^+ + e \longrightarrow C_2H_2 + H_2$	3.3(-5)/$T^{0.5}$	"
217) $C_2H_5^+ + e \longrightarrow C_2H_2 + H_2 + H$	3.3(-5)/$T^{0.5}$	Krauss & Julienne (1973)
218) $\longrightarrow C_2H_4 + H$	3.3(-5)/$T^{0.5}$	"
219) $C_2H_6^+ + e \longrightarrow C_2H_4 + H_2$	3.3(-5)/$T^{0.5}$	used in Capone *et al* (1976)
220) $C_2H_7^+ + e \longrightarrow C_2H_6 + H$	3.3(-5)/$T^{0.5}$	"
221) $C_2H_9^+ + e \longrightarrow C_2H_6 + H_2 + H$	3.3(-5)/$T^{0.5}$	"
222) $C_nH_m^+ + e \longrightarrow C_nH_{m-1} + H \ (n \geqslant 3)$	6.6(-5)/$T^{0.5}$	*VIII*

Remarks in Table 8

I. The reaction is of vital importance in determining the abundance of H^+, a predominant ion in the topside ionospheres of the giant planets. No experimental or theoretical suggestions have been given about the rate coefficient. All the existing works dealing with ion chemistry in those outer planets have examined the effect of this process on ion density profiles by tentatively changing the rate coefficient by several orders of magnitude. Here we have simply followed the most conventional value so far assumed. The importance of the study for this reaction system can never be overemphasized.

II. Upper limit anticipated by Huntress (1974).

III. Fehsenfeld *et al* (1966) set an upper limit, $10^{-13}\,cm^3 \cdot s^{-1}$ for He^+ loss rate and this value was allotted to the reactions *7~9* with a proportion of 8 : 1 : 1 (Prasad & Tan, 1974).

IV. Hereafter, in all the cases where the column for rate coefficient is left unfilled, it means that the reaction path is being thought probable but the rate is not actually known and at the same time that the process has not been taken into account in our calculations.

V. $k_{24} < 0.1 k_{22}$ by Saporoschenko (1965). Use is made of the data at equality.

VI. Hereafter (from reaction *51* to *143*), if reference is not explicitly given, it shows that the rate value is taken from Huntress (1977)—the compilation of ion-molecule reactions of astrophysical interest, where one can find the appropriate original references.

VII. It is well known that H_3^+ is initially formed in vibrationally excited states by the reaction $H_2^+ + H_2$ and the rates listed in the table (*80–86*) are those for such excited H_3^+ ions. Note that the generation mechanism of that ion in the planetary ionospheres is just the same as that in the experimental conditions under which those rates were measured.

VIII. For all the ions of $C_n H_m^+$ ($n \geqslant 3$), it is assumed that the recombination with electron results in the fragments as $C_n H_{m-1} + H$, except for the particular ions of C_3^+, $C_3 H_{10}^+$, $C_3 H_{11}^+$, of which the following decompositions are assumed (see, also Chap. III, § 6)

$$C_3^+ + e \longrightarrow C_2 + C$$
$$C_3 H_{10}^+ + e \longrightarrow C_3 H_8 + H_2$$
$$C_3 H_{11}^+ + e \longrightarrow C_3 H_8 + H + H_2.$$
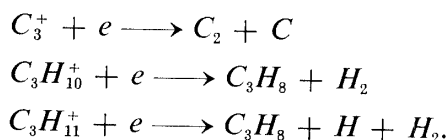
The rate coefficients are uniformly assumed to be twice the rate of reaction *221*.

Chapter IV. ATMOSPHERIC MODEL AND METHOD OF COMPUTATION

1. Equation Describing Density Distribution of Molecule

Dynamics is, together with photochemistry, an important factor in determining the distribution of molecule with altitude. Mathematically these dynamical and photochemical processes may be expressed, when we restrict ourselves to the one dimensional variation along the vertical direction, as follows

$$\frac{\partial n_i}{\partial t} = \frac{\partial}{\partial z} D_i n_i \left(\frac{1}{n_i} \frac{\partial n_i}{\partial z} + \frac{1}{H_i} + \frac{1}{T_+} \frac{\partial T_+}{\partial z} \right) + \frac{\partial}{\partial z} K n_i \left(\frac{1}{n_i} \frac{\partial n_i}{\partial z} + \frac{1}{H} + \frac{1}{T_n} \frac{\partial T_n}{\partial z} \right)$$
$$+ \sum_\ell \sum_k \frac{\Phi_k}{R^2} e^{-\tau_k \sec \chi} \sigma_k^{\ell,i} n_\ell - \sum_k \frac{\Phi_k}{R^2} e^{-\tau_k \sec \chi} \sigma_k^i n_i + \sum_{a,b} \alpha_{a,b}^i n_a n_b - \left(\sum_a \alpha_{i,a} n_a \right) n_i$$

where the notations are:

n_i: the number density of i-th molecule

H_i: the diffusive scale height defined by $H_i = kT/m_i g$ (T, the neutral or ion temperature depending on whether the i-th molecule is neutral or ionic species (T_n or T_+, respectively), k, the Boltzmann constant, g, the gravitational constant)

K: eddy diffusion coefficient

H: mixing scale height defined by $H = kT_n/m_a g$ (T_n, the neutral temperature, m_a, the atmospheric mean mass defined by $m_a = \sum_j m_j n_j / \sum_j n_j$)

Φ_k: the solar photon flux at the earth's orbit in k-th wavelength interval

R: the heliocentric distance to the planet

τ_k: the vertical optical depth in k-th wavelength interval

$\sigma_k^{\ell, i}$: the cross section of the specific photoprocess which, in the act of the photons whose wavelength is characterized by k on ℓ-th molecule, results in the production of i-th molecule

σ_k^i: the total cross section of the photoprocesses in k-th wavelength interval, through which i-th molecule is changed to non i-th molecules (due to such as photodissociation and/or photoexcitation)

$\alpha_{a,b}^i$: the rate coefficient of the reaction between a-th and b-th molecules which produces i-th molecule

$\alpha_{i,a}$: the rate coefficient of the reaction between i-th and a-th molecules which alters the former to non i-th molecules.

The terms in the righthand side[*], in sequence, represent molecular diffusion, eddy diffusion, input and output by photoprocesses, and input and output by chemical reactions. All the above quantities must of course be definite before actual calculations. In the following we describe, particularly on the molecular and eddy diffusions, how they have been assessed.

i) *Molecular diffusion*

Molecular diffusion works upon each species in such a way as it establishes a diffusive separation according to the scale height of its own, and its importance relative to the other effects is controlled by the molecular diffusion coefficient D_i. In the first approximation of the classical gas kinetic theory (Chapman & Cowling, 1970), this is given by

$$D_i = 3kT(m_i + m_j)/16n\Omega_{ij}m_i m_j,$$

where n is the total concentration of gas particles and Ω_{ij} the so-called collision integral between i-th and j-th particles (in our calculations, either of them is molecular hydrogen because of the predominant abundance).

Precise determination of Ω_{ij} is of course dependent on the detailed knowledge of an interaction potential between both particles, although it would not be available

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[*] Here by dynamics we have considered only those bulk motions resulting from molecular diffusion and atmospheric turbulence, the latter are characterized by the so-called eddy diffusion and have not included the motions associated with something like general circulation.

in most systems of our concern. Except for a limited number of binary gas systems for which diffusion coefficients are known by experiment, rigid elastic sphere characterized by the effective interaction radius of 3Å has been uniformly applied to Ω_{ij} for the neutral binary mixtures. Then we would obtain,

$$D_i = 1.52 \times 10^{18} (1/M_i + 1/M)^{1/2} T^{1/2}/n \quad \text{cm}^2 \text{ s}^{-1}$$

with the mass measured in atomic mass unit.

As for the ionic species, the diffusion coefficients have been calculated by

$$D_i = \frac{kT_+}{m_i} \sum_a \frac{1}{\nu_{i,a}}$$

where, T_+ is the ion temperature and $\nu_{i,a}$ the collision frequency between i-th ion and a-th neutral molecule (H_2, He and H in the present case). Here the frequency has been assumed to obey Langevin's expression (Langevin, 1905), an expression obtained when a pure polarization interaction is postulated to prevail between them,

$$\nu_{i,a} = 2.6 \times 10^{-9} n_a (\alpha_a/\mu)^{1/2} \quad \text{s}^{-1}$$

where, μ is the reduced mass of the colliding system in atomic mass unit and α_a the polarizability of a-th particle in unit of 10^{-24}cm^3.

Furthermore, in the case of such ionic species, the term describing the molecular diffusion is subject to some modifications owing to the so-called ambipolar nature of diffusion and also owing to the inability of their diffusing across the magnetic line of force. The required modification can be taken into account as follows,

$$D_i \sin^2 I \cdot n_i \left(\frac{1}{n_i} \frac{\partial n_i}{\partial z} + \frac{(T_e/T_+)}{n_e} \frac{\partial n_e}{\partial z} + \frac{1}{H_i} + \frac{1}{T_+} \frac{\partial}{\partial z} (T_e + T_+) \right)$$

where, I is the inclination of the field line to the horizontal, T_e the electron temperature and n_e, the electron density.

ii) *Eddy diffusion*

By eddy diffusion is meant the mass transport arising from the various scales (in space and time) of turbulent eddies existing in the atmosphere. In the tenuous part, these are usually the *in-situ* features of the propagative and dissipative waves which originated, at the deeper levels of altitude, in atmospheric disturbances such as internal gravity waves, planetary waves and tidal waves. Care must, however, be taken in that the above expression of eddy diffusion represented in the similar form as molecular diffusion is somewhat of an empirical nature, since the equations of motion are not very useful for describing the complexity that arises from the inertial interaction of different mass elements. The eddy diffusion appears, in mechanisms and in magnitudes, as yet to include some controversial aspects even in the terrestrial case. In the planetary cases, such a diffusion coefficient has been conjectured by observing the intensity of $Ly\,\alpha$ albedo from the planetary disk. This is due to the fact that the abundance of atomic hydrogen in the upper atmosphere suffers a reduction in a predictable way in principle with the increasing coefficient. In Table 9

Tabie 9. *Ly* α observations on Jupiter

Investigators	Date of obs.	Instrument	Intensity (kR)
Moos *et al* (1969)	1967, Sep. 5	rocket	4
Rottman *et al* (1973)	1971, Jan. 25	rocket	4.4 ±2.6
Giles *et al* (1976)	1972, Sep. 1	rocket	2.1 ±1.0
Jenkins *et al*[1]	1973, May 2–3	Copernicus	0.66±0.35
Carlson & Judge (1974)	1973, Dec.	Pioneer 10	0.40±0.12
Bertaux *et al* (1979)	1976, Jan. 5	Copernicus	2.8 ±1.0
	1976, Aug.–Sep.	Copernicus	4.0 ±1.4
Cochran & Barker (1979)	1978, Mar.	Copernicus	8.3 ±2.9
Clarke *et al*[2] (1979a, b)	1978, Dec. 1	rocket	13
	1978, Dec. 7	IUE	14
Broadfoot *et al* (1979)	1979, Jan.	Voyager 1	14
Clarke *et al* (1979b)	1979, Feb. 28	IUE	15

1) Jenkins. E. B., L. Wallace and J. F. Drake, quoted by Carlson & Judge (1974) as a private communication.
2) Clarke. J. T., W. G. Fastie, P. G. Feldman, H. W. Moos, H. A. Weaver and C. B. Opal, 1979a, EOS, **60**, 307; 1979b, private communication to Cochran & Barker (1979).

we show the observational results so far obtained with the Jovian $Ly\,\alpha$ brightness. The values of eddy diffusion coefficients derived from such observations in earlier days have yielded a dispute about the plausible strength of turbulence in the Jovian atmosphere (for instance, see, Wallace & Hunten, 1973, Shimizu, 1974 and French & Gierasch, 1974). Apparently the table reveals a large variability of the brightness. Although this may be partly ascribed to the real variation of the concentration of atomic hydrogen (Cochran & Barker, 1979) in the atmosphere, the accuracies of measurement (significantly limited by instrumental origins) may be also related to it. More important is, however, that the theoretical models commonly used for analyzing observational results are oversimplified ones: Conversion of observed $Ly\,\alpha$ intensity (or, under some spectroscopic assumptions, of the total atomic hydrogen concentration) to eddy diffusion coefficient is not necessarily a matter of readiness. It requires detailed knowledge of the photochemical processes prevalent in the H_2/CH_4 atmosphere, those processes as a source and a sink of free hydrogen—such processes themselves are, in turn, greatly affected by the eddy diffusion. Remember the argument made in Chap. II, where it was stated that the $Ly\,\alpha$ occupies a fraction as much as about 80% of the photons whose wavelengths are shorter than that, and also that CH_4 (a substantial absorbing agent of $Ly\,\alpha$) produces in effect one atomic hydrogen every event of photoabsorption, due to $^1CH_2 + H_2 \longrightarrow CH_3 + H$.

Anyway the values usually discussed on the eddy diffusion coefficient have ranged from 10^5 to $10^8\,\mathrm{cm^2\,s^{-1}}$. Even more intense turbulence exceeding, in magnitude, $10^9\,\mathrm{cm^2\,s^{-1}}$ has been suggested by Prasad (1975), who interpreted the electron density profiles observed by Pioneer 10 (where the density peak located far above the levels so far predicted theoretically) in terms of the underlying neutral atmosphere having been substantially heated to a temperature higher than was radiatively determined: Prasad (1975) assessed the effect of atmospheric heating by a dissipation of intense

turbulence and in consequence the high eddy diffusion coefficient as mentioned was obtained. We, however, note that such a high value of K (the parametric quantity used in his heat equation) cannot be directly applied without alteration to the mass conservation equation. If use is made of the value as high as $10^9\,cm^2\,s^{-1}$ or more, the peak electron density would be too diminished to be reconciled with observations, since methane would then have become distributed to greatly high altitudes and as a result molecular ions would overwhelm atomic ions.

In the present study, altitude profile of eddy diffusion coefficient has been taken as: $10^4\,cm^2\,s^{-1}$ at the lower boundary ($p=0.01$ atm level), the magnitude increases with altitude after the scale height of mixing equilibrium, and if it reaches a value fixed beforehand (maximum eddy diffusion coefficient) at a certain height, then the same value as that is applied at all altitudes above the level. This maximum value in the eddy diffusion profile has been variously changed in our models so as to see the effects on final results ($10^5 \sim 10^8\,cm^2\,s^{-1}$).

2. Atmospheric Compositions and Thermal Structures

In this section we briefly overview the knowledge of the compositions[++] and temperatures so far obtained with the major planets. It has an obvious importance for our present purpose what compositions an atmosphere has, while on the thermal structure it affects our results more directly than might be thought at first glance. For temperature often controls chemical reactions so vitally that how an atmosphere vertically extends (depending on temperature) is of a secondary importance there.

i) *Compositions*

As described in the introductory chapter, our main concern is in investigating how and to what extent hydrocarbons would be created from methane photochemistry. For this purpose, we have simplified our problem by fixing the densities of the three

Table 10. Mixing ratios of atmospheric constituents in Jupiter

Constituent	Mixing ratio	Investigators
NH_3	$(0.7 \sim 2.0) \times 10^{-4}$	Marten *et al* (1980)
CO	$10^{-9}(1.6 \times 10^{-2}\,cm\,atm)$	Beer & Taylor (1978)
PH_3	$(1 \sim 2) \times 10^{-7}$	Tokunaga *et al* (1979)
GeH_4	6×10^{-10}	Fink *et al* (1978)
H_2O	10^{-6}	Larson *et al* (1975)
H_2S	$<5 \times 10^{-5}$	
HCN	$<1.1 \times 10^{-6}$	
CO_2	$<2.0 \times 10^{-7}$	Treffers *et al* (1978)
N_2O	$<3.0 \times 10^{-8}$	upper limit at 5 μm observation based
AsH_3	$<4.5 \times 10^{-9}$	on 100 km am H_2
SiH_4	$<2.5 \times 10^{-9}$	

[++] Here *compositions* means of the atmospheric species such as H_2, He, CH_4, NH_3 etc., which are to be regarded as a background or framework of the present calculation, but not of those minor constituents whose productions are to be expected from the former.

Table 11. Neutral and ionic species taken into account in the present calculation

neutrals: H, C, CH, CH_2, CH_2^*, CH_3, C_2, C_2H, C_2H_2, $C_2H_2^*$, C_2H_3, $C_2H_3^*$, C_2H_4, C_2H_6,
C_2H_6, C_3H_3, C_3H_4, C_3H_5, C_3H_6, C_3H_7, C_3H_8, C_4H_2, C_4H_3, C_4H_4, C_4H_5, C_4H_6,
C_4H_7, C_4H_8, C_4H_9, C_4H_{10}

ions: H^+, H_2^+, H_3^+, $(H_3^+)^*$, H_5^+, He^+, He_2^+, HeH^+, HeH_2^+, He_2H^+, C^+, CH^+, CH_2^+,
CH_3^+, CH_4^+, CH_5^+, C_2^+, C_2H^+, $C_2H_2^+$, $C_2H_3^+$, $C_2H_4^+$, $C_2H_5^+$, $C_2H_6^+$, $C_2H_7^+$,
$C_2H_9^+$, C_3^+, C_3H^+, $C_3H_2^+$, $C_3H_3^+$, $C_3H_4^+$, $C_3H_5^+$, $C_3H_6^+$, $C_3H_7^+$, $C_3H_8^+$, $C_3H_9^+$,
$C_3H_{10}^+$, $C_3H_{11}^+$, $C_4H_2^+$, $C_4H_3^+$, $C_4H_5^+$, $C_4H_7^+$, $C_4H_9^+$, $C_5H_9^+$, $C_6H_9^+$

major atmospheric constituents as H_2, He and CH_4. In other words, they have been assumed as not influenced by the minor constituents that are photochemically produced from the former. This would be a sound assumption usually adopted for calculating the abundances of minor constituents as far as they are exceedingly small compared with those of the fixed major components—only except for the greatly high altitude region where atomic hydrogen comes to outnumber molecular hydrogen. Table 11 lists those neutral and ionic hydrocarbon species whose densities are to be determined upon such 'model atmosphere'.

Concerning the bulk constituents, in order to get smooth transitions of the densities from a perfect mixing to a perfect diffusive equilibrium, the following expression is used (Banks & Kocharts 1973)

$$n_i(z) = (T(0)/T)n_i(0)\exp\left\{-\left[\int_{z_0}^z \left(\frac{1}{H_i} + \frac{A_i}{H}\right)(1+A_i)^{-1}dz + \int_{z_0}^z \alpha_{i,T}(1+A_i)^{-1}\frac{dT}{T}\right]\right\}$$

where, $T(0)$ and $n_i(0)$ are the temperature and density, respectively, at $z=z_0$, $\alpha_{i,T}$ the thermal diffusion factor and $A_i = K/D_i$. This is the expression simply obtained by integrating the familiar equation in aeronomy that describes the bulk motion of gas, under the supposition that the velocity is zero.

