No. 61.

(Published May, 1930.)

Action of Antioxydants in Oxidation of Unsaturated Fatty Oils.

I. Mechanism of Inhibitory Action of Diphenylhydrazine and α-naphtylamine.

By

Bunnosuke YAMAGUCHI, *Rigakusi*,

Member of the Institute.

Abstract.

This paper describes the results of the investigations on the effects of unsymmetrical diphenylhydrazine and α-naphtylamine on the oxidation of unsaturated fatty oils such as olive oil and castor oil at 100°C. The rate of oxidation has been determined by the measurement of the decrease in iodine value resulting from the oxidation. The oxidation does not apparently start at once, i.e., oil remains seemingly unchanged during a period of incubation. Diphenylhydrazine acts as a strong inhibitor, prolonging the incubation period in a remarkable degree. The oxidation, when once started, always proceeds at the same rate whether or not the reaction has been delayed by the antioxydant. α-naphtylamine does not inhibit so completely the oxidation for a certain length of time as diphenylhydrazine does, and therefore the incubation period is not prolonged by α-naphtylamine, although the initial rate of the oxidation is much lowered by it. Theoretical considerations on the mechanism of the inhibitory action have been made. It has been shown that the actual rate of the inhibited oxidation can be expressed exactly by the equation which has been established on the basis of Christiansen's theory of the chain mechanism. The results of this investigation seem to furnish a new proof of the existence of thermal chain reactions.

Introduction.

Although the oxidation of unsaturated fatty oils has hitherto been much studied, it is only recent that the accurate quantitative study of their rate of oxidation has been undertaken. Besides the investigations on the oxidation of various fatty oils carried out by Ingle,[1] Poster & Holmes,[2] Hyland & Lloyd,[3] and Peter & Danilovich,[4] a number of studies concerning the oxidation of drying oils have been carried out. Recently Roger and Taylor,[5] in their investigation on the oxidation of linceed oil, have introduced an excellent device into the method of measuring the rate with which the oil absorbs oxygen. But, however accurately the measurement of oxygen-absorbing rate of oil can be made, such a method, like the measurement of the increase in weight of oil on exposure to oxygen, is not suitable for determining the rate of oxidation. For, the peroxide into which unsaturated fatty oil is primarily oxidized by absorbing oxygen molecules to the places of unsaturated linkages decomposes, as has been shown by Ingle,[6] into aldehydes by the action of heat in the manner

$$\begin{matrix} -CH-O \\ | \quad | \\ -CH-O \\ \text{peroxide} \end{matrix} = \begin{matrix} -CH=O \\ \\ -CH=O \\ \text{aldehydes} \end{matrix},$$

and the aldehydes thus formed are further transformed into acids by the absorption of oxygen. Oxygen, therefore, is absorbed not only by the unsaturated linkages of oil but also by the decomposition products of oxidized oil and accordingly the measurement of oxygen-absorbing rate does not give the rate with which the oil is oxidized simply into its peroxide but the rate of complicated consecutive oxidation, the

(1) Jour. Soc. Chem. Ind., **32** (1913), 639.
(2) Ibid., **24** (1905), 1287.
(3) Ibid., **34** (1915), 62.
(4) Zeit. deut. Oel-Fett-Ind., **45** (1925), 669, 688, 703, 723.
(5) Jour. Phys. Chem., **30** (1926), 1334.
(6) loc. cit.

theoretical analysis of which is almost impossible. From the point of view, in order to determine the rate of oxidation, it is desirable to measure by some method the decrease in unsaturated linkages resulting from the oxidation. The author has intended to study the rate of oxidation of unsaturated fatty oils such as olive oil and castor oil and also to study the effects of antioxydants on the rate of oxidation by means of the measurement of the change in iodine value due to oxidation.

As regards the mechanism of auto-oxidation reactions, our constantly increasing knowledge of them since the inception of the Engler-Bach[1] theory, has brought forth new but conflicting and at times irreconcilable interpretations of the mechanism of such reactions. The recent, prevalent investigations on the inhibition of auto-oxidation reactions, namely the action of antioxydants which is a very interesting and important problem in both theoretical and practical sides lead us to pay our fresh attention on the mechanism of auto-oxidation. Moureu[2] and his co-workers including Dufraisse have studied so brilliantly and exhaustively the phenomenon of inhibition in the oxidation of numerous substances including hydrocarbons. The inhibition in the oxidation of unsaturated organic compounds has been also studied by Smith and Wood.[3] The other reactions in which the mechanism of inhibition has been researched are the oxidation of substances such as benzaldehyde, investigated in detail by a number of workers including Bächström,[4] Reiff[5] and Brunner[6] as well as the slow combustion of various substances investigated by Callendar[7] and by Gill and his co-workers.[8]

(1) Engler and Wild: Ber., **30** (1897), 1669; Engler and Weiserberg: "Kinetische Studien über die Vorgänge der Autoxydation," (1904); Bach: Compt. rend., **124** (1897), 951; "Fortschritt. d. naturw. Forsch," (Edited by Abderhalden), **1** (1910), 85.

(2) Rapport du Conceil de Chimie Solvay, Bruxelles, (1925); Compt. red., **174** (1922), 258 and other articles.

(3) Jour. Ind. Eng. Chem., **18** (1926), 691.

(4) Jour. Am. Chem. Soc., **49** (1927), 1460.

(5) Ibid., **48** (1926), 2893.

(6) Hev. Chim. Act., **10** (1928), 707.

(7) Engineering, **123** (1927), 147, 182, 210.

(8) Trans. Faraday Soc., **24** (1928), 574.

A number of theories concerning the mechanism of inhibition in auto-oxidation reactions has been established and discussed[1] not only by these workers but also by other investigators such as Taylor,[2] Rideal,[3] Hinshelwood,[4] Dhar,[5] Christiansen[6] and Milas.[7] The conclusions which we may draw at present time from the results of those very interesting investigations and discussions are that it is most favourable to the general interpretation of the results of numerous investigations on auto-oxidation reactions to consider that the oxidation of auto-oxidable substances proceeds by the chain mechanism of Christiansen, and that all auto-oxidable substances form always their unstable peroxides in the primary stage of oxidation (such peroxides are called unstable moloxyd, primary peroxide[8] or dative peroxide[9]). Striking chemical evidence has been found in favour of the latter conclusion in the successful attempt to isolate organic peroxides from auto-oxidation reactions.[10] Christiansen's theory of chain mechanism has its favorable applicability not only in photochemical reactions but also in thermal reactions such as auto-oxidation reactions, providing us the means to explain the phenomenon of negative catalysis in such reactions. In favour of this theory the author has ascertained that the actual rate of oxidation of olive oil containing an antioxydant can be expressed exactly by the equation which has been established on the basis of Christiansen's theory.

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(1) Trans. Faraday Soc., **24** (1928), 697.
(2) Jour. Phys. Chem., **27** (1923), 322.
(3) Trans. Faraday Soc., **24** (1928), 570.
(4) Ibid., **24** (1928), 552.
(5) Ibid., **24** (1928), 567.
(6) Z. Phys. Chem., **104** (1923), 451; Jour. Phys. Chem., **28** (1924), 145; Trans. Faraday Soc., **24** (1928), 595; Dissertation, Copenhagen (1921).
(7) Jour. Phys. Chem., **33** (1929), 1204.
(8) Hev. Chim. Act., **10** (1928), 709.
(9) Jour. Phys. Chem., **33** (1929), 1207.
(10) Callendar: Engineering, **123** (1927), 147; Milas: Jour. Phys. Chem., **33** (1929), 1205.

Experimental.

The method adopted for oxidizing oil consists of bubbling dry oxygen at a rate of 10 liters per hour through 90-gram samples of oil contained in a tube submerged in an oil bath. The temperature of oil samples has been kept constant at 100°C in all cases except one in which the effect of temperature on the rate of oxidation has been studied. In the preliminary experiment (the result of which will be described in the following part) a number of 90-gram samples of oil have been oxidized separately for different times in order to examine the change of its properties such as iodine value, acid value, saponification value, density and refractive index resulting from oxidation. But in the other experiments in which the rate of oxidation has been studied merely by the measurement of the change in iodine value, one sample has been continuedly oxidized by bubbling dry oxygen and at intervals small quantities of the sample have been withdrawn for the determination of iodine value. Oxidation causes the increase in weight of oil. Therefore, when the fall of iodine value is used as measure for the rate of oxidation, a correction corresponding to the increase of weight must be added to each observed iodine value. The correction can be easily calculated from the increases of weight and the amounts of oil withdrawn for analysis at each oxidation time. Iodine value has been determined by the method of Wijs. Since oxidized oil contains peroxide, it is observed that when solution of potassium iodide is added to the carbon tetrachloride solution of oxidized oil and the mixture is left in a dark room after being shaken, iodine is liberated very slowly by the action of the peroxide from the potassium iodide. It has however been ascertained that there is no fear of error due to the presence of peroxide in the case of determination of iodine value, for the mixture of carbon tetrachloride solution of oxidized oil and solution of iodine monochloride is quickly titrated with sodium thiosulphate immediately after solution of potassium iodide and water is added to the mixture. Repeated determinations of iodine value of an oxidized

oil have been found to give consistent results, showing that the experimental error of iodine value does not exceed ±0.2%.