Before we further advance a modeling procedure relevant to the present study, there is one thing what is desirable to be examined: Is our methane photochemistry really not affected by several other atmospheric constituents whose presence in the outer planets has been proved? Table 10 shows the abundances reported for such molecules in the case of Jupiter, excepting hydrocarbons (where comparatively recent data alone are shown to avoid any confusion that may arise from simply listing many diversed data. A more general argument on compositions in the outer planets is found, *e.g.*, in the reviews of Prinn & Owen, 1976, Ridgway *et al*, 1976 and Newburn & Gulkis, 1973). So far as we judge from the mixing ratios in the table, ammonia is the sole candidate that may give rise to an influence over the present methane photochemistry. We should, however, note that those reported mixing ratios are mostly of the values to be referred to the heights below the tropopause. Above the level, the abundances of the molecules listed in the table suffer extremely large reductions. As for ammonia, for instance, the mixing ratio has been estimated to be about $10^{-7} \sim 10^{-8}$ in the Jovian stratosphere and $\lesssim 10^{-10}$ in the Saturnian stratosphere (Tokunaga *et al*, 1979, Marten *et al*, 1980). One explanation is the

so-called 'cold trap' which states, in the present example, that gaseous ammonia is frozen to cloud particles due to the low temperatures realized at levels near the tropopause and, in consequence, that it is depleted in the stratosphere. The other explanation is an irreversible destruction of ammonia in the stratosphere by the solar UV (Strobel, 1973c, Prasad & Capone, 1976, Strobel, 1977), such as

$$NH_3 + h\nu \ (\lambda < 2300A) \longrightarrow NH_2 + H$$

$$NH_2 + NH_2 + M \longrightarrow N_2H_4 \ (\text{hydrazine})$$

$$NH_2 + H + M \longrightarrow NH_3$$

$$(N_2H_4)_{gas} \xrightarrow[\text{condensation}]{} (N_2H_4)_{solid}, \text{ due to the low permissible vapor}$$
$$\text{pressure of hydrazine}$$
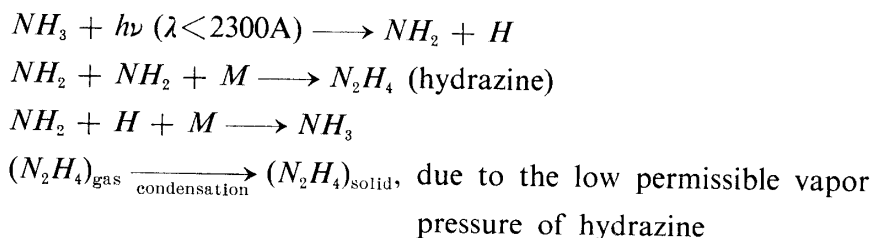
(the similar mechanism was also applied to phosphine (PH_3) and there the irreversible conversion to a red phosphorus (P_4) was suggested as responsible for possible coloration of the Great Red Spot—Prinn & Lewis, 1975). Therefore we are probably right to conclude that our methane photochemistry in and above the stratosphere is hardly affected by the other known atmospheric constituents.

Lastly we must talk about the mixing ratio of methane itself to be used in the present work, which is of a fundamental importance in the quantitative determination of hydrocarbon abundances. For the inner two of the four major planets, this can be done without particular difficulty. There are an extensive number of the available references about methane absorption on these two planets. It now seems that the mixing ratios of methane roughly fall between the solar value[+] (7×10^{-4}) to twice or thrice the value. Hence we have simply used the value of 0.001 as a methane mixing ratio in those inner major planets.

On the other hand, the situation is more controversial in the cases of the outer two planets as Uranus and Neptune. These planets are so remote and faint that quite a restricted number of observations have resulted in large discrepancies about methane abundance (and about its mixing ratio to hydrogen). The discrepancies, apart from the remoteness of planets, result from the lack of appropriate laboratory data on methane absorption in the very long path length and the very low temperature both of which the planets show. Notable fact is that almost all existing data indicate a considerable enrichment of methane compared with those of Jupiter and Saturn (*e.g.*, Mecy & Trafton, 1975, Bergstralh, 1975, Danielson *et al.*, 1977, Macy *et al*, 1978, Courtin *et al*, 1979, Benner & Fink, 1980, Macy, 1980).

We, however, should also note that these methane abundances reported are usually the ones belonging to the deep atmosphere below the tropopause. On the contrary, at the pressure levels of our concern ($p < 0.01$ atm), it is very likely that the mixing ratio is considerably small compared with those of the inner two major planets, for the minimum temperature which is realized near the tropopause is thought to be extremely low (40~60K) and hence the cold trap will work strongly, preventing methane distribution above the stratosphere. In fact, Trafton (1976), Danielson

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[+] Of course, for carbon atom but not for methane.

(1977), Gillet & Rieke (1977) and Fink & Larson (1979) suggest a large depletion of methane above the levels of $0.4 \sim 1.5$ atm. In particular, Gillet & Rieke (1977) estimated the methane mixing ratios to be 10^{-6} for the Neptunian stratosphere and $\leq 3 \times 10^{-6}$ for the Uranian stratosphere, and these values we have used as our standard mixing ratios of methane for the both planets.

ii) *Thermal structures*

The heights relevant to our present research locate, at the lowest, at a level three to four scale heights above the visible cloud top and, at the highest, at a level far above the ionospheric electron peak. Unfortunately, the knowledge commonly obtained from infrared and microwave observations is mostly concerned with the regions far below such altitudes. Thermal structures in the upper stratosphere and mesosphere[++] are very uncertain when compared with that of the troposphere. Very little knowledge we currently have about such high altitude regions is that derived from star occultations by a mere chance or derived from pure theoretical studies. Neither, however, appears to have yielded a fruitful information as a whole.

In the former star occultations, temperature obtained by inverting raw data rich in spikes is strongly dependent on an assumed form with altitude (isothermal, linear increase, etc.) and on the assumed mean molecular weight of atmosphere. In fact, in the case of Jupiter, the earlier star occultation experiments gave rise to somewhat erroneous results.

On the other hand, theoretical study too, has its own difficulties. It is usually thought that in the upper stratospheric and mesospheric regions, heat input to atmosphere is due to the near-*IR* absorption by methane (mainly ν_3 band at $3.31\,\mu$) or due to the absorption of *UV* by aerosol particles (Axel dust) floating high in the atmosphere (Gillet *et al*, 1969, Hogan *et al*, 1969, Cess & Khetan, 1973, Wallace *et al*, 1974)—as for the latter point, however, quantitative discussion beyond a mere speculation may be rather difficult. These heat inputs must be balanced by some heat losses and the most common idea will be that of utilizing a fundamental band of methane (ν_4) at $7.7\,\mu$. However, as indicated by McGovern (1968) and Strobel & Smith (1973b), ethane and/or acetylene is very likely to dominate methane in the effect of cooling atmosphere, depending on the abundances (this would be true, even if they are as few as 10^{-2} to 10^{-3}, in abundance, of methane because of the low-lying *IR*-active vibrational bands inherent to those molecules). This can further offer the potential that there might be other such hydrocarbons which are effective in cooling atmosphere—incidentally, our present research would contribute to arguing about such molecular species.

One of the constraints which we have imposed on our calculation is an isothermal nature of atmosphere. This is entirely due to a practical reason as the present research is made feasible numerically. In the Jovian case, we have fixed this isothermal temperature to 150K. We appreciate that many an objection is possible to

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[++] In the outer planets, there is no observational evidence suggestive of the second minimum in temperature profile with respect to altitude, as found in the case of the earth. The name 'mesosphere', here and in the followings, is only used to designate the heights corresponding to the atmospheric pressures by which the terrestrial mesosphere is characterized.

such a selection. The value, however, is conservative and reasonable one if altitudes are specified to those of the upper stratospheric and mesospheric regions; the Pioneer missions reported high plasma temperatures (800 ~ 1150K) in the Jovian and Saturnian ionospheres (Kliore *et al*, 1974, Fjeldbo *et al*, 1976, Kliore *et al*, 1980a, b) and simultaneously, the data further implied a much warmer environment of neutral atmosphere underlying the ionosphere than had previously been thought—see discussions by Ashihara & Shimizu (1977). Nevertheless, we emphasize that in the present research a stress is being placed on investigating the physico-chemical processes which initiate with the photodissociation of methane and lead to the production of a variety of higher hydrocarbons. For such a purpose, the most suitable selection of temperature would be the one just made above, as far as an isothermal condition is required—we have, though, tentatively changed this isothermal temperature to those other than 150K, testing the effects on the final results (see, Chap. V, § 5).

For Saturn, we have assumed the same temperature as for Jupiter, while for Uranus and Neptune it needs some explanations.

For such remote planets as Uranus and Neptune, it was not until the late 1970's that the measurements of the *IR*-brightness temperatures, in a substantial sense, started. And the effective temperatures have been reported to be 58K for Uranus (Fazio *et al*, 1976), 55.5K for Neptune (Loewenstein *et al*, 1977) and 58.5K for Uranus, 59.7K for Neptune (Stier *et al*, 1978), results confirming the presence of internal heat source in Neptune but the absence in Uranus(!). These temperatures were derived from the observations made in the far *IR* wavelength region of $40\,\mu \sim 250\,\mu$, while Gillet & Rieke (1977) examined those planets in the wavelength region of $5\,\mu \sim 22\,\mu$ and for Neptune they observed strong emission features at $8\,\mu$m and $12\,\mu$m (at the former wavelength, 150K or even higher temperatures was indicated). They interpreted the emission features as indicating that strong temperature inversion is occurring in the upper atmosphere (the emissions at $8\,\mu$m and $12\,\mu$m were then thought as due to the transitions of $CH_4(\nu_4)$ and $C_2H_6(\nu_9)$, respectively). It is very unlikely for the emission layer to be maintained only by the solar radiation, and heat from the interior of planet must be contributing to it somehow. Whereas, for Uranus, Gillet & Rieke (1977) observed in those wavelength regions much less prominent spectrum compared with that of Neptune, a result suggestive of weaker temperature inversion (this is consistent with the absence of intrinsic heat source of the planet as mentioned above but not consistent with the Wallace (1975a)'s model, which predicted a temperature of about 140K at heights above 10^{-4} atm level).

Uranus and Neptune occulted the stars of SAO158687 and BD-17°4388, respectively, in the past. By analyzing the changing light curves of star with time in immersion or emersion, one can derive useful information on the temperature of upper atmosphere. Shown below are the results reported for such events of '*star occultation*',
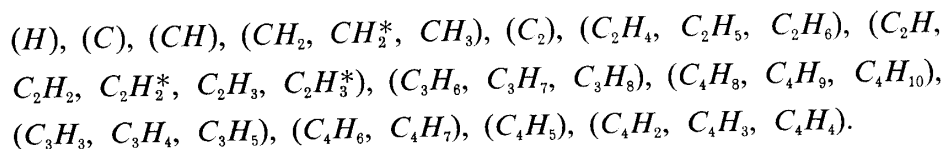
Veverka *et al* (1974)   Neptune; 135K at the density level of 10^{15} cm^{-3} (assumes pure H_2); suggests a small positive temperature gradient of ~ 0.1 K/km

Wallace (1975b)   Neptune; scale height $\sim 49\,\mathrm{km}$ at $10^{14}\,\mathrm{cm}^{-3}$ level;
   $128\mathrm{K}$ for pure H_2
   $140\mathrm{K}$ for $[He]/[H_2] \sim 0.1$

Elliot & Dunham (1979)   Uranus;
   $109\mathrm{K}$ for immersion (peak to peak variation $\sim 45\mathrm{K}$)
   $96\mathrm{K}$ for emersion (peak to peak variation $\sim 35\mathrm{K}$)
   at $10^{-4} \sim 10^{-2}\,\mathrm{mbar}$ levels.

Referencing these and the preceding Gillet & Rieke (1977)'s argument, we have assigned 100K and 130K as temperatures of our model atmospheres (isothermal) for Uranus and Neptune, respectively.

3. Numerical Method

Although an actual atmosphere is not free from various dynamical effects, the solution derived by taking into account the photochemical processes alone is quite useful for two reasons. One is that an insight is readily obtained for the chemical reactions which are effective in determining the concentrations of hydrocarbons (inclusion of transport effects more or less obscures the analysis of elementary chemical reactions occurring in model calculations). The other is that such a solution in local photochemical equilibrium can be used as an appropriate initial density distribution of molecules in order to solve diffusion equations by means of an iterative method, where a smooth transition to the final solution is to be expected in quite a natural way. If the initial distribution should be somewhat arbitrarily given with little attention being paid to chemical reactions, we note there is a possibility that a numerical scheme may break down in the course of iterative cycles owing to an overstability which is bred by several nonlinear terms involved in the scheme. Therefore, the primary step in our calculation is to prepare the density distribution of hydrocarbons in a pure photochemical equilibrium for every fixed altitude. At first we have attempted this for a system of neutral molecules. Such a neutral system (consists of 30 species except for H_2, He and CH_4) has been divided into 13 subsets, by inspecting chemical intimacies between each pair of molecules. These are

$$(H), \ (C), \ (CH), \ (CH_2, \ CH_2^*, \ CH_3), \ (C_2), \ (C_2H_4, \ C_2H_5, \ C_2H_6), \ (C_2H,$$
$$C_2H_2, \ C_2H_2^*, \ C_2H_3, \ C_2H_3^*), \ (C_3H_6, \ C_3H_7, \ C_3H_8), \ (C_4H_8, \ C_4H_9, \ C_4H_{10}),$$
$$(C_3H_3, \ C_3H_4, \ C_3H_5), \ (C_4H_6, \ C_4H_7), \ (C_4H_5), \ (C_4H_2, \ C_4H_3, \ C_4H_4).$$

With this classification, the molecular densities in each specified subset can be analytically expressed only by solving quadratic (or at most cubic) equations provided that those belonging to the other subsets are all known. This would enable us to get a solution for the whole system of neutral molecules by the method of iteration. That is, starting from the very crudely estimated values of densities, we need only continue the calculation of the above mini-cycles successively and repeatedly until

sufficient convergences are attained. We have set a criterion for convergence at relative variation of 10^{-4}. At most altitudes, convergence has been fulfilled with fairly small number of cycles but at those transitional altitudes where methane abundance rapidly diminishes, it has required several hundred times iterations, reflecting a departure of real chemical couplings from those on which the above classification of molecules has been done.

On the basis of the neutral densities thus obtained, the next step is to derive a local solution for ionic species (totally of 44 ions). For this purpose, we change the equations of ions, from $q_j - l_j n_j = 0$ to the time-dependent equations as

$$\frac{dn_j}{dt} = q_j - l_j n_j$$

where q_j and l_j are the production and loss rates of j-th ion, respectively (they depend on the abundances of ionic species other than j and those of neutral hydro-carbons). We solve, again, by using the iterative method, difference equations which are obtained by discretizing the above equations. This can be done quite easily since it suffices for our purpose to only solve a simple linear equation for each ion—there is no need to simultaneously solve the whole ionic densities (*i.e.*, matrix inversion). Here, we have monitored the production and loss of electrons. For a perfect convergence, it is necessary for the equality to be satisfactory. To confirm only the convergence of the individual ionic density is not enough since it can still hold even if some important errors were contained in the program in the course of coding ion-molecule reactions.

To say from our experiences of the present and the past studies, it is very likely that almost all calculations which attempt to determine the densities of ions end successfully by any of the existing methods, contrasted to the case of the neutral system. Presumably this is due to the fact that the system describing ion-molecule reactions is essentially linear with respect to ionic species (except for recombination reaction with electrons)—whereas, the system describing neutral-neutral reactions is quadratic and sometimes cubic with respect to neutral species. The convergence, on the contrary, is rather slow compared with the neutral case because any analytical processing has not been introduced there to accelerate conversion—a processing upon which principal chemical paths are to be reflected.

Once the ion densities have been determined in this way, the iterative scheme previously employed to obtain the neutral densities must again be used, since the input and output terms of the neutrals in the relevant part to ion-molecule reactions, suffer changes owing to the renewed abundances of ions. And then, if a sufficient convergence has been obtained for the neutral abundances, such altered densities are once more used for evaluating the production and loss terms of ionic species thereby to recalculate the ionic densities. After all, both iterative schemes for the neutrals and the ions are alternately applied and repeated until convergence of the whole system is attained.

The local equilibrium solution thus obtained is, in turn, available as an initial

distribution for the subsequent step of solving diffusion equations where the solution is sought again iteratively. Mathematically the present problem including diffusion effects is characterized by a system of non-linear differential equations of the second order. For a numerical purpose, the derivatives involved in the equations should be replaced by finite difference scheme. The choice of the best suitable difference scheme is often of a primary concern in the actual processing of numerical computation, not only because it limits accuracies of the obtained results (under given mesh intervals of discrete variables) but also because, this is to be more important, an instability arises numerically for an inadequate selection of the scheme. The system of equations of our concern may be written as

$$\frac{\partial n_i}{\partial t} = \frac{\partial}{\partial z} K\left(\frac{\partial n_i}{\partial z} + \frac{n_i}{H}\right) + P_i - L_i n_i + P_i' - L_i' n_i \quad (i = 1, \cdots, N)$$

(the term corresponding to molecular diffusion is removed in the above expression to simplify the following argument). Here P_i and P_i' are the production terms of i-th molecule due to photodissociations and chemical reactions, respectively, and $L_i n_i$ and $L_i' n_i$, the loss terms due to these processes. With respect to n_i, a variable representing the number density, these four terms have the dependences as follows,

P_i: independent of, or linearly dependent on n_j for $j \neq i$

L_i: independent of all n_j

P_i': bilinear* in n_j and $n_{j'}$ for $j \neq i$ amd $j' \neq i$

L_i': linear in n_j (except for the only one case corresponding to the reaction,

$H + H + H \longrightarrow H_2 + H$).

In the actual numerical scheme of iteration, the values of n_j appearing in the terms of P_i, P_i' and L_i' are replaced by those which have been derived at the just previous iterative cycle (*explicit* in numerical terminology), while those appearing in the other places are disposed in the complete *implicit* scheme, that is, in the following manner,

$$\frac{\partial n}{\partial t} = \frac{n_k^{\ell+1} - n_k^{\ell}}{\Delta t} \qquad \frac{\partial n}{\partial z} = \frac{n_k^{\ell+1} - n_{k-1}^{\ell+1}}{\Delta z} \qquad \text{etc.,}$$

where the superscript and subscript attached to n refer to the coordinates of time and space, respectively, and Δt and Δz are the increments of these discrete variables. This is the most conventional way of linearizing the above type of equations and of guaranteeing a fair stability for the broad range of selections of ratio between time step and space step.

Nevertheless, it is known that a numerical breakdown sometimes occurs in simulating chemical reactions that progress under the aeronomical conditions or laboratory conditions. Such an instability is found to occur first among those molecular species

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* Bilinearity is not lost even if one considers an altitude-dependent reaction coefficient for three-body association, since collisional stabilization is assumed to occur only by the bulk atmospheric constituents, such as H_2, He and CH_4.

which are chemically closely connected to each other but are characterized by their quite different lifetimes. This has usually been avoided by assuming that the species with shorter lifetimes are chemically equilibrated with those with longer lifetimes and then by solving transport equations only for such long-lived molecules. The procedure is a kind of 'approximation' and more or less includes some errors depending upon the actual conditions in calculation. We have not resorted to such an approximate procedure in the present calculations, but allowed every species to distribute with altitude according to its own ability to diffuse. Then the potentiality of causing the instability as mentioned above has been eased by introducing the following sophistications:

i) *Active introduction of photodissociation processes*

Our several preliminary calculations suggest that a numerical scheme tends to be stabilized by photodissociation processes taken into calculation, particularly for those molecules with short lifetimes (namely, radicals). Hence such photodissociation processes have been incorporated into the calculation scheme as far as possible (*cf.* Chap. II).

ii) *Variable time step*

The instability has a root, in that chemical lifetimes are very different among those species which are chemically coupled. We have thus assigned the best suitable time increment to every each specie. This would be justified because our present study concerns only the stationary concentrations of molecules to be obtained finally and not the time-dependent features.

iii) *Ordering of species*

Experiences suggest that at least in our present numerical scheme the order in which species are calculated at the fixed iteration cycle can greatly benefit the stability, if it is deliberately chosen, allowing *redundancy*. In the scheme of neutral hydrocarbons, they have been ordered as,

$$C_2H_6, \ C_3H_8, \ C_4H_{10}, \ C_2H_2, \ C_3H_4,$$

$$\left. \begin{array}{l} CH_2^*, \ CH, \ C_2H_2^*, \ C_2H_3^*, \ C_2, \ C, \ C_2H, \ H, \ C_3H_3, \ C_3H_7, \\ C_2H_3, \ C_2H_5, \ CH_2, \ C_3H_5, \ C_4H_3, \ C_4H_5, \ C_4H_7, \ CH_3, \ C_4H_9 \end{array} \right\} = A$$

$$C_3H_6, \ C_2H_4, \ C_4H_2, \ C_4H_8, \ C_4H_4, \ C_4H_6,$$
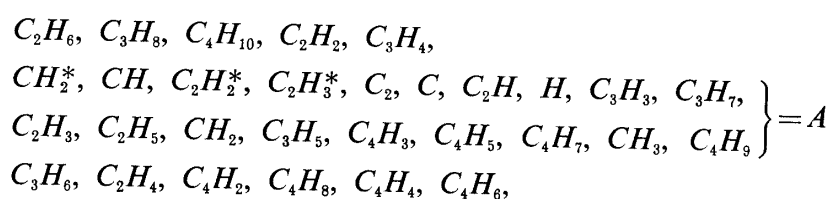
again calculates the molecules of set A.

Probably, the frequent adjustments of densities for short-lived radicals (A) before and after those for the long-lived molecules, have removed a kind of numerical *strain* that might otherwise have accumulated. With the above improvements, our numerical scheme has been considerably strengthened against latent instabilities.

When appropriate boundary conditions are imposed, the present problem reduces to solving a matrix equation, such as, $A \cdot N = C$ for each species in every iteration cycle. Here, A is characterized by tridiagonal matrix, and N and C are, respectively, unknown and known vectors. The quite rapid method to solve it, which does not need a matrix inversion, can be found in the comprehensive book by Richtmyer (1957).
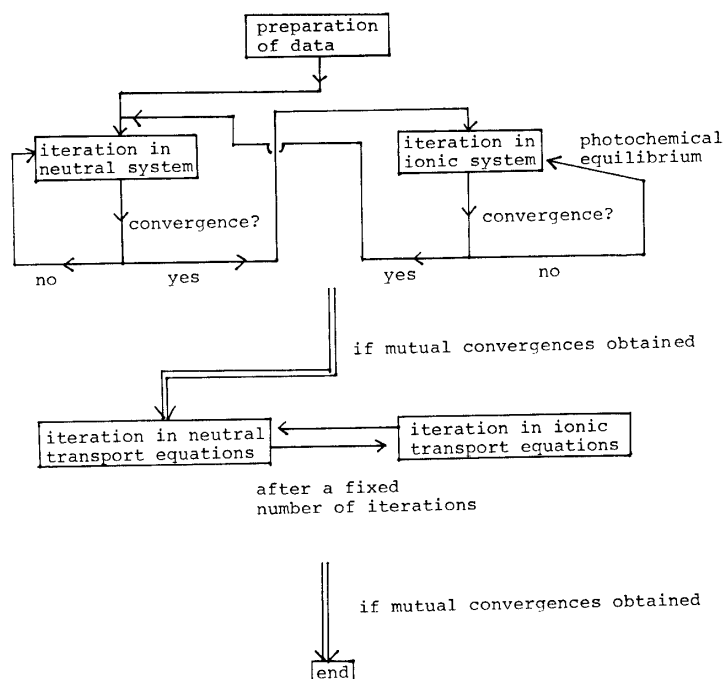
Fig. 12. Flow Diagram of Numerical Method.

The analysis of the obtained results is a matter of complexity because so many processes of photodissociations and chemical reactions are taken into account in this study. For convenience of their analyses, a substantial part of the program (some 7000 statements in Fortran 77 language) has been devoted to monitoring these processes in the course of numerical calculation. Computationally, each job (consists of the procedures shown in Fig. 12) has spent, on the average, three hours on Facom M-180 II AD computer.

Chapter V. RESULTS AND DISCUSSIONS

1. Solutions in Local Photochemical Equilibrium

Dynamical effect such as the eddy diffusion affects in quite a different manner the densities of molecules of our consideration, depending upon their photochemical lifetimes. Moreover, the magnitude of the eddy diffusion coefficient and its variation with altitude are very uncertain in the outer planets compared with those in the terrestrial case. Hence it would be adequate to discuss elementary processes of chemical reactions at first on a basis of the solutions which have been obtained by assuming a *"local photochemical equilibrium"*. Fig. 13 and Fig. 14 show the reaction diagrams for these local equilibrium solutions obtained at the two altitudes, characterized by the total densities of $9.84 \times 10^{13}/cm^3$ and $4.95 \times 10^{17}/cm^3$ respectively. In the figures, only the reactions of some importance are indicated (the numbers attached to arrows show the reaction numberings used in Table 7). The former
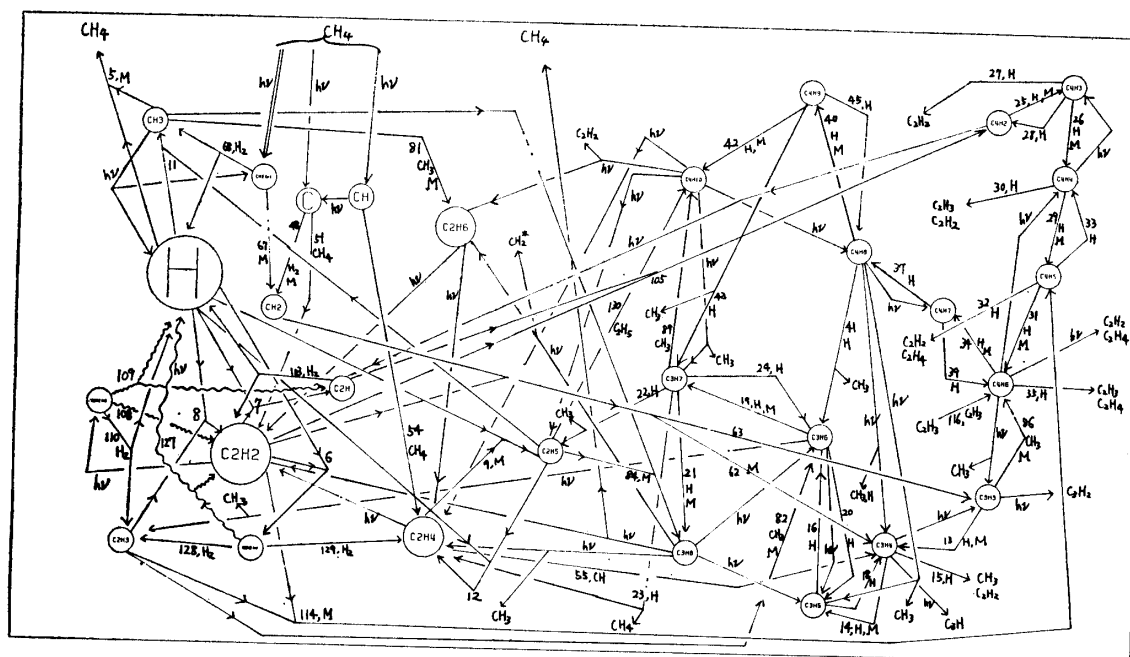
Fig. 13. Chemical flow diagram of principal neutral reactions at density level of 9.84×10^{13} cm^{-3}, which applies to the result shown in Fig. 15 (local equilibrium solution). The numbers attached to arrows indicate reaction numberings used in Table 7.
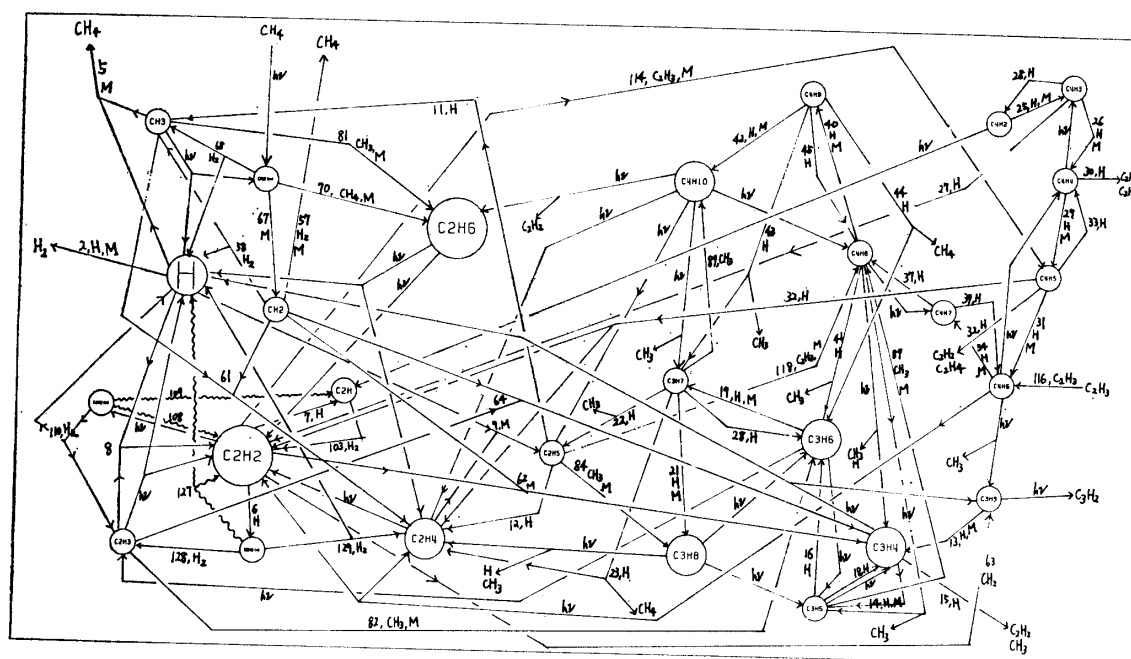

Fig. 14. Chemical flow diagram of principal neutral reactions. It is derived from the same calculation as in Fig. 13, excepting that the present figure corresponds to height level with higher pressure of 4.95×10^{17} cm^{-3}. The numbers attached to arrows indicate reaction numberings used in Table 7.

corresponds to the situation where $Ly\,\alpha$ photons are most strongly absorbed by CH_4, but the ambient pressure is not so high that the stabilization in association reaction is incomplete, while, the latter represents the situation where only a very small absorption is possible for CH_4 but the third-body requirement for stabilization is well satisfied in most reactions. We shall start our discussions by following the bulk flows of chemical reactions.

As described in Chap. II, 2.2, methane, by UV irradiation, mainly produces a pair of $^1CH_2$ (singlet methylene) and H_2, and slightly produces CH or CH_3 radicals. This singlet methylene, interacting with H_2, yields $CH_3^{*)}$, unless it is simply stabilized (the former rate is about fifty times as fast as the latter). Methyl radical thus formed plays quite an important role as a starting radical in forming a variety of hydrocarbons. The efficiency, however, is limited by the three-body addition reaction,

$$H + CH_3 + M \xrightarrow{\alpha 5} CH_4.^{\#\#)}$$

If the reaction proceeds rapidly compared with methyl combination reaction, $CH_3 + CH_3 + M \xrightarrow{\alpha 81} C_2H_6$, in a substantial altitude range, the stability problem of methane atmosphere can be greatly eased—the similar problem annoyed past investigators in the cases of Mars and Venus: Why the present atmosphere could be stable for a geolgic time against the incessant UV irradiation. But if the former reaction ($\alpha 5$) that recycles a methyl radical to methane is not so efficient as the latter methyl association ($\alpha 81$), this stability problem of methane atmosphere deserves a special interest. The last situation occurs, if it happens that a free hydrogen is substantially depleted from 'photochemical zone' due to a strong downward tranport by eddy diffusion or due to some chemical reactions which effectively promote hydrogen addition. This would also occur if, even allowing for abundant free hydrogens, it happens that methyl radical is not so efficiently formed, as would be the case where triplet methylene ($^3CH_2$) does not react with molecular hydrogen but preferentially reacts with heavier hydrocarbons: Note that the rates for $^3CH_2$ $+ H_2 + M \xrightarrow{\alpha 57} CH_4$ and $^3CH_2 + H_2 \xrightarrow{\alpha 58} CH_3 + H$ are actually not known, though they may be exceedingly small (Table 7, Remark $XXVI$). We will return to this topic of methane stability in a later section.

Self-combination of methyl radicals results in ethane (C_2H_6) and it is always one of the predominant hydrocarbons in every case of our calculations. Why such a high abundance can be maintained for C_2H_6 is due to two reasons, one, that the combination reaction between methyls is quite rapid, even in the tenuous part of the atmosphere (three-body association rate shows a remarkable increase with decreasing temperature as found in Remark $XXXVII$ in Table 7), and the other, that saturated hydrocarbons generally undergo the UV absorption only at the shortest wavelength side (Chap. II). In addition, any significant chemical reaction that
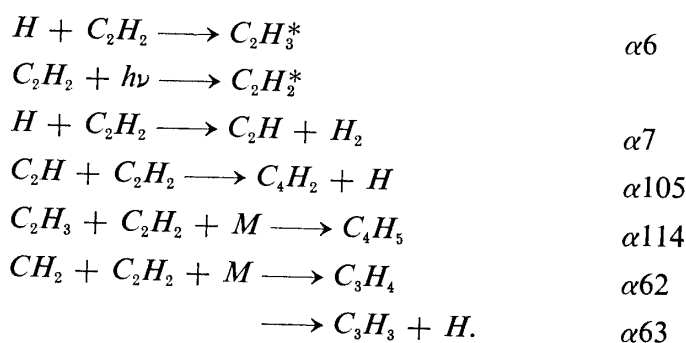
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*) It was thought before the 1960's that the photoabsorption of methane resulted mainly in the production of CH_3 and H. It is, however, to be noted that the difference on primary photolytic act does not significantly change the results of our calculation, since the reaction, $^1CH_2 + H_2$ $\xrightarrow{\alpha 68} CH_3 + H$ is quite rapid in the environments of the outer planets.

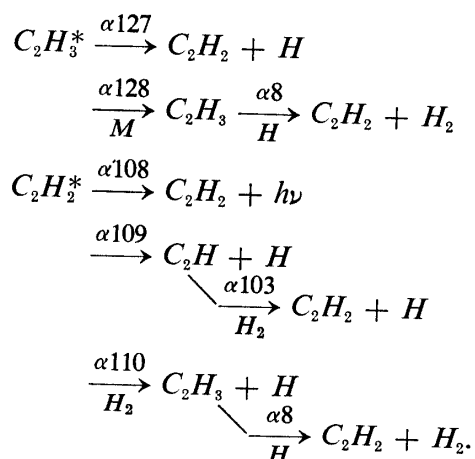##) α_i indicates the reaction numberings used in Table 7.

promotes the loss of saturated hydrocarbons is not likely to occur in a low temperature condition because of the large activation energy for such a reaction system.

Ethane thus formed absorbs the solar UV and produces C_2H_2, and C_2H_4. We will postpone discussions of the latter compound and discuss acetylene (C_2H_2) and those molecules closely related to it $(C_2H_2^*, C_2H_3, C_2H_3^*, C_2H, H)$. In Figs. 13 and 14 we have illustrated the principal chemical flows for the typical cases of our calculations and one may easily discern that there are several internal chemical cycles. These, so to speak, catalytic reactions are most conspicuous and complicated in the system consisted of acetylenic compounds. Shown below are the reactions that apparently cause the loss of acetylene,

$$H + C_2H_2 \longrightarrow C_2H_3^* \qquad \alpha 6$$

$$C_2H_2 + h\nu \longrightarrow C_2H_2^*$$

$$H + C_2H_2 \longrightarrow C_2H + H_2 \qquad \alpha 7$$

$$C_2H + C_2H_2 \longrightarrow C_4H_2 + H \qquad \alpha 105$$

$$C_2H_3 + C_2H_2 + M \longrightarrow C_4H_5 \qquad \alpha 114$$

$$CH_2 + C_2H_2 + M \longrightarrow C_3H_4 \qquad \alpha 62$$

$$\longrightarrow C_3H_3 + H. \qquad \alpha 63$$

Particularly, the first two reactions are fast and so is the third if temperature is increased more than that assumed here (150K). Those C_2-products appearing in the righthand side, however, soon restore to acetylene through the following reactions

$$C_2H_3^* \xrightarrow{\alpha 127} C_2H_2 + H$$

$$\xrightarrow[M]{\alpha 128} C_2H_3 \xrightarrow[H]{\alpha 8} C_2H_2 + H_2$$

$$C_2H_2^* \xrightarrow{\alpha 108} C_2H_2 + h\nu$$

$$\xrightarrow{\alpha 109} C_2H + H$$
$$\searrow \xrightarrow[H_2]{\alpha 103} C_2H_2 + H$$

$$\xrightarrow[H_2]{\alpha 110} C_2H_3 + H$$
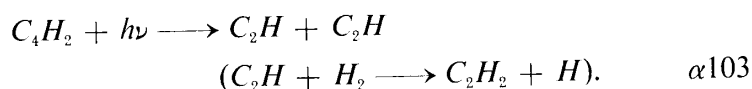$$\searrow \xrightarrow[H]{\alpha 8} C_2H_2 + H_2.$$

Such a recycling is nearly complete and the resulting important fact is that these acetylenic compounds play the role as an effective catalyst for recombining free hydrogens; $H + H \longrightarrow H_2$.