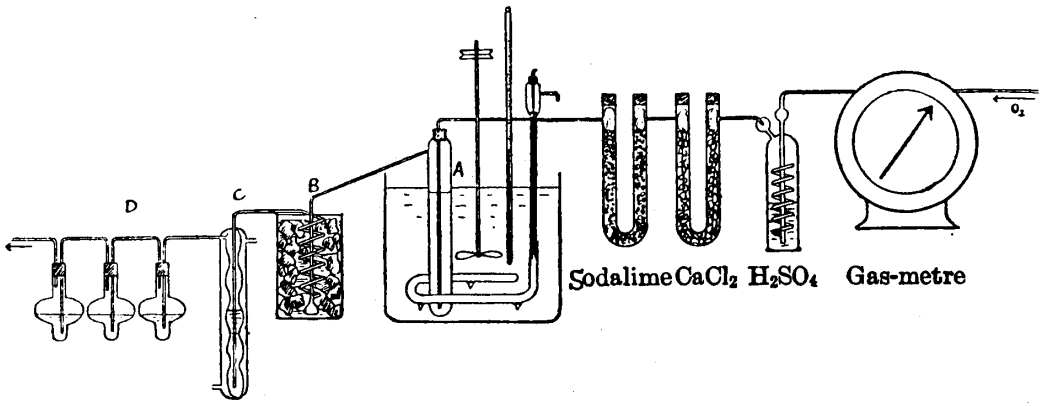


Fig. 1.

Fig. 1 shows the apparatus used for the experiment. *A* is a tube for containing a sample of oil and is submerged in an oil bath held at a constant temperature. *B* is a condensor cooled by ice for collecting the most part of the distilled products resulting from the oxidation of oil. The other part of the distilled products which escape condensation in the condensor *B* is caught by alcohol contained in the tube *C*. *D* consists of three flasks containing baryta water and serves to absorb carbon dioxide resulting from the oxidation.

Two kinds of olive oil have been employed in the experiments: the one which has been used chiefly in the preliminary experiment has an iodine value of 86.6 (Olive Oil A), and the other one has an iodine value of 86.2 (Olive Oil B). Both the oils have been purified as follows.

Olive oil is dissolved in ether and the solution is shaken with the powder of calcium hydroxide. After the solution has been filtered, the ether is removed by evaporation.

I. Preliminary Experiments.

In these experiments the change of various properties of olive oil and castor oil resulting from their oxidation and the effect of diphenyl-

hydrazine on the oxidation have been preliminarily examined.

(*a*) *Oxidation in the absence of antioxydant.*

The results of examinations on the changes of iodine value, acid value, saponification value, density and viscosity resulting from the oxidation of Olive Oil A are shown in Table 1. The iodine numbers

TABLE 1.

Oxidation time (t) (hours)	Corrected iodine value ($a-x$)	$k=\frac{1}{t-4}\ln\frac{a}{a-x}$	Acid value		Density at 14·5°C	Kinetic viscosity at 35°C	Saponification value
			Acid in oil	Acid in distillate			
0	86·6		0	0	0·917	0·461	191·8
2	86·8		0	0·03	0·918	0·468	192·5
4	86·6		0	0·04	0·919	0·477	192·6
5·5	83·8	—	0·37	0·18	0·925	0·565	195·9
7·5	78·5	0·0282	1·48	0·58	0·932	0·729	202·6
10·0	72·2	0·0304	3·12	1·56	0·941	0·983	
15·0	61·5	0·0312	9·11	5·26	0·953		
17·0	57·8	0·0311	11·97	5·26	—		
21·0	51·8	0·0302	17·83	7·00	—		
26·0	44·8	0·0301	23·77	8.96	—		
30·0	39·7	0·0299	28.70	10·45	—		
35·0	32·5	0·0315	33·23	12·39	—		
40·0	27·4	0·0319	39·89	14·09	—		
45·0	24·2	0·0310	—	15·83	—		
47·5	21·7	0·0317	45·67	16·49	—		
53·0	17·4	0·0326	51·80	18.18	—		
63·0	15·4	0·0293	55·21	20·80	—		
75·0	10·5	0·0297	—	23·27	—		
98·0	5·65	0·0294	65·70	25 67	1·042		
		mean 0·0305					