As for the remaining products of C_3- and C_4-compounds, the substantial portions react to free hydrogens and with a large probability decompose unimolecularly as
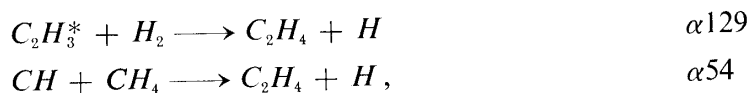
$$C_4H_5 + H \longrightarrow C_2H_2 + C_2H_4 \qquad \alpha 32$$

$$C_3H_4 + H \longrightarrow CH_3 + C_2H_2 \qquad \alpha 15$$

or photodissociate as

$$C_4H_2 + h\nu \longrightarrow C_2H + C_2H$$

$$(C_2H + H_2 \longrightarrow C_2H_2 + H). \qquad \alpha 103$$
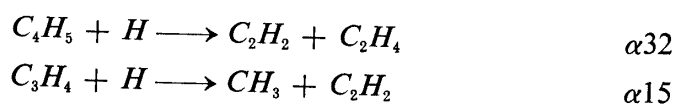
Acetylene, in all the cases, rather quickly restores.

As previously mentioned, another main product of ethane photolysis is ethylene (C_2H_4). This and the following reactions make major input terms for ethylene

$$C_2H_3^* + H_2 \longrightarrow C_2H_4 + H \qquad\qquad \alpha 129$$

$$CH + CH_4 \longrightarrow C_2H_4 + H , \qquad\qquad \alpha 54$$

and it is consumed by a hydrogen addition reaction at any height, with a probability more than half

$$H + C_2H_4 + M \longrightarrow C_2H_5 . \qquad\qquad \alpha 9$$
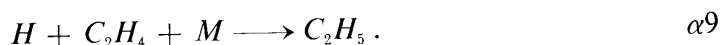
The remaining ethylene is usually brought back to acetylene by photodissociation

$$C_2H_4 \xrightarrow{h\nu} C_2H_2 + H + H \text{ (or } H_2) .$$
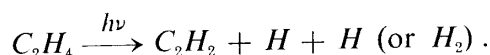
C_3-compounds

As for ethyl radicals, a balance is attained by the production due to the reaction ($\alpha 9$) and the loss due to the following reactions, which are arranged in the order of decreasing importance,

$$H + C_2H_5 \longrightarrow 2CH_3 \qquad\qquad \alpha 11$$

$$\longrightarrow C_2H_4 + H_2 \qquad\qquad \alpha 12$$

$$CH_3 + C_2H_5 + M \longrightarrow C_3H_8 \qquad\qquad \alpha 84$$

$$\longrightarrow CH_4 + C_2H_4 \qquad\qquad \alpha 85$$

$$H + C_2H_5 + M \longrightarrow C_2H_6 . \qquad\qquad \alpha 10$$
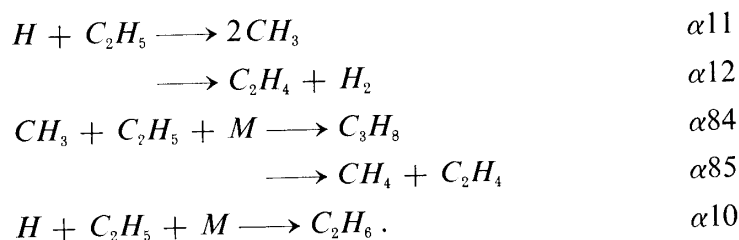
About 95% of ethyl consumption is done through the first, and the last three processes occupy a fraction as few as a ten thousandths of it. All the reactions except for the third, however, are in effect a repetition of a series of the processes of which we have been describing. The formation of C_3-hydrocarbons is essentially made possible upon this ($\alpha 84$) and the following reactions

$$CH + C_2H_4 \longrightarrow C_3H_4 + H \qquad\qquad \alpha 55$$

$$CH_2 + C_2H_2 + M \longrightarrow C_3H_4 \qquad\qquad \alpha 62$$

$$\longrightarrow C_3H_3 + H \qquad\qquad \alpha 63$$

$$CH_3 + C_2H_3 + M \longrightarrow C_3H_6 . \qquad\qquad \alpha 82$$
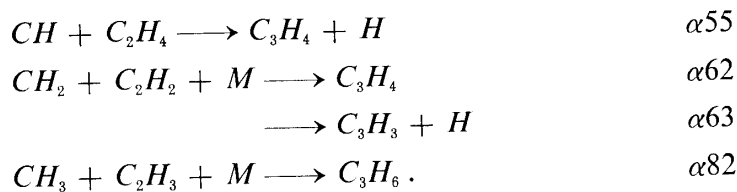
Before continuing discussions, we note a pattern that is often found in the chemical reaction diagrams (Figs. 13 and 14), such as
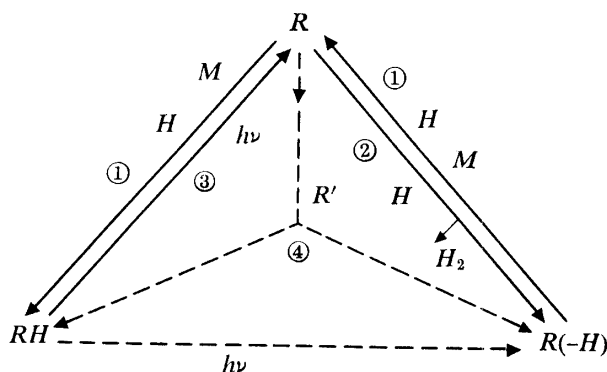
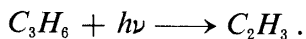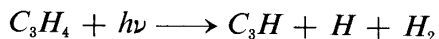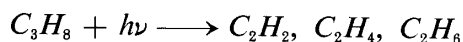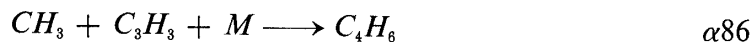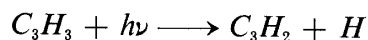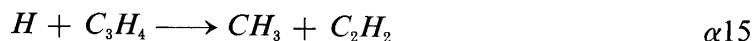where, R and R' denote radical species. The broken lines show that the processes are not so universal as those indicated by the solid lines. The reactions appeared in this triangular figure are of the types:

① hydrogen addition reaction, which increases a degree of saturation.

② abstraction reaction by a free hydrogen, which returns radicals to less saturated molecule.

③ free hydrogen elimination by UV absorption (a decomposition pattern frequently found in the longest wavelength region).

④ disproportionation reaction between radical R and another radical R' (less frequent).

We have often confirmed in numerical computations that with the species of the longest chemical lifetime, the densities of the remaining two molecules internally equilibrate.

The five reactions stated above ($\alpha55$, $\alpha62$, $\alpha63$, $\alpha82$ and $\alpha84$) yield the effective inputs to C_3-compounds (respectively, to C_3H_4, C_3H_4, C_3H_3, C_3H_6 and C_3H_8). In a steady state, these are redistributed among C_3-compounds according to the reaction flows illustrated in Figs. 13 and 14, and their absolute densities are controlled by the rates of the following reactions through which such C_3-molecules leak out from the category. They are, in the order of decreasing importance,

$$H + C_3H_4 \longrightarrow CH_3 + C_2H_2 \qquad\qquad \alpha15$$

$$C_3H_3 + h\nu \longrightarrow C_3H_2 + H$$

$$CH_3 + C_3H_3 + M \longrightarrow C_4H_6 \qquad\qquad \alpha86$$

$$C_3H_8 + h\nu \longrightarrow C_2H_2,\ C_2H_4,\ C_2H_6$$

$$C_3H_4 + h\nu \longrightarrow C_3H + H + H_2$$

$$C_3H_6 + h\nu \longrightarrow C_2H_3 .$$

The second and the fifth reactions were included here, since the C_3-compounds with hydrogen atoms fewer than two were not taken into account in our calculation scheme due to the lack of available information of the related elemental reaction data.[*] Fig. 15 (local equilibrium solution) reveals that the abundances of C_3H_8,

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[*] Hence, our calculation cannot pursue those extremely unsaturated molecules about their possible comeback to the more saturated. For a conceptual convenience, it may be thought that those species have contributed directly in forming polymeric products. A simiiar situation is also applicable for C_4-hydrocarbons.
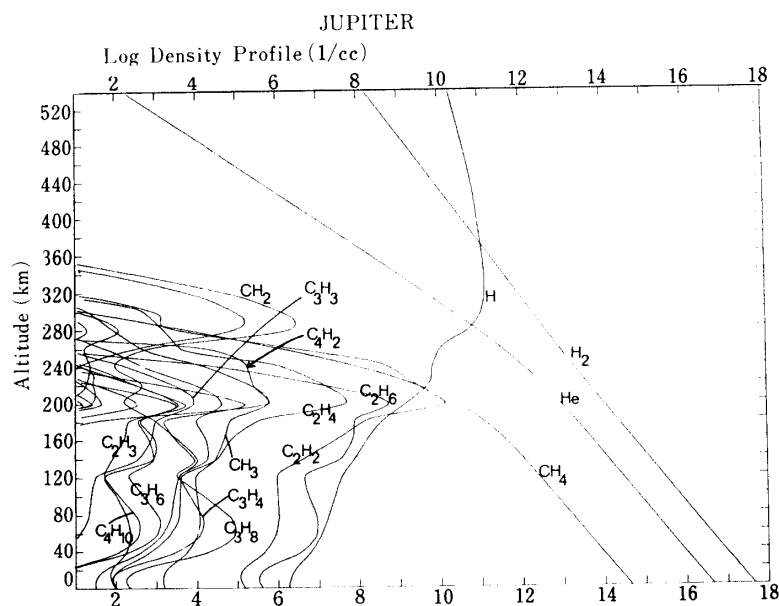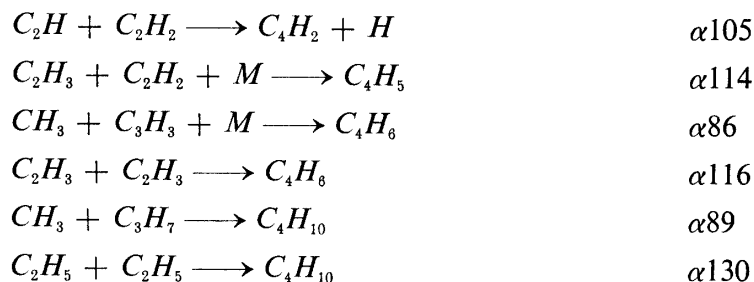
JUPITER
Log Density Profile (1/cc)

Fig. 15.   Neutral hydrocarbon densities in Jupiter (local equilibrium solution).
Mixing ratio of methane (f_{CH_4}) is 0.001 and temperature is 150K
(isothermal).   Here and in all the following figures (except 22 & 26),
the numbers on the abscissa indicate number densities in the
common logarithms and a reference level for altitude is fixed at
$p = 0.01$ atm.

C_3H_4 and C_3H_3 stand out from those of the other members of C_3-group. The
inclusion of eddy diffusion, however, greatly alters the density profile and the saturated
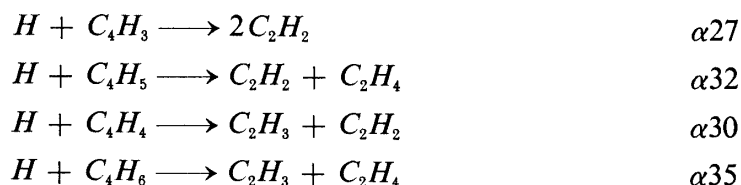molecule as C_3H_8 becomes predominant there.   The reason will be considered in § 2.

C_4-compounds

As for the C_4-compounds, we have taken nine species into account (C_4H_{10}, C_4H_9,
C_4H_8, C_4H_7, C_4H_6, C_4H_5, C_4H_4, C_4H_3, C_4H_2).   It is conspicuous in the features of
the chemical flow diagrams that the more saturated C_4-compounds are successively
produced by a hydrogen addition and at the same time that an abstraction reaction
by free hydrogen is working to return a radical to products consisting of hydrogen
molecule and less saturated hydrocarbon.   Hence the internal density distribution
among those C_4-hydrocarbons is fundamentally determined by these two kinds of
mutually reversed reactions, although the relative importance would be quite different
with altitude—note that the rate of the former (addition reaction) is density-dependent,
while the latter is not.   There are other kinds of reactions, such as disproportionation
and combination which occur between a pair of radicals.   This is expected when
the overall abundance of acetylenic compounds (and in proportion to it, those of
C_4-compounds) is substantially enhanced somehow, for instance, due to the reason
as described at the part relevant to CH_2 and CH_3: In such a circumstance, it can
be shown that the abundance of the species like diacetylene (C_4H_2) and vinylacetylene
(C_4H_4) greatly increases.   Similar behavior is also obtained when the rate of hydrogen
addition to acetylene is smaller than the value listed in Table 7.

The C_4-hydrocarbons are supplied by the following reactions; in the order of decreasing importance,

$$C_2H + C_2H_2 \longrightarrow C_4H_2 + H \qquad \alpha 105$$

$$C_2H_3 + C_2H_2 + M \longrightarrow C_4H_5 \qquad \alpha 114$$

$$CH_3 + C_3H_3 + M \longrightarrow C_4H_6 \qquad \alpha 86$$

$$C_2H_3 + C_2H_3 \longrightarrow C_4H_6 \qquad \alpha 116$$

$$CH_3 + C_3H_7 \longrightarrow C_4H_{10} \qquad \alpha 89$$

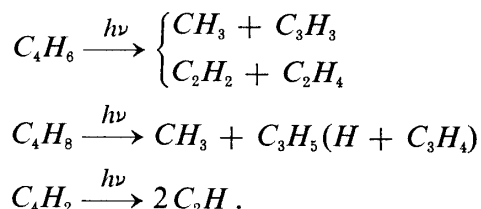$$C_2H_5 + C_2H_5 \longrightarrow C_4H_{10} \qquad \alpha 130$$

They are, except for the first, characterized by combination type reaction. The contribution from photo- and chemical processes related to the C_5- and higher hydrocarbons is not taken into account in the present work. It would not be an easy task to estimate even crudely what a fraction of the species outgoing from within C_3- and C_4-compounds are, in steady state, returned to within the category (C_3- and C_4-compounds). I believe, however, that such a contribution would not be very important in determining the densities of the hydrocarbons of our interest. This is inferred from the way that the amount of the species belonging to each C_i-group is decreasing with increasing number of i (Fig. 15), and also inferred from a number of experimental results which report the principal products in photolysis (in most of them, such products of C_nH_m as $n \geqslant 5$ are much reduced compared with those of $n \leqslant 4$).

On the other hand, the C_4-hydrocarbons are mainly destructed by unimolecular decompositions that are usually involved in the reactions with a free hydrogen,
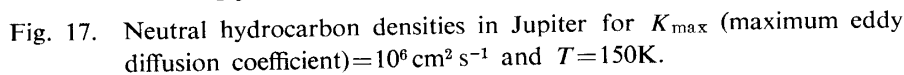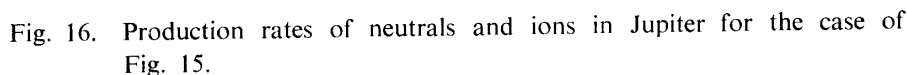
$$H + C_4H_3 \longrightarrow 2C_2H_2 \qquad \alpha 27$$

$$H + C_4H_5 \longrightarrow C_2H_2 + C_2H_4 \qquad \alpha 32$$

$$H + C_4H_4 \longrightarrow C_2H_3 + C_2H_2 \qquad \alpha 30$$

$$H + C_4H_6 \longrightarrow C_2H_3 + C_2H_4 \qquad \alpha 35$$

and to the less extent destructed by photodissociations

$$C_4H_6 \xrightarrow{h\nu} \begin{cases} CH_3 + C_3H_3 \\ C_2H_2 + C_2H_4 \end{cases}$$

$$C_4H_8 \xrightarrow{h\nu} CH_3 + C_3H_5 (H + C_3H_4)$$

$$C_4H_2 \xrightarrow{h\nu} 2C_2H .$$

2. Effect of Eddy Diffusion

In the local equilibrium solutions it is commonly found that the densities become largest for most hydrocarbons at the mesospheric altitude levels. This is simply due to their production being most actively done at the heights where the $Ly\,\alpha$ photons are absorbed out, as is evident from Fig. 16. It is not due to something

specific like increased chemical losses at the deeper levels. On the contrary, most reactions progress rather slowly at these altitudes, since the production of radical species as an important reaction agent is greatly reduced there. It is, however, to be noted that the rate coefficient itself is generally enhanced at such deep altitudes because a condition for collisional stabilization is more favorable.

The effect of the inclusion of eddy diffusion is, therefore, evident from the above argument. That is, molecules tend to distribute with a larger abundance at the

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Log Production Profile of Neutral and Ion Species by UV (1/cc/s)

Fig. 16. Production rates of neutrals and ions in Jupiter for the case of Fig. 15.

JUPITER

Log Density Profile (1/cc)

Fig. 17. Neutral hydrocarbon densities in Jupiter for K_{max} (maximum eddy diffusion coefficient)$=10^6$ cm^2 s^{-1} and $T=150$K.

lower heights than in the cases of the local equilibrium solutions. This is particularly true for the saturated hydrocarbons like C_2H_6, C_3H_8 and C_4H_{10} whose *UV* absorption is no longer expected in such a deep layer. Moreover, due to the original chemical inactiveness, it is very likely that those saturated molecules distribute on altitude,
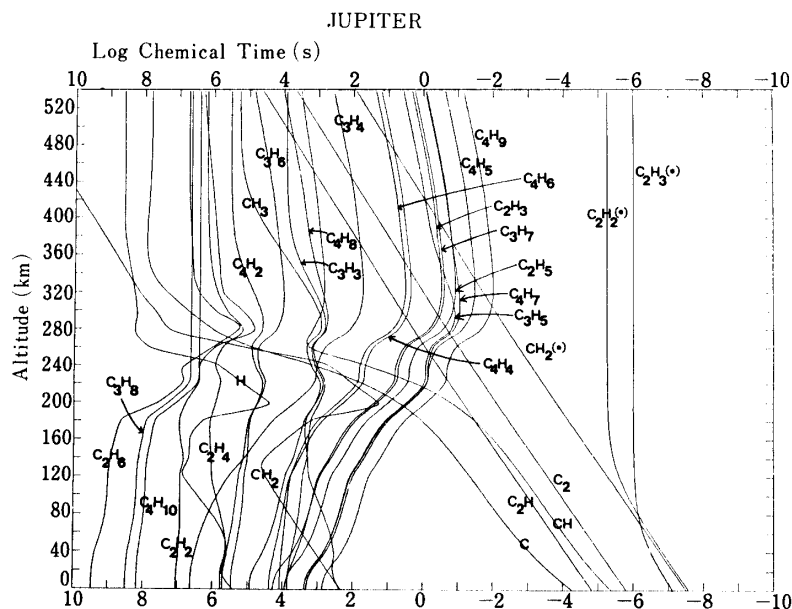

Fig. 18. Chemical time constants of neutrals for the Jovian case; $K_{max}=$ $10^6\,cm^2\,s^{-1}$ and $T=150K$. For the *i*-th species, this is defined as L_i^{-1} in its loss term expression, $L_i n_i$.
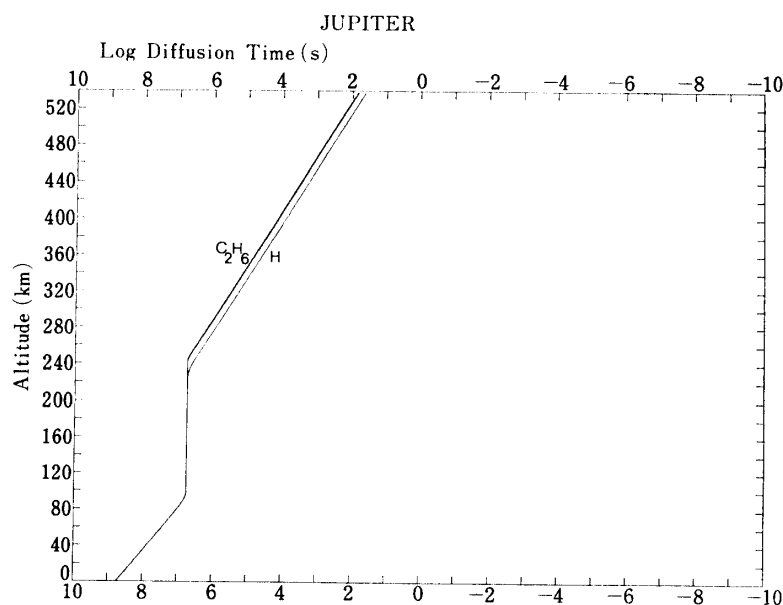
Fig. 19. Diffusion time constants for the Jovian case; $K_{max}=10^5\,cm^2\,s^{-1}$ and $T=150K$. It is defined as min $(H^2/K, H^2/D)$, where H is the mixing scale height of atmosphere, K the eddy diffusion coefficient and D the molecular diffusion coefficient.

in accordance with the mixing scale height of atmosphere.