in the table are the values to which the corrections corresponding to the weight increase due to oxidation have been added. Besides the acid values of the oxidized oils themselves given in the right-hand side of the fourth column of Table 1, the amount of the acid which has been distilled out as a result of the oxidation and caught by the condesor B and the alcohol-containing tube C has been measured at each of the oxidation times. The acid values which the original 90-gram sample

would have if the distilled acid were contained in it, are also given in the left-hand side of the same column. The sum of such two acid values at each time of oxidation is obviously the total increase of acid resulting from the oxidation. Fig. 2 also shows the changes of various

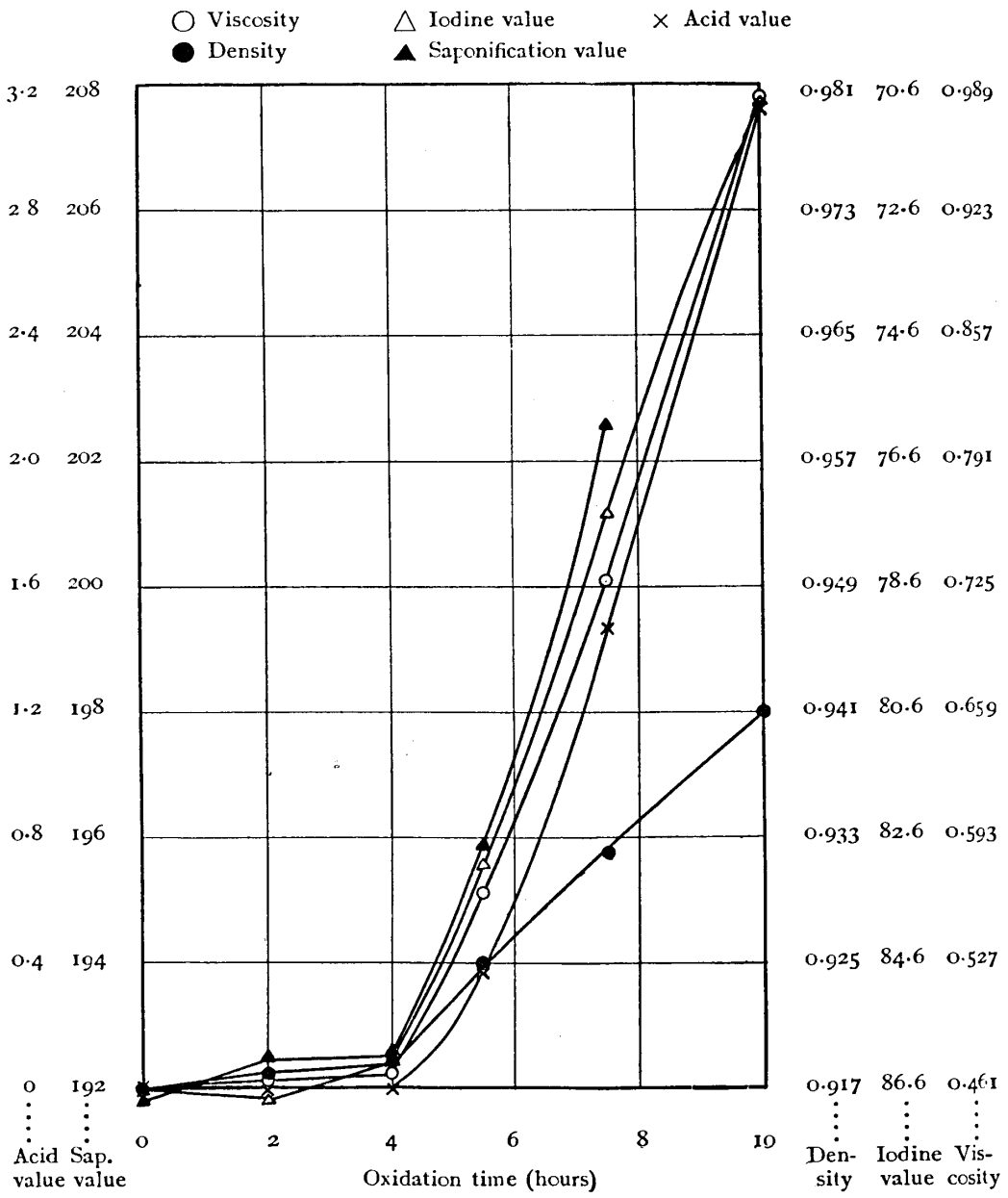


Fig. 2.

properties in the time of oxidation up to 10 hours. It is perceived from the diagram that the properties of olive oil do not practically change beyond the range of experimental error untill the oxidation duration amounts to 4 hours, but after the incubation period (or induction period) their changes distinctly begin to arise simultaneously with appreciable rates. Although a change in one of the properties seems to be invariably connected with a corresponding change in the others, the curves showing these changes are not quite similar with one another. This is reasonable because these changes do not actually depend on the same chemical or physical change in the oil. The left-hand three curves in Fig. 3 show the

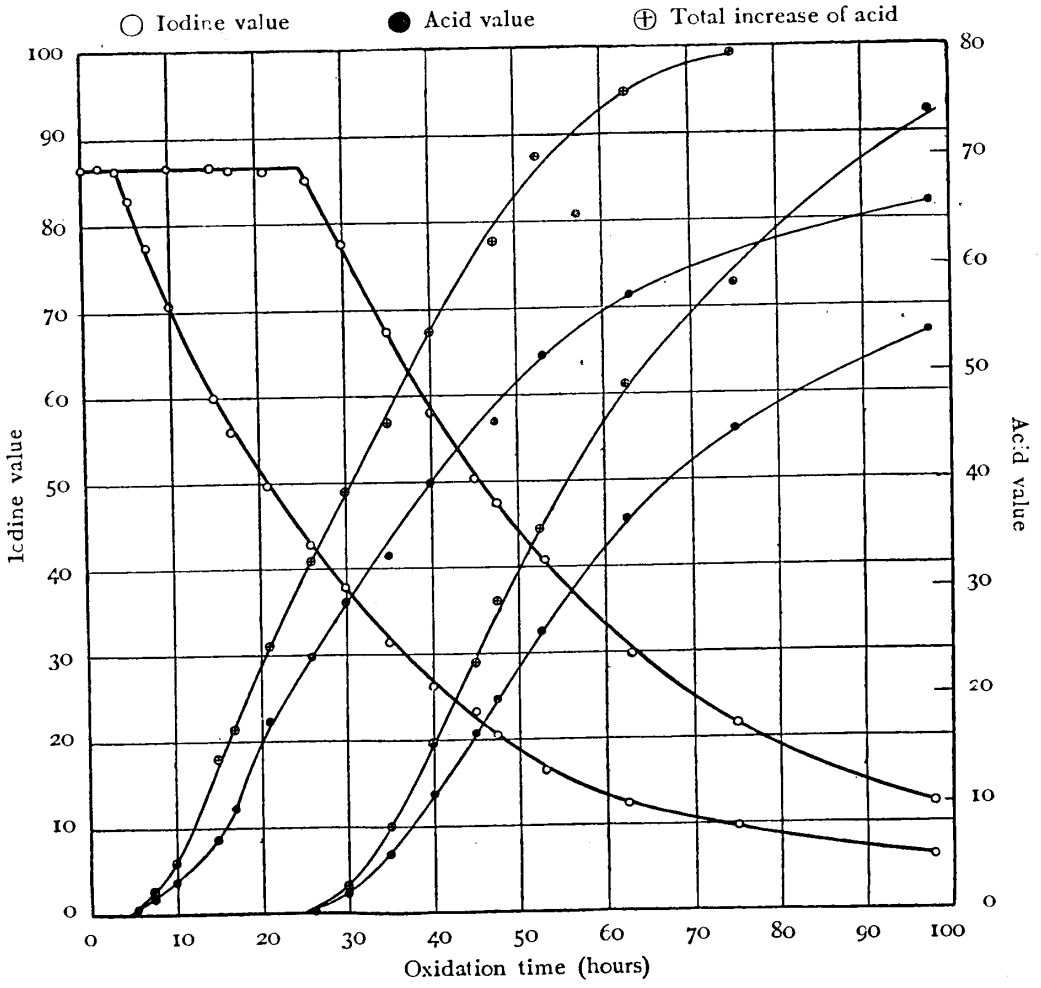


Fig. 3.