For free radicals, things are not so simple and the lifetimes can widely change on altitude and on species. Some radicals may be transported down to the regions with higher pressures and there by chemical reaction they may keep abundances chemically equilibrated with some more stable species. Or, else, they may react with other radicals locally before they suffer transport effect. It would require too lengthy pages to give a full account of the relative importance of these two processes for every hydrocarbon and I only suggest here that one is able to deduce enough information by inspecting Figs. 15 and 17, and Figs. 18 and 19.

When we compare the result obtained by assuming a local photochemical equilibrium, with that obtained by including an eddy diffusion of the maximum coefficient of 10^6 cm^2 s^{-1} (Fig. 17 for Jupter and Fig. 20 for Saturn), we find marked differences: In the latter case, the fairly stable molecules such as C_2H_6, C_3H_8, C_4H_{10}, C_3H_4, C_3H_6 will get a mixing distribution in the low altitude region and consequently the abundance alternation arises between the high and low altitude regions for most of these hydrocarbons. This tendency becomes more remarkable with increasing eddy diffusion coefficient (see, Fig. 21), because they are rapidly transported down to the lower atmosphere where their chemical consumptions are extremely slow.

A free hydrogen deserves special attention, relating to the problem of the $Ly\ \alpha$ albedo from the planetary disk (Chap. IV, § 1). As is evident in Fig. 16, such hydrogen atoms are mostly those which were initially produced from photodissociation of H_2. Direct effect of eddy diffusion on hydrogen atoms is also the downward transport, which carries them to the heights where a significant loss can be chemically expected. Then the density of hydrogen atom comes to reduce at the tenuous part of the atmosphere where the third-body recombination is quite slow,
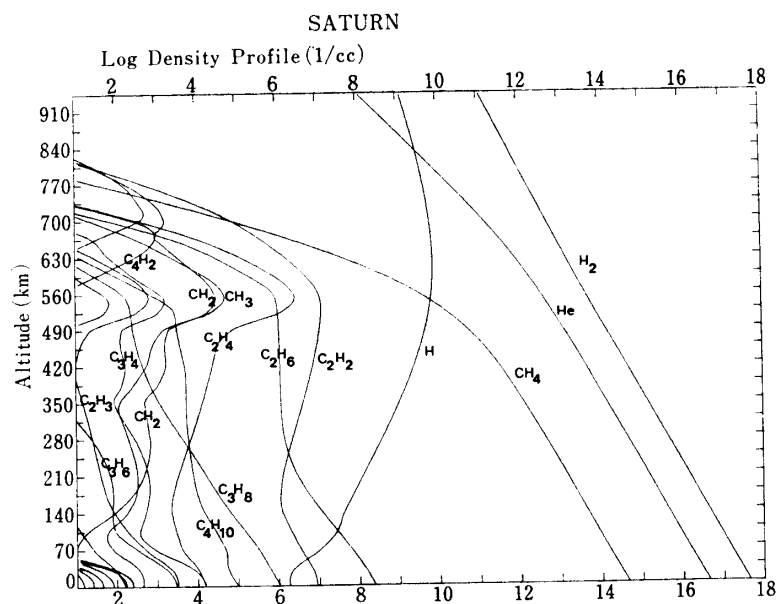

Fig. 20. Neutral hydrocarbon densities in Saturn for $K_{max}=10^6$ cm^2 s^{-1}, $T=$ 150K and $f_{CH_4}=0.001$.

while at the denser part, it, instead, comes to increase (Figs. 15 and 17). The chemical loss of hydrogen atom has usually been considered due to the reaction, $H + H + M \xrightarrow{\alpha 2} H_2$. Although the process is as important in the present case as ever, there are several reactions that can contribute in consuming free hydrogens. We have already stated in the foregoing section that a number of chemical cycles would work as an effective catalyst to recombine hydrogen atoms. We can enumerate such reactions as

$$H + CH_3 + M \xrightarrow{\alpha 5} CH_4$$

$$H + C_2H_2 + M \xrightarrow{\alpha 6, \alpha 128} C_2H_3 \xrightarrow{\alpha 8}{}^{H} H_2 + C_2H_2$$

$$H + C_2H_4 + M \xrightarrow{\alpha 9} C_2H_5 \xrightarrow{\alpha 12}{}^{H} H_2 + C_2H_4$$
$$\xrightarrow{\alpha 11} CH_3 + CH_3$$
$$\xrightarrow{\alpha 5}{}^{H,M} CH_4$$

$$H + C_4H_5 \xrightarrow{\alpha 32} C_2H_2 + C_2H_4$$

$$H + C_4H_3 + M \xrightarrow{\alpha 26} C_4H_4$$

$$H + C_3H_5 \xrightarrow{\alpha 16} C_3H_6$$

$$\xrightarrow{\alpha 18} H_2 + C_3H_4 .$$

We have actually confirmed by analyzing numerical results that the consumption and the production, respectively, of atomic and molecular hydrogen are at work through these reactions (their relative importance, however, depends on altitudes).

Fig. 21. Neutral hydrocarbon densities in Jupiter for $K_{max} = 10^8 \, cm^2 \, s^{-1}$ and $T = 150K$.
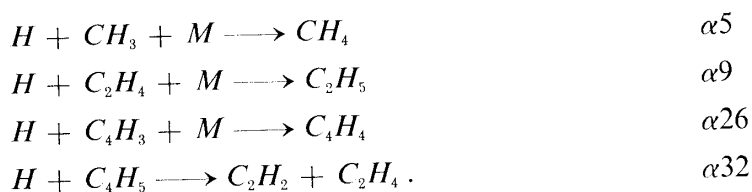
As a summary, we conclude that hydrogen atoms are returned to hydrogen molecules directly through $H + H + M \xrightarrow{\alpha 2} H_2$ and indirectly (but comparably in effect) through the catalytic systems consisting of such minor hydrocarbons as yielded from methane photochemistry. In the both mechanisms, the strength of eddy diffusion is essential in controlling the rate at which the hydrogen atoms are transported and consumed, which will explain the difficulty of theoretical prediction of the total content of hydrogen atoms *vs* eddy diffusion coefficients, as mentioned in Chap. IV, § 1, ii).

The role played by eddy diffusion may be more intuitively understood by comparing Fig. 17 ($K_{\text{max}} = 10^6 \, \text{cm}^2 \, \text{s}^{-1}$) with the result obtained for higher eddy diffusion coefficient. Fig. 21 is the neutral density profile obtained for such an intense turbulence as characterized by $K_{\text{max}} = 10^8 \, \text{cm}^2 \, \text{s}^{-1}$. In the latter case, methane distributes to the altitudes much higher than in the former, since the location of the turbopause is approximately determined by a level where its molecular and eddy diffusion coefficients are equal. The characteristic features found in the latter are a reduction of free hydrogen content and a general enhancement of hydrocarbon abundance (the increase of C_4-compounds is particularly remarkable). These two features are closely related to each other: Depletion of free hydrogens in the upper atmosphere caused by intense turbulence means a lack of important reaction partner for methyls, which, in cases of less intense turbulence, constituted the predominant loss mechanism ($H + CH_3 + M \xrightarrow{\alpha 5} CH_4$). Hence the methyl radicals are mostly lost by the self-combination reaction, $CH_3 + CH_3 + M \xrightarrow{\alpha 81} C_2H_6$, resulting in a considerable increase of ethane. This increase spreads over the other compounds through the reactions as follows (see, also Fig. 22),

$$C_2H_6 \xrightarrow{h\nu} C_2H_4$$

$$\left\lceil \begin{cases} H + C_2H_4 + M \xrightarrow{\alpha 9} C_2H_5 & \text{increase of } C_2H_5 \text{ production}^{+)} \\ H + C_2H_5 \longrightarrow (\alpha 10, \alpha 11, \alpha 12) & \text{decrease of } C_2H_5 \text{ loss} \end{cases} \right.$$

$$\longrightarrow \text{resultant increase of } C_2H_5$$

$$CH_3{}^{\#)} + C_2H_5 \xrightarrow{\alpha 84} C_3H_8$$

$$C_2H_5 + C_2H_5 \xrightarrow{\alpha 130} C_4H_{10}, \quad \text{particularly, at low altitudes.}$$
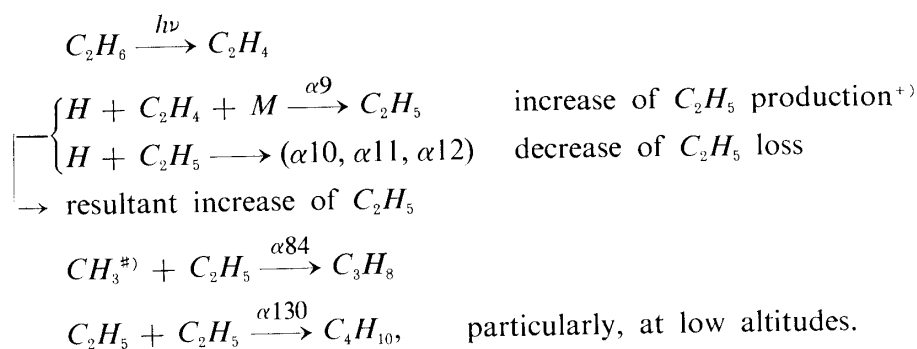
On the other hand, hydrogen atoms transported down into the stratospheric altitudes, in the present case, disappear through the reactions as follows,

$$H + CH_3 + M \longrightarrow CH_4 \qquad\qquad \alpha 5$$

$$H + C_2H_4 + M \longrightarrow C_2H_5 \qquad\qquad \alpha 9$$

$$H + C_4H_3 + M \longrightarrow C_4H_4 \qquad\qquad \alpha 26$$

$$H + C_4H_5 \longrightarrow C_2H_2 + C_2H_4 . \qquad\qquad \alpha 32$$

+) The increase of C_2H_4 exceeds, in magnitudes, the decrease of H.
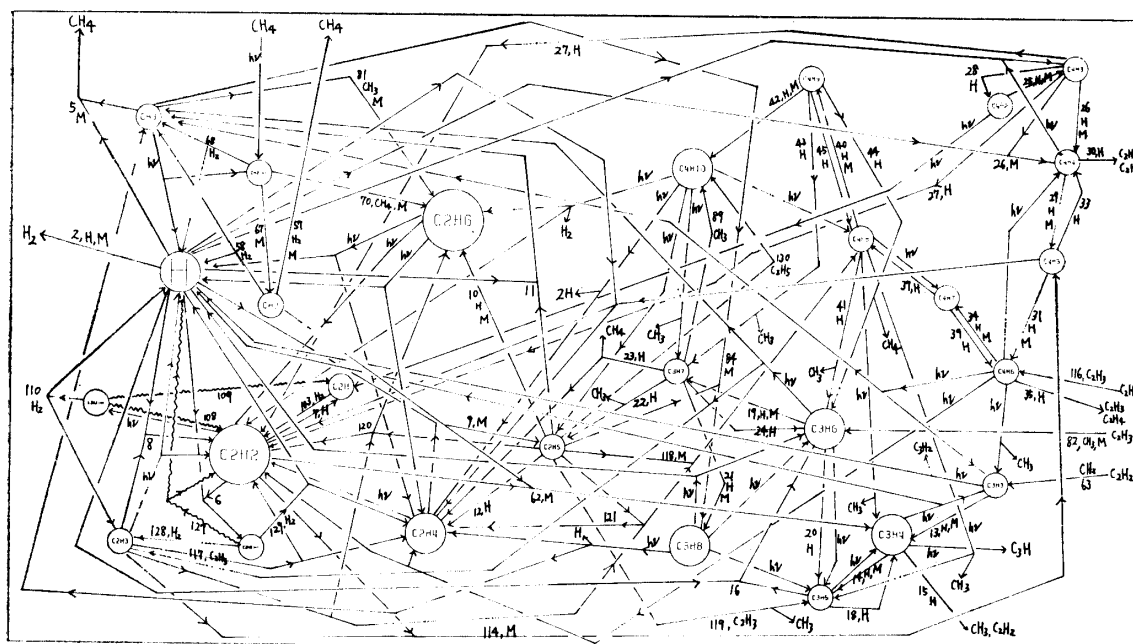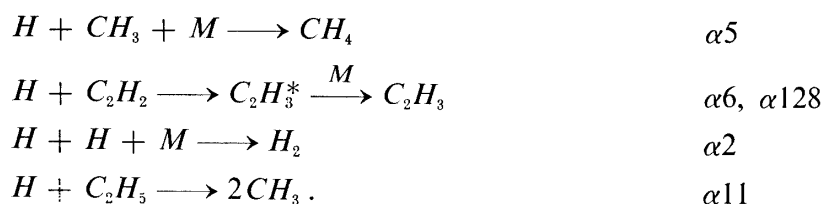#) Increased due to the delay of the reaction, $H + CH_3 + M \longrightarrow CH_4$, as noted.

Fig. 22. Chemical flow diagram of principal neutral reactions at density level of 4.95×10^{17} cm^{-3}, which applies to the result shown in Fig. 17 (inc. transport effect). The numbers attached to arrows indicate reaction numberings used in Table 7.

Such a loss is rather different in mechanism from those found at higher altitudes where it disappears through,

$$H + CH_3 + M \longrightarrow CH_4 \qquad\qquad \alpha 5$$

$$H + C_2H_2 \longrightarrow C_2H_3^* \xrightarrow{\ M\ } C_2H_3 \qquad\qquad \alpha 6,\ \alpha 128$$

$$H + H + M \longrightarrow H_2 \qquad\qquad \alpha 2$$

$$H + C_2H_5 \longrightarrow 2CH_3 . \qquad\qquad \alpha 11$$

3. Ion Chemistry

Fig. 23 and Fig. 24 show the density profiles of ionic species that have been obtained, respectively, with and without transport effects (as molecular and eddy diffusion) included. We can further show in Fig. 25 the ion densities obtained for the more intense turbulence characterized by $K_{max} = 10^8$ cm^2 s^{-1}. Although the difference may be thought large, it is essentially due to the change of neutral densities, which too, has resulted from the inclusion of such transport effects. Since the chemical lifetimes of ions are rather small compared with those characteristic to diffusions, they can quickly follow the change of neutral densities. (The situation is, however, not necessarily applicable to the atomic ions such as H^+ and He^+, because the characteristic times of recombining with electrons are larger than those for molecular diffusions which rapidly become small with increasing altitude.)

The present calculation for hydrocarbon ions is new in the point that it contains

a number of ion-molecule reactions for C_2H_2, C_2H_4 and C_2H_6, the principal neutral products expected from methane photochemistry. Ion chemistry incorporating these reactions into calculation, as far as the author knows, has not been done in the atmospheric environments. We show the density profile and the diagram illustrating the chemical reactions that prevail in our present chemistry, respectively, in Fig. 24
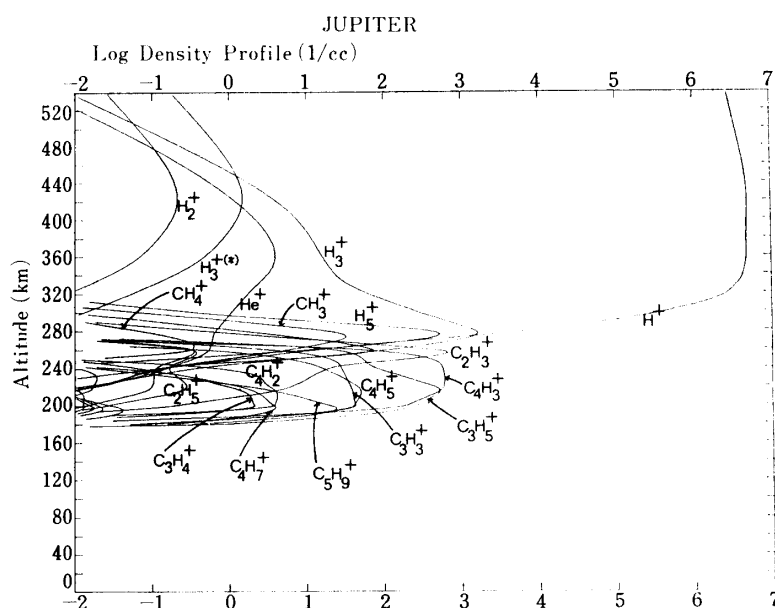

Fig. 23.   Ion densities in Jupiter (local equilibrium solution) for $F_{10.7}$ (index of solar activity)$=150$ and χ (solar zenith angle)$=60^{\circ}$. The profile is self-consistent with that of Fig. 15 in that the both are obtained as a result of simultaneous convergences.
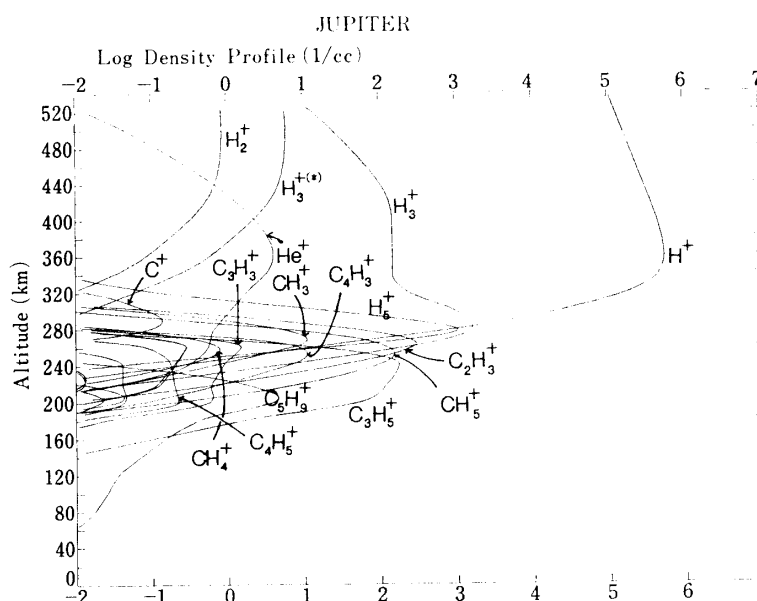
Fig. 24.   Ion densities in Jupiter for $K_{max}=10^6\,cm^2\,s^{-1}$. The profile is self-consistent with that of Fig. 17.

and Fig. 26. One can see there that the hydrocarbon ions as $C_2H_3^+$, $C_3H_3^+$, $C_3H_5^+$, $C_4H_3^+$ and $C_4H_5^+$ constitute a group of major ions below altitudes where H^+ becomes a predominant ion. Here I emphasize the facile alteration of the dominant ionic species, which occurs if the relative abundance of the major neutral C_2-compounds is changed: this is to be expected when the parameters such as temperature and
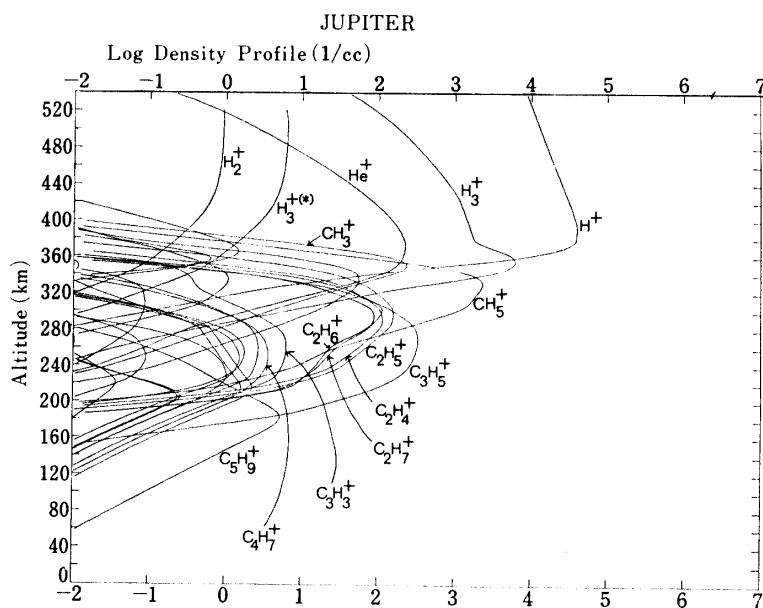

Fig. 25. Ionic hydrocarbon densities in Jupiter for $K_{max}=10^8\,\mathrm{cm^2\,s^{-1}}$. All the other calculational conditions are same as in Fig. 17.
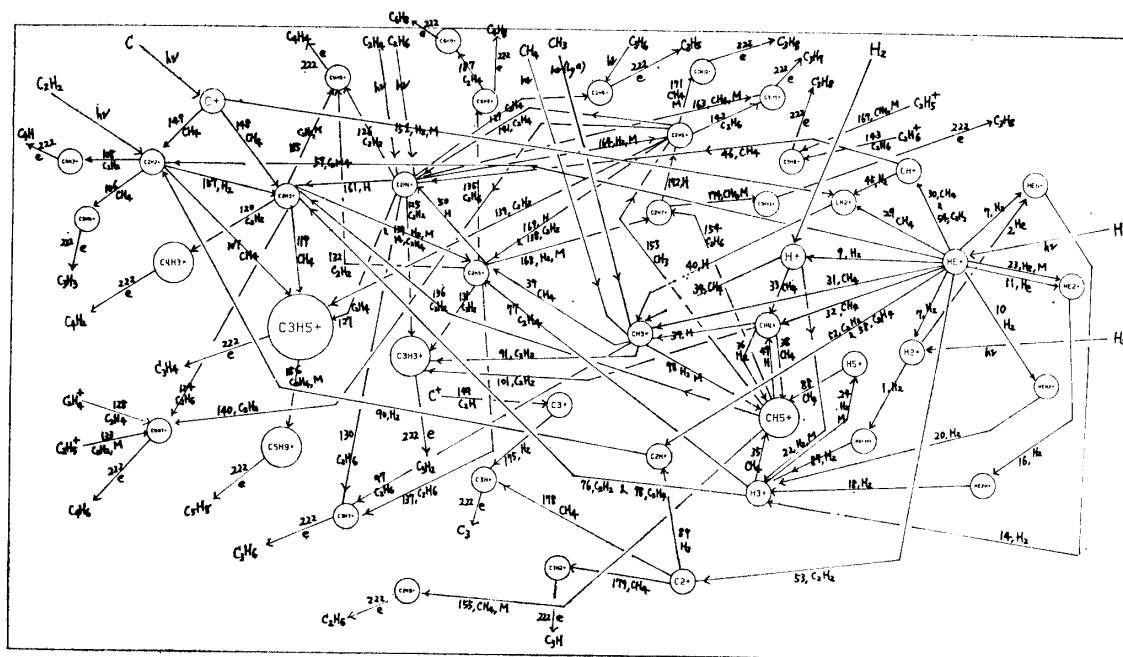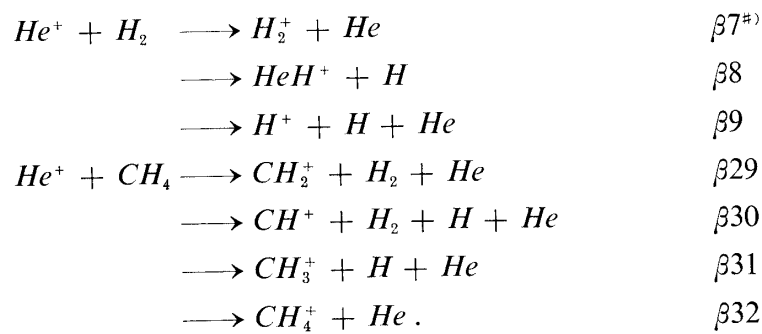

Fig. 26. Chemical flow diagram of principal ion-neutral reactions at density level of 4.22 $\times 10^{13}\,\mathrm{cm^{-3}}$, which applies to the result shown in Fig. 24. The numbers attached to arrows indicate reaction numberings used in Table 8.

eddy diffusion coefficient are varied to a certain degree. Owing to the above situation, it may be a little too early to conclusively argue the identification of the ionic species which are responsible for the electron density profiles obtained from the radio occultation experiments in Pioneer 10 and 11 missions, only except that some density peaks observed beneath the main peak are probably due to hydrocarbon ions. Keeping this in mind, we shall discuss the chemical flows of ion-molecule reactions in our typical case.
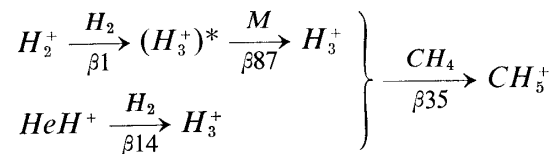
Ion-molecule reactions originate from ionization of the major atmospheric constituents such as H, He, H_2 and CH_4. In addition to these neutrals, we have considered the ionization of C_2H_2, C_2H_4, C_2H_6, CH_3 and C_3H_6 (propylene). The reason is, for the first three hydrocarbons, that they are usually the neutrals expected to be abundant and for the rest, that they are the molecules which are capable of being ionized by $Ly\,\alpha$. Fig. 26 illustrates the flow diagram of ion-molecule reactions for the case: Jupiter, max. eddy diffusion coeff. $= 10^6$ cm^2 s^{-1}, temperature $= 150$K, altitude $= 220$ km (total density $= 4.22 \times 10^{13}$ cm^{-3}), medium solar activity ($F_{10.7} = 150$), solar zenith angle $= 60°$, and relating to it, an averaging factor of solar radiation $= 1/2$ (*i.e.*, day-night average due to the rapid planetary rotation). At this height, the solar EUV photons capable of ionizing H_2 and He are already absorbed out and ionization occurs only from the extremely high energy photons being absorbed by these molecules, or from the photons whose energies are below their ionization thresholds being absorbed by C_2H_2, C_2H_4 and C_2H_6, or from the strong $Ly\,\alpha$ photons being absorbed by CH_3. It can be shown that all these processes contribute to a similar extent to the occurrence of ionization ($10^{-1} \sim 10^{-2}$ cm^{-3} s^{-1}).
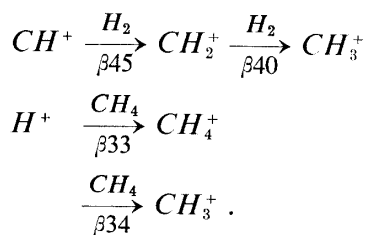
i)   *Routes from* He^+

He^+ can react with almost all the abundant neutrals as inferred from its high ionization potential. The following reactions are particularly important because of the abundant neutrals
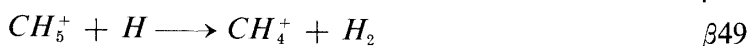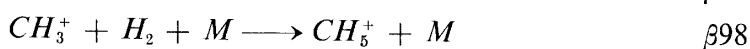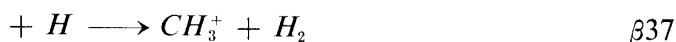
$$He^+ + H_2 \longrightarrow H_2^+ + He \qquad\qquad \beta7^{\#)}$$

$$\longrightarrow HeH^+ + H \qquad\qquad \beta8$$

$$\longrightarrow H^+ + H + He \qquad\qquad \beta9$$

$$He^+ + CH_4 \longrightarrow CH_2^+ + H_2 + He \qquad\qquad \beta29$$

$$\longrightarrow CH^+ + H_2 + H + He \qquad\qquad \beta30$$

$$\longrightarrow CH_3^+ + H + He \qquad\qquad \beta31$$

$$\longrightarrow CH_4^+ + He\,. \qquad\qquad \beta32$$

The product ions can further continue to react with H_2, He and CH_4 and the resultant ions tend to converge to the ions such as CH_3^+, CH_4^+, and CH_5^+ *via* the routes

$$H_2^+ \xrightarrow[\beta1]{H_2} (H_3^+)^* \xrightarrow[\beta87]{M} H_3^+ \left.\begin{array}{c} \\ \\ \end{array}\right\}$$

$$HeH^+ \xrightarrow[\beta14]{H_2} H_3^+ \qquad\qquad \left.\begin{array}{c} \end{array}\right\} \xrightarrow[\beta35]{CH_4} CH_5^+$$

#) β_i indicates the reaction numberings used in Table 8.

$$CH^+ \xrightarrow[\beta45]{H_2} CH_2^+ \xrightarrow[\beta40]{H_2} CH_3^+$$

$$H^+ \xrightarrow[\beta33]{CH_4} CH_4^+$$

$$\xrightarrow[\beta34]{CH_4} CH_3^+ .$$

Among these three ions, CH_3^+, CH_4^+ and CH_5^+, it is found that a (somewhat incomplete) chemical cycle is established due to the reactions,

$$CH_4^+ + H_2 \longrightarrow CH_5^+ + H \qquad\qquad \beta36$$

$$\qquad\quad + H \longrightarrow CH_3^+ + H_2 \qquad\qquad \beta37$$

$$CH_3^+ + H_2 + M \longrightarrow CH_5^+ + M \qquad\qquad \beta98$$

$$CH_5^+ + H \longrightarrow CH_4^+ + H_2 \qquad\qquad \beta49$$

The incompleteness arises from there being a few loss processes of these ions which lead to the formation of C_2-hydrocarbon ions (for instance, $CH_3^+ + CH_4 \xrightarrow{\beta39} C_2H_5^+ + H_2$, $CH_5^+ + C_2H_2 \xrightarrow{\beta156} C_2H_3^+ + CH_4$). As for the reactions of these C_2-ions, we postpone the discussion to item v).

ii) *Routes from H^+ and H_2^+*

As described in Chap. II, 2.1, molecular hydrogen produces H_2^+ by absorbing *EUV*, simultaneously yielding a small amount of H^+ as a result of the accompanying dissociative ionization. The description of their subsequent reactions is included in i).
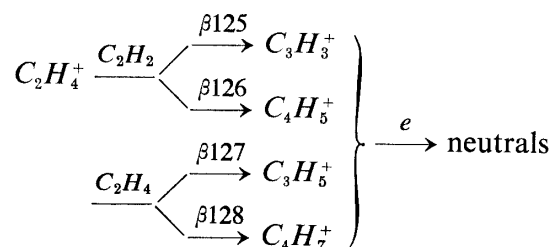
iii) *Routes from CH_3^+*

The ion is produced by the dissociative ionization of CH_4, or directly by the ionization of CH_3 due to $Ly \alpha$. The discussion also reduces to i).
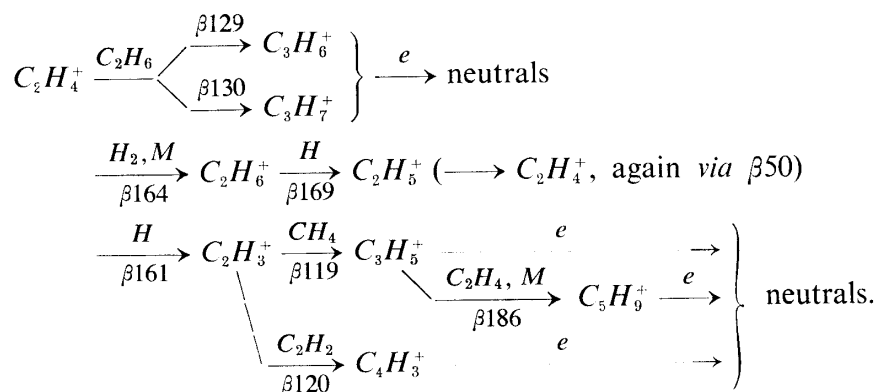
iv) *Routes from $C_2H_2^+$*

$C_2H_2^+$ is produced by the photoionization of acetylene. Almost all the acetylene ions become $C_2H_3^+$ due to $C_2H_2^+ + H_2 \xrightarrow{\beta157} C_2H_3^+ + H$. Only a very small fraction of it reacts with CH_4 and C_2H_2 (respectively, yielding, $C_3H_4^+$, $C_3H_5^+$, and $C_4H_2^+$, $C_4H_3^+$ — $\beta106 \sim \beta109$).

v) *Routes from $C_2H_4^+$*

$C_2H_4^+$ can be produced from the photoionization of ethylene or ethane. The process, however, is not a major route in forming the ion. Mostly it comes from the ion-molecule reaction, $C_2H_5^+ + H \xrightarrow{\beta50} C_2H_4^+ + H_2$. Successive flow from the ion, $C_2H_4^+$, branches into several different ways depending upon the neutral reactants, as follows,

$$C_2H_4^+ \underset{\begin{array}{c} C_2H_4 \end{array}}{\overset{\begin{array}{c} C_2H_2 \end{array}}{\rightleftharpoons}} \begin{cases} \xrightarrow{\beta125} C_3H_3^+ \\ \xrightarrow{\beta126} C_4H_5^+ \\ \xrightarrow{\beta127} C_3H_5^+ \\ \xrightarrow{\beta128} C_4H_7^+ \end{cases} \xrightarrow{e} \text{neutrals}$$

$$C_2H_4^+ \xrightarrow{C_2H_6} \begin{cases} \xrightarrow{\beta129} C_3H_6^+ \\ \xrightarrow{\beta130} C_3H_7^+ \end{cases} \left.\phantom{\begin{cases}\\\\\end{cases}}\right\} \xrightarrow{e} \text{neutrals}$$

$$\xrightarrow[\beta164]{H_2,M} C_2H_6^+ \xrightarrow[\beta169]{H} C_2H_5^+ \ (\longrightarrow C_2H_4^+, \text{ again } via \ \beta50)$$

$$\xrightarrow[\beta161]{H} C_2H_3^+ \begin{cases} \xrightarrow[\beta119]{CH_4} C_3H_5^+ \searrow \xrightarrow[\beta186]{C_2H_4, M} C_5H_9^+ \xrightarrow{e} \\ \xrightarrow[\beta120]{C_2H_2} C_4H_3^+ \phantom{\xrightarrow{C_2H_4}} \xrightarrow{e} \end{cases} \left.\phantom{\begin{cases}\\\\\\\end{cases}}\right\} \text{neutrals.}$$

Especially, the last sequence which begins from a reaction with H is quite important, as is understood from that in the present example $C_3H_5^+$ becomes one of the dominant ionic species.

It can be said that every other ion which we have not mentioned arises from minor processes, which leak from the principal chemical reaction flows as described in i) ~ v), and therefore their densities are generally low. Beyond the altitude where we have given the above discussion of ion-molecule reactions, the photochemistry occurring in the atmosphere becomes simpler, since the abundances of methane and of hydrocarbons that originate from the former both diminish there. Such a photochemistry and a modification needed when high energy electron precipitation on atmosphere is evoked, were discussed by Ashihara & Shimizu (1977).

4. Lower Boundary Condition and Associated Stability Problem of Methane Atmosphere

In any planet with a substantial atmosphere in our solar system we will meet with a similar problem as in the above title. An attempt, whatever it may be, to get some useful result is usually possible within the restricted range of altitudes, provided that the formalism of problem is not allowed to change spatially. For example, in the outer planets, temperatures vary from those far below room temperature to several hundred or several thousand degrees Kelvin (towards the deep interiors), and the conventional methods to treat the chemistry largely differ depending on the environments which we are concerned with. It is quite common for the calculation based on a certain method in a certain altitude range to require, as a necessary input, the information obtained from calculations which are made on the different methods and conditions. From such a mutual dependence of boundary conditions it would be difficult, without any observational constraint imposed, to obtain a self-consistent picture on atmospheric structure through the whole altitude range.

We shall specify a subject to our present one that treats the density distribution of minor constituents at the altitudes above stratosphere. As previously seen, methane is destructed by a variety of the processes of photodissociation, neutral-neutral reaction and ion-molecule reaction, and at the same time it is restored by

these chemical reactions and by photodissociation of larger hydrocarbons. The both rates for the destruction and restoration, however, need not balance in general and actually differ in our calculations (the former is larger than the latter, see Fig. 27). In the cases of the local equilibrium solutions or the solutions obtained with no boundary fluxes imposed on diffusion equations, such a difference is numerically due to the existence of output terms towards the compounds with more than four carbon atoms (Fig. 28). These heavier compounds may continue reactions eventually
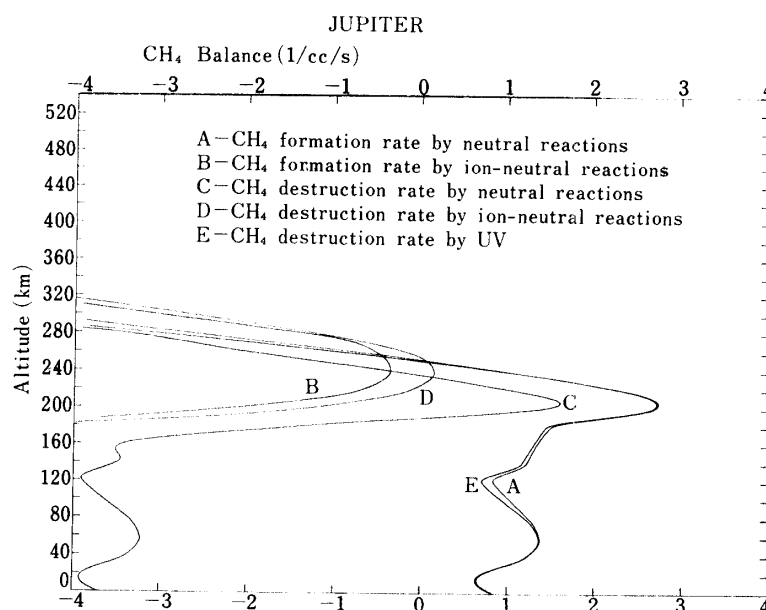
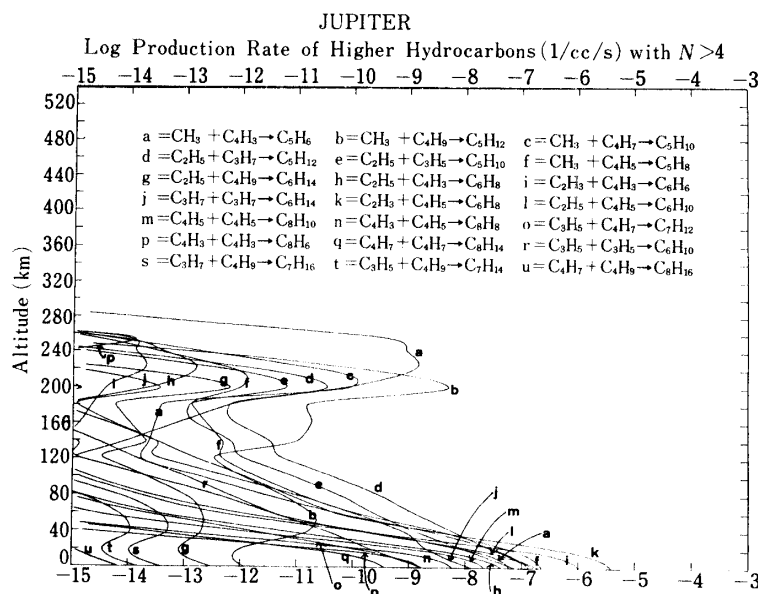Fig. 27. Formation and destruction rates of methane for the case given in Fig. 15.

Fig. 28. Production rates of hydrocarbons with more than four carbon atoms, for the case given in Fig. 17.

to form polymeric products, or may on the way be returned to lighter hydrocarbons by photochemical processes, or may be transported down to the deep troposphere passing the lower boundary—the first may have a connection with the existence of dust layer in the stratosphere, which was strongly suggested from the spectral feature of the Jovian UV albedo (Axel, 1972). It, however, appears that those routes have not a specific importance in discussing the following stability problem of methane, at least in our nominal case ($T = 150K$ and $K_{max} = 10^6 \, cm^2 \, s^{-1}$). The problem is more essentially affected by the distribution of saturated hydrocarbons near the lower boundary.

We have already seen that near the lower boundary most hydrocarbons have shorter chemical lifetimes compared with that for the eddy diffusion, but not so for the saturated hydrocarbons. As a result, the species like C_2H_6, C_3H_8 and C_4H_{10} are considerably influenced by transport effect and their actual fluxes beyond the lower boundary are governed by the physico-chemical processes occurring in the lower stratosphere and troposphere. Since the information on these hydrocarbons in such deep levels is currently not obtained both theoretically and observationally, our argument is inevitably qualitative. Anyway, the total flux of these hydrocarbons that are carried downward beyond the lower boundary, if it exists, has to be compensated by the net destruction of methane, as far as the former originates from the latter (except for the small fraction with which they may *in situ* polymerize, or come to be restored by vaporization or UV irradiation of dust particles). Hence the present assumption of fixing a methane concentration is equivalent to implicitly assuming that an upward transport of methane exists to the same extent as the above total downward (unknown) flux of those heavier hydrocarbons, since, otherwise, methane would have vanished from the upper atmosphere within a time much shorter than the age of the planet. This, however, does not necessarily imply that the total methane content in the planetary atmosphere has been kept constant throughout its geologic history. Whether such an assertion is correct or not depends on the difference between the total destruction and restoration of methane, when accumulated during the time history, would be smaller or not, compared with the whole methane content possessed by the planet in the early stage of its formation. Unfortunately current knowledge of the total amount of methane in the outer planets includes considerable uncertainty. In Jupiter, if one estimates it to be 150 m·amagat, referring to Kuiper (1952) and Lutz *et al* (1976), then the rate necessary for destructing the methane atmosphere in 4.5×10^9 years is $1.5 \times 10^4 \cdot$ (Loschmidt NO.)/ $(4.5 \times 10^9 \cdot 3 \times 10^7$ (1 year))$= 3 \times 10^6 \, cm^{-2} \, s^{-1}$. This is undoubtedly a small rate compared with the solar UV fluxes on Jupiter which are capable of destructing methane. Considering that the above 150 m·amagat of CH_4 would probably be an upper limit (Chamberlain, 1977) it is evident that some efficient processes to recycle hydrocarbons to CH_4 are operating in the deep troposphere characterized by high temperatures of a thousand degree or more—pyrolysis or thermal decomposition may be the most usual way of *purifying* higher hydrocarbons to smaller ones in such an environment. As for Uranus and Neptune, they seem not so troubled by this stability problem

of methane atmosphere as Jupiter has, since the methane contents suggested for the former planets exceed those for Jupiter and Saturn by one to two orders of magnitudes, and moreover, since the *UV* fluxes capable of dissociating methane greatly diminish in these planets because of the remoteness from the sun.

Finally we show in Fig. 29 an example of non-zero downward fluxes having been imposed on the saturated hydrocarbons at the lower boundary. According to the context so far described, these fluxes are currently unknown parameters and in the example they are taken as $-5 \times 10^8 \, \mathrm{cm^{-2} s^{-1}}$ for C_2H_6, $-2 \times 10^5 \, \mathrm{cm^{-2} s^{-1}}$ for C_3H_8 and $-2 \times 10^5 \, \mathrm{cm^{-2} s^{-1}}$ for C_4H_{10}. When we compare Fig. 29 with Fig. 21 it is clear that the saturated hydrocarbon contents have suffered a reduction at heights near the lower boundary in such a way as predicted from*[)]

$$n_i(z) = C n_i(z_0) e^{-(z-z_0)/H} - \Phi_i/K,$$

where H is the mixing scale height, K the eddy diffusion coefficient and Φ_i the number flux of the i-th hydrocarbon at the lower boundary. For downward flux ($\Phi_i < 0$), the second term dominates, realizing a density distribution nearly independent of height. Responding to such a density alteration of the saturated hydrocarbons, it is also clear that the abundances of those hydrocarbons which are photochemically connected to the former, have changed.
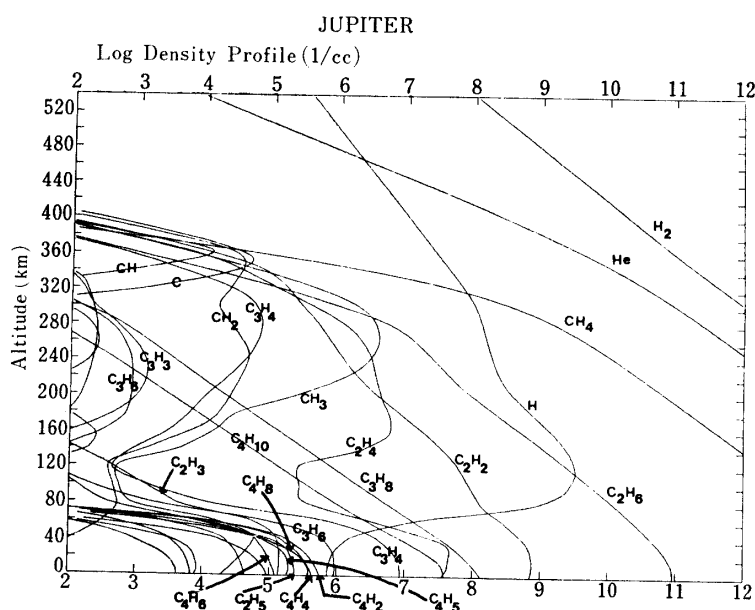

Fig. 29. Neutral hydrocarbon densities in Jupiter in the case where nonzero downward fluxes at the lower boundary have been assumed; $-5 \times 10^8 \, \mathrm{cm^{-2} s^{-1}}$ for C_2H_6, and $-2 \times 10^5 \, \mathrm{cm^{-2} s^{-1}}$ both for C_3H_8 and C_4H_{10}. $K_{max} = 10^8 \, \mathrm{cm^2 \, s^{-1}}$ and $T = 150 \mathrm{K}$.
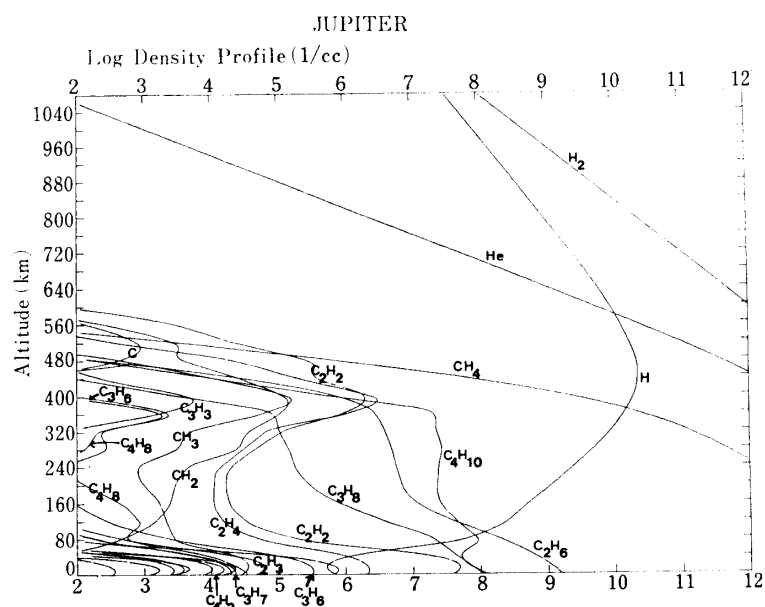
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* Strictly speaking, the expression is correct only for constant eddy diffusion coefficient and for no production and loss terms included.

5. Temperature Effect

We have carried out a number of test calculations by changing the various physical parameters characterizing planetary atmospheres and also by changing some important elementary reaction data. From such calculations, it is known that temperature is one of the parameters which most sensitively affect final results. Although we have usually assumed a temperature of 150K for the Jovian cases, the possibility of higher mesospheric temperature is not excluded *a priori* (Chap. IV, § 2, ii)). On the other hand, to the more distant planets as Uranus and Neptune, we have assumed 100K and 130K, respectively, the temperatures lower than those in Jupiter and Saturn. These two extreme cases of temperature (higher and lower than 150K) will be discussed separately below.

i) *A result obtained under the supposition of warmer Jovian atmosphere*

Fig. 30 shows the Jovian density profile for the tentative case of isothermal atmosphere of 300K. By comparison with Fig. 17, it can be found that higher temperature has brought about a general increase of abundance for most hydrocarbons. Only the densities of the molecules such as CH_2 (triplet) and C_3H_4 have exceptionally diminished. The density increase of those hydrocarbons has its origin in that methyl radicals have been made abundant due to the delay of the reaction, $H + CH_3 + M \xrightarrow{\alpha 5} CH_4$, which, instead, resulted in the growth of ethane density $(CH_3 + CH_3 + (M) \xrightarrow{\alpha 81} C_2H_6{}^{*)})$. Such a delay of the reaction ($\alpha 5$) is, one, due

Fig. 30. Neutral hydrocarbon densities in Jupiter in the tentative case where temperature is as high as 300K. All the other calculational conditions are same as in Fig. 17.

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*) In the altitude region where ethanes are most actively produced, the reaction proceeds, nearly as a second-order reaction.

to the strong negative temperature dependence of the three-body association rate coefficient and, the other, due to the reduced atomic hydrogen abundance; the latter mainly comes from the enhanced role of the reactions with acetylene,

$$H + C_2H_2 \xrightarrow{\alpha 6} C_2H_3^* \quad \text{and} \quad \xrightarrow{\alpha 7} H_2 + C_2H .$$
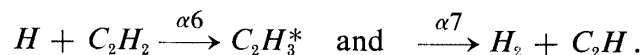
As for acetylene and some C_4-compounds such as C_4H_4 and C_4H_6, the increases are much larger than may be simply expected from the above density increase of ethane (*e.g.*, $C_2H_6 \xrightarrow{h\nu} C_2H_2$). The reason is not necessarily the same for different altitudes and the analysis is somewhat complicated by diffusion effects. Furthermore, the argument on those hydrocarbons depends on the most uncertain part of the reaction models which we have formulated in the present work. The following, however, is clearly one of the causes; at high temperatures the production of methylacetylene ($H + C_3H_3 + M \xrightarrow{\alpha 13} C_3H_4$) is considerably reduced because of the diminution of free hydrogen content and of the delay of addition reaction rate, fully compensating the increase of C_3H_3 which has resulted from $CH_2 + C_2H_2 \xrightarrow{\alpha 63} C_3H_3 + H$. Methylacetylene produces C_3H_2 by photoabsorption. Since the radical is not incorporated into our model, the more the abundance of methylacetylene decreases, the more the chance that a hydrocarbon stays as non-acetylenic compounds reduces (remember that there is many a chemical cycle which is very efficient to return heavier hydrocarbons to acetylene). Under such a circumstance, acetylene tends to react with ethynyl radical that resulted from photoabsorption of acetylene or its reaction with atomic hydrogen,

$$C_2H + C_2H_2 \longrightarrow C_4H_2 + H . \qquad \alpha 105$$

The product, diacetylene, however, is easily returned to acetylene, or, again, to ethynyl radical by

$$C_4H_2 \xrightarrow[H,M]{\alpha 25} C_4H_3 \xrightarrow[H]{\alpha 27} 2C_2H_2$$

and

$$C_4H_2 \xrightarrow{h\nu} 2C_2H .$$
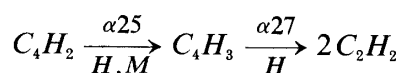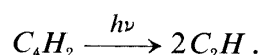
Hence, acetylene and some C_2- and C_4-hydrocarbons that are closely related to the former by chemical reactions become maintained on high abundance.

After all, we can conclusively argue that why the overall abundance of hydrocarbons increases is because the more efficient chemical cycles have been used in the present case, with respect to a restoration of acetylene.

The density increase of the species like C_4H_6, C_2H_4, C_2H_5, C_3H_8 and C_4H_{10} can all be understood upon the enrichment of those compounds as described above, by considering the following reactions,

$$C_2H_3 + C_2H_3 \longrightarrow C_4H_6 \qquad \alpha 116$$

$$(H + C_2H_2 \xrightarrow{\alpha 6}) C_2H_3^* \xrightarrow[H_2]{\alpha 129} C_2H_4 + H$$

$$H + C_4H_6 \longrightarrow C_2H_3 + C_2H_4 \qquad\qquad \alpha 35$$

$$H + C_2H_4 + M \longrightarrow C_2H_5 \qquad\qquad \alpha 9$$

$$CH_3 + C_2H_5 + M \longrightarrow C_3H_8 \qquad\qquad \alpha 84$$

$$CH_3 + C_3H_7 \longrightarrow C_4H_{10} \qquad\qquad \alpha 89$$

$$C_4H_6 \xrightarrow[H,M]{\alpha 34} C_4H_7 \xrightarrow[H,(M)]{\alpha 37} C_4H_8 \xrightarrow[H,M]{\alpha 40} C_4H_9 \xrightarrow[H,M]{\alpha 42} C_4H_{10} \, ,$$
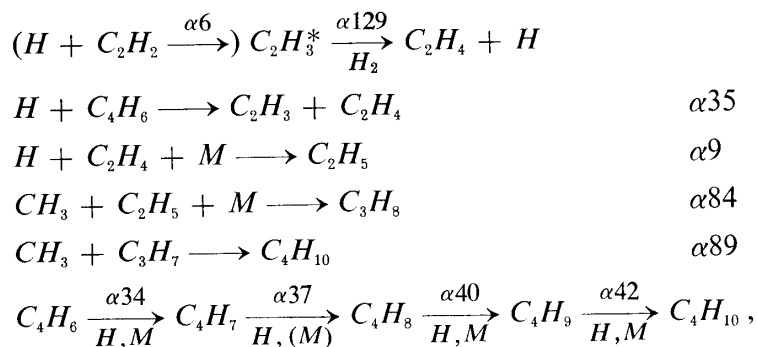
where the increase of C_3H_7 in the lefthand side comes from the reaction sequence as follows,

$$C_4H_9 \xrightarrow[H]{\alpha 44} C_3H_6 \xrightarrow[H,M]{\alpha 19} C_3H_7 \, .$$
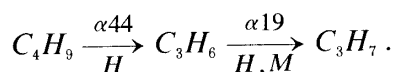
ii)   *Results in the Uranian and Neptunian atmospheres*

   Figs. 31 and 32 show the neutral density profiles obtained for Uranus and Neptune, respectively.   Conspicuously found is that the C_3- and C_4-compounds with high degree of saturation, such as C_3H_8, C_3H_6, C_3H_4, C_4H_{10} and C_4H_8 are much more abundant in these planets than in Jupiter and Saturn.   In contrast, the densities of C_2-compounds have reduced.

   As has been described in the previous chapter, we have chosen mixing ratio of methane as $(1 \sim 3) \times 10^{-6}$ for those distant planets.   From such a small value, the results shown in Figs. 31 and 32 may appear somewhat unexpected.   We discuss the reasons for Uranus.

   Photochemistry occurring in the Uranian atmosphere will be characterized by the following two features when it is compared with that in the inner major planets.

   One is the reduced photodissociation rate, which arises from the diluted solar radiation intensity.   This effect, however, could not, in itself, bring about a result significantly deviated from those obtained for the other planetary cases, if the photoprocesses were postulated to prevail over the chemical processes.   This is due to the trivial reason that the production and destruction of molecules by photo-processes are then similarly affected by the same diluted solar radiation and therefore the molecular densities can be maintained on certain levels, fairly independent of the heliocentric distance of planet. (In the above, transport effects are left untouched but its inclusion may bring about an additional complexity to the density distribution of molecules, depending upon the relative importance between the transport effects and photochemical effects.)

   The other is the marked increase of the rates for combination.   This can be understood from that such rate coefficients generally become large towards low temperatures, and also from that the pressure condition to stabilize an excited intermediate is more satisfactory in Uranus and Neptune than in Jupiter and Saturn: Since we have modeled the former planetary atmospheres by assuming quite small mixing ratios of methane, the ambient pressure in zone of active methane photolysis—

which is roughly characterized by an unit optical depth of $Ly\,\alpha$ in a gaseous methane—is much larger than in Jupiter and Saturn. Shown below are the reactions of this kind due to which a substantial increase of the product species at the right-hand side arises.

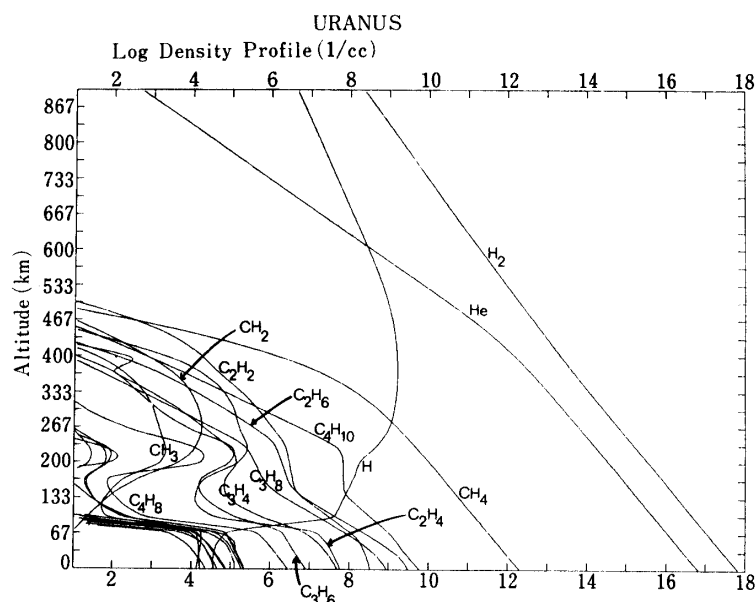Fig. 31. Neutral hydrocarbon densities in Uranus for $K_{max}=10^6$ cm^2 s^{-1}, $T=100$K and $f_{CH_4}=3\times10^{-6}$.

Fig. 32. Neutral hydrocarbon densities in Neptune for $K_{max}=10^6$ cm^2 s^{-1}, $T=130$K and $f_{CH_4}=10^{-6}$.

$$CH_3 + C_2H_5 + M \longrightarrow C_3H_8 \qquad\qquad \alpha 84$$

$$C_2H_5 + C_2H_5 \longrightarrow C_4H_{10} \qquad\qquad \alpha 130$$

$$C_2H_3 + C_2H_2 + M \longrightarrow C_4H_5 \qquad\qquad \alpha 114$$

$$CH_3 + C_3H_3 + M \longrightarrow C_4H_6 \qquad\qquad \alpha 86$$

$$CH_2 + C_2H_2 + M \longrightarrow C_3H_4 \qquad\qquad \alpha 62$$

Such an increase would be more strengthened if the loss should happen to be suppressed. This is the case for C_4H_6 and C_3H_4 among the above products. Their principal losses are,

$$H + C_3H_4 \xrightarrow{k_1} C_3H_5^* \xrightarrow{M} C_3H_5 \qquad\qquad \alpha 14$$

$$\searrow CH_3 + C_2H_2 \qquad\qquad \alpha 15$$

$$H + C_4H_6 \longrightarrow C_4H_7^* \xrightarrow{M} C_4H_7 \qquad\qquad \alpha 34$$

$$\searrow C_2H_3 + C_2H_4 \qquad\qquad \alpha 35$$

where, the first rate k_1 is much smaller in Uranus than the corresponding rate value used in Jupiter ($k_1 \propto e^{-1000/T}$). Nevertheless, note that it does not necessarily mean that the allyl radicals (C_3H_5) are produced less in Uranus. As already described, the stabilization reaction ($\alpha 14$), compared with the unimolecular reaction ($\alpha 15$), is more important in Uranus than in Jupiter. Quite similar argument is also valid for the reaction system of $H + C_4H_6$ ($\alpha 34$, $\alpha 35$).

The decrease of atomic hydrogen is also remarkable. Detailed analysis shows that it is not caused by the change of the loss rate; in its principal loss reactions such as, $H + CH_3 + M \xrightarrow{\alpha 5} CH_4$ and $H + H + M \xrightarrow{\alpha 2} H_2$, the paucity of reaction partners available for free hydrogens is, in effect, nearly compensated by more abundant third-bodies. The decrease of free hydrogen essentially comes, one, from the decreased production of $^1CH_2$ that owes to the reduced photodissociation rate of methane,

$$CH_4 \xrightarrow[\text{weaker}]{h\nu} {}^1CH_2 + H_2$$
$$\searrow{}^{H_2^{\#)}} CH_3 + H$$
$$\searrow \text{decrease}$$

and, the two, from the decreased abundance of C_1- and C_2-compounds, that is, from the delays of

$$C_2H + H_2 \longrightarrow C_2H_2 + H \qquad\qquad \alpha 103$$

$$CH + CH_4 \longrightarrow C_2H_4 + H. \qquad\qquad \alpha 54$$

#) Note that singlet methylene almost completely reacts with molecular hydrogen in any atmospheric environment of the outer planets. Therefore, the enrichment of hydrogen molecule at each fixed altitude in Uranus and Neptune is nothing to do with the total consumption rate (cm^{-2} s^{-1}) of $^1CH_2$. It is only determined by the total production rate (cm^{-2} s^{-1}) of $^1CH_2$.

There is one more characteristic feature in the present case, which was not found in calculations for the other planets. This is the role of ion-moecule reactions in yielding some C_3- and C_4-hydrocarbons, such as

$$C_3H_9^+ + e \longrightarrow C_3H_8 + H$$
$$C_3H_{11}^+ + e \longrightarrow C_3H_8 + H + H_2 \qquad \Big\} \quad \beta222$$
$$C_4H_7^+ + e \longrightarrow C_4H_6 + H .$$

In the Uranian atmosphere, these ions are relatively more abundant compared with the other ions, although the total ion density is much smaller than in the Jovian atmosphere. We note that such a difference in the different planets eventually results from: a) dissimilar relative abundance of the dominant neutrals such as H, C_2H_2, C_2H_4 and C_2H_6 (see, § 3). b) large separation existing between the heights where H_2/He photolysis and CH_4 photolysis occur respectively. Since Uranus and Neptune are given quite small mixing ratios of methane, the photons which are incapable of ionizing any of H, H_2 and He, can penetrate deep into the atmosphere where absorption by methane first occurs. At these altitudes, because of the high ambient pressures, such an ion-neutral reaction as necessitates a stabilization by third-bodies is much faster in the cases of Uranus and Neptune than in the other planetary cases.

6. Comparison with Observational Results and Theoretical Implications for Future Research

From the results obtained in the foregoing sections, we now know that many hydrocarbons can actually be created in the chilly circumstances of the outer planets, but, at the same time, also know that their abundances are strongly influenced by the parameters characterizing our model atmospheres such as temperature, eddy diffusion coefficient and methane mixing ratio and by several currently unavailable reaction rates.

A comparison with observational results is not necessarily an easy task. As is seen in Table 3, the earlier determinations of the abundance for C_2H_2 and C_2H_6 have probably brought about too large values. In the succeeding observations, there is some systematic trend that the more lately they are made, the smaller mixing ratios are obtained. In the present argument, we shall continue discussions by tentatively adopting the values of $10^{-8} \sim 10^{-7}$ for ethane and 10^{-9} for acetylene, as the most probable average mixing ratios in the outer planets.

Table 12 shows the mixing ratics of hydrocarbons derived from the calculations for different eddy diffusion coefficients and temperatures. In reality, those species as listed in the table do not distribute after constant mixing ratios with height. The values are deduced first by calculating the column abundances $(cm^{-2} s^{-1})$ for such hydrocarbons and next by dividing them by the total density of H_2 and He.

So far we have discussed mostly the results obtained for a moderate strength of eddy diffusion. This is simply due to the comparison of the present work with

those performed in the past being easier. A better agreement with observational results, however, appears to be obtained, in the present work, for more intense turbulence as is seen in Table 12. The mixing ratios of acetylene and ethane, for the case of $K = 10^6 \, cm^2 \, s^{-1}$, are insufficient for detection. This is also valid for methylacetylene (C_3H_4), and propane (C_3H_8), the species whose existence on Saturn was suggested by Voyager 1.

Our results for $K = 10^6 \, cm^2 \, s^{-1}$ are rather different from those of previous investigators in that the latter calculations produced, in spite of such a low eddy diffusion coefficient, acetylene and ethane sufficient for explaining the observed abundances. Although the exact reason is not necessarily clear, two factors are probably related to it; the adoption of rate coefficients (particularly of $\alpha 5$ and $\alpha 81$) different from ours, and the entire neglect of the reaction paths that yield C_3- and C_4-hydrocarbons. The importance of the relative rate values between those two reactions $(\alpha 5$ and $\alpha 81)$ was repeatedly discussed in the previous sections. One can see an example in Fig. 33, which has been derived by tentatively reducing the rate value $(\alpha 5)$ given in Table 7 by a factor of 10. The overall increase of hydrocarbons is evident.

Our chemical model here formulated for the atmospheres of the outer planets may, or certainly will, include a number of debatable assumptions on chemical reaction schemes and the rate values. The selection of the different rate values for some of those processes would change our present conclusions not only quantitatively but even qualitatively. As to such, anyway, we must await the advance of future research. Here, only based on the results obtained from the selection of chemical
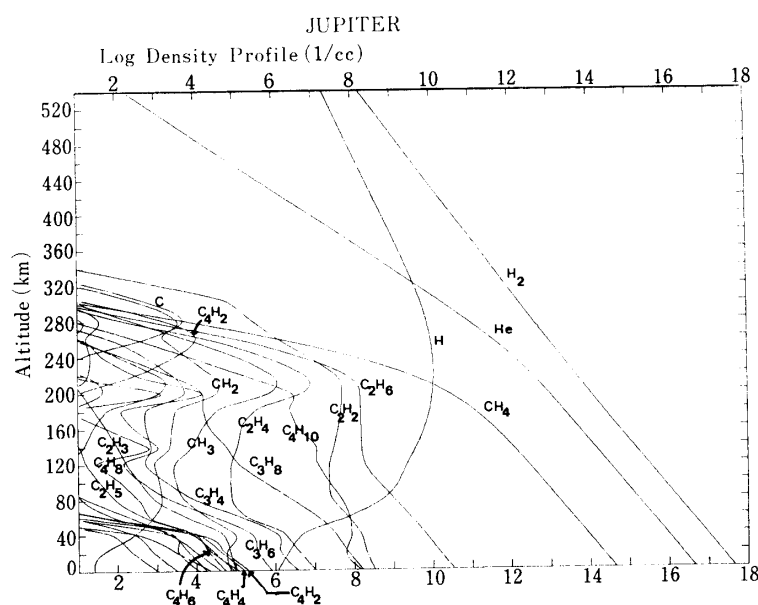

Fig. 33. Neutral hydrocarbon densities in Jupiter in the artificial case where the rate of the reaction, $H + CH_3 + M \rightarrow CH_4$ has been reduced by a factor of 10. All the other calculational conditions are same as in Fig. 17.

data listed in Tables 7 and 8, we shall discuss the hydrocarbons that may be thought abundant in the atmospheres of the outer planets.

Table 12 shows that there would be no hydrocarbons detectable under the current capabilities of the earth-based observations, other than those already described in this section. The *IR* observation by Voyager 1 obtained a result, strongly suggesting the existence of methylacetylene and propane. As far as we refer to Table 12, it appears that C_2H_4 (ethylene) and C_4H_{10} (butanes) are also marginal in abundance from a viewpoint of detectability by *in situ* observations. Next abundant compounds are C_3H_6, C_4H_2 and C_4H_8—here, C_3H_6 usually means propylene, and C_4H_2 diacetylene, while for C_4H_8, it represents butene compounds and, in the present work, cannot specify the isomers. It, however, must be added that the actual possibility of detection is another matter, not necessarily proportioning to abundance. Normally the following conditions must be favorable in order that a specific vibrational transition of molecule may be detected: a) have a large band strength (usually, infrared-active band). b) not interrupted by such telluric absorptions as due to H_2O and CO_2. c) the characteristic absorption or emission is not mingled with those of the dominant atmospheric constituents of planets, *e.g.*, due to CH_4 and NH_3.

Although no hydrocarbons with five or more carbon atoms have yet been suggested in existence in the outer planets, we know from laboratory experiments that photolyses of C_2- to C_4-compounds yield many such heavier products. For future reference, we have compiled in Table 13 those hydrocarbons which had been so far ident fied as photolysis products. As all the molecules in the first column are, conceptually, the ones that have been modeled in the present work, existence of the molecules given in the product column would be not inconceivable in the planetary environments by virtue of the solar *UV* photolysis working on the former materials. On a basis of this table and some available information of experimental yields, we can enumerate several most promising candidates of abundant C_5- and C_6-hydrocarbons, as follows

C_5H_{10}	pentenes (1-, 2-)
	3-methyl-1-butene
	2-methyl-2-butene
C_5H_{12}	pentanes (*n*-, *iso*-, *neo*)
C_6H_6	benzene
C_6H_{12}	hexenes (1-)
	4-methyl-1-pentene
C_6H_{14}	hexanes (*n*-)
	dimethylbutane.

Table 12.   Mixing ratios of hydrocarbon in Jupiter derived from the present calculations

	$K=10^6$, $T=150$	$K=10^8$, $T=150$	$K=10^6$, $T=300$
H	1.0(-7)	1.6(-8)	2.7(-7)
C_2H_2	2.0(-10)	6.3(-9)	1.3(-10)
C_2H_4	1.2(-11)	4.1(-10)	1.6(-11)
C_2H_6	7.4(-10)	8.0(-7)	4.2(-9)
C_3H_4	1.1(-13)	7.4(-11)	1.3(-12)
C_3H_6	2.4(-14)	9.1(-12)	7.4(-13)
C_3H_8	9.7(-12)	1.4(-9)	3.1(-10)
C_4H_2	8.0(-15)	3.2(-12)	3.5(-14)
C_4H_4	7.4(-16)	2.6(-12)	2.6(-14)
C_4H_6	5.1(-16)	7.4(-13)	1.9(-14)
C_4H_8	2.4(-16)	2.7(-12)	8.5(-14)
C_4H_{10}	4.3(-13)	5.1(-10)	8.5(-10)

Table 13. C_5- and higher hydrocarbons observed in photolyses of C_2- to C_4- hydrocarbons
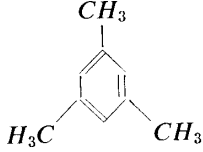
materials	products	
acetylene (C_2H_2)	benzene (C_6H_6)	
ethylene (C_2H_4)	1-pentene (C_5H_{10})	$CH_3(CH_2)_2CH=CH_2$
	2-pentene (C_5H_{10})	$CH_3CH_2CH=CHCH_3$
	n-pentane (C_5H_{12})	$CH_3CH_2CH_2CH_2CH_3$
	n-hexane (C_6H_{14})	$CH_3CH_2CH_2CH_2CH_2CH_3$
	C_7, C_8	
methylacetylene (C_3H_4)	1, 5-hexadiyne (C_6H_6)	$HC\equiv C(CH_2)_2C\equiv CH$
	C_6H_8, C_6H_{10}	
	mesitylene (C_9H_{12})	
propylene (C_3H_6)	1, 4-pentadiene (C_5H_8)	$CH_2=CHCH_2CH=CH_2$
	3-methyl-1-butene (C_5H_{10})	$(CH_3)_2CHCH=CH_2$
	1-pentene	
	isopentane (C_5H_{12})	$CH_3CH(CH_3)CH_2CH_3$
	1, 5-hexadienne (C_6H_{10})	$CH_2=CHCH_2CH_2CH=CH_2$
	4-methyl-1-pentene (C_6H_{12})	$(CH_3)_2CHCH_2CHCH_2$
	2, 3-dimethyl-butane (C_6H_{14})	$(CH_3)_2CHCH(CH_3)_2$
propane (C_3H_8)	3-methyl-1-butene	
	1-pentene	
	n-pentane	
	isopentane	
	1, 3, 5-hexatriene (C_6H_8)	$CH_2=CHCH=CHCH=CH_2$
	4-methyl-1-pentene	
	1-hexene (C_6H_{12})	$CH_3(CH_2)_3CH=CH_2$
	n-hexane (C_6H_{14})	$CH_3(CH_2)_4CH_3$
	2, 4-dimethyl-butane (C_6H_{14})	$(CH_3)_2CHCH_2CH_2CH_3$

Table 13. *Continued*

materials	products	
1, 3-butadiene (C_4H_6)	pentenes two kinds of C_6H_6 two kinds of C_6H_{12} one kind of C_7H_{10}	
1-butene (C_4H_8)	1-pentene	
	cis $\Big\}$-2-pentene trans	
	2-methyl-1-butene (C_5H_{10})	$CH_3CH_2C(CH_3)=CH_2$
	2-methyl-2-butene (C_5H_{10})	$(CH_3)_2C=CHCH_3$
	3-methyl-1-butene	
	n-pentane	
	isopentane	
	1, 5-hexadiene (C_6H_{10})	$CH_2=CHCH_2CH_2CH=CH_2$
	3-methyl-pentane (C_6H_{14})	$CH_3CH_2CH(CH_3)CH_2CH_3$
	3-methyl-1, 5-hexadiene (C_7H_{12})	$CH_2=CHCH_2CH(CH_3)CH=CH_2$
	1, 5-heptadiene (C_7H_{12})	$CH_3CH=CHCH_2CH_2CH=CH_2$
	4-methyl-1-hexene (C_7H_{14})	$CH_3CH_2CH(CH_3)CH_2CH=CH_2$
2-butene (C_4H_8)	2-pentene 3-methyl-1-butene *n*-pentane isopentane C_8	
isobutene (C_4H_8)	1-pentene	
	cis $\Big\}$-2-pentene trans	
	2-methyl-2-butene 3-methyl-1-butene isopentane	
	neopentane (C_5H_{12})	$(CH_3)_4C$
	C_6, C_7, C_8	
n-butane (C_4H_{10})	*n*-pentane isopentane C_6H_{14} (hexanes) C_8H_{18}	
isobutane (C_4H_{10})	isopentane neopentane	

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