changes of acid value and iodine value more clearly. Both the two values remain apparently unaltered during four hours, but as soon as the incubation period expires, the fall of iodine value and the rise of acid value proceed with appreciable rates. The curve of iodine value is obviously different from that of the acid value. The curve which shows the total increase of acid is S-shaped as if it showed an auto-catalytic reaction, while the curve of iodine value has a shape peculiar to unimolecular reactions, indicating that no auto-catalytic effect[1] is practically present in the oxygen-addition reaction of the oil after the incubation period. The course which the decrease of iodine value takes can be expressed by the equation

$$ln\frac{a}{a-x}=k(t-b) \qquad \text{(I)}$$

where x represents the decrease of iodine value in time t, a the initial iodine value of the oil (86·6) and b the incubation period (4 hours). The values of velocity coefficient k which have been calculated by the equation for each oxidation time are found to be in good coincidence as shown in Table 1. Although the greater part of the unsaturated fatty acids which exist in olive oil as glycerides are oleic acid, a little percentage of linolic acid is also contained in the oil. The fact that the fall of iodine value of olive oil can be expressed by the equation of unimolecular reaction notwithstanding that the oil contains such different unsaturated acids makes us to admit that the respective unsaturated linkages of oleic acid and linolic acid have almost equal oxygen-absorbing powers at least at such a temperature as that used in the present experiment.[2] In the case of oxidation of castor oil, the fall in iodine value due to oxidation similarly proceeds unimolecularly as will be shown later on.

The increase of saponification value after the incubation period is very striking. An increase in acid value, of course, causes a corres-

(1) The autocatalytic effect, if present at all, is neglegibly slight.

(2) The author is now studying on the oxidation of chemically pure triolein. It is of course expected that the fall in iodine value of triolein will proceed unimolecularly.

ponding rise in saponification value. But the actual increase of saponification value at an oxidation time of 7.5 hours amounts to more than 10, while the increase in acid value at the same time of oxidation is only 1.48 (see Table 1), and the extraordinary rise of saponification value can not be explained only by the change of acid value. It is, however, explained easily by the assumption suggested by Ingle[1] that the peroxide which has been formed by the oxidation in the oil breaks up under hydrolysis, forming acids in the following manner.

$$\begin{array}{l} \text{HC}-\text{O} \\ \quad | \quad | \\ \text{HC}-\text{O} \\ \quad | \end{array} + \text{H}_2\text{O} = \begin{array}{l} \\ \cdot\text{COOH (acid)} \\ \\ \cdot\text{CH}_2\text{OH}. \end{array}$$

The refractive index of olive oil like the other properties begins to change after a period of incubation. Fig. 4 and Table 2 illustrate the

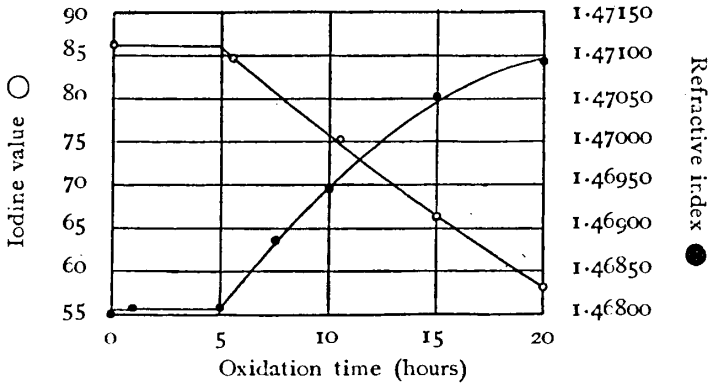


Fig. 4.

TABLE 2.

Oxidation time (hours)	Refractive index at 26·5°C
0	1·46800
1	1·46807
5	1·46807
7·5	1·46886
10·0	1·46945
15·0	1·47053
20·0	1·47092

(1) loc. cit.

result of investigation on the change in refractive index resulting from the oxidation of Olive Oil B. As the oil used in this experiment is different from that used in the preceding experiments, the observed incubation period accordingly is different from that in the preceding case, and is found to be nearly 5 hours. The change in iodine value resulting from the oxidation of this oil is also shown in Fig. 4 (the numerical data are given in Table 9.).

(*b*) *Oxidation of olive oil and castor oil containing diphenylhydrazine as an antioxydant.*

Olive Oil A to which was added 0.1% unsymmetrical diphenylhydrazine has been oxidized at 100°C in the same manner as before, and the changes of its properties have been examined. The results are given in Table 3. The right-hand side three curves in Fig. 3 show the

TABLE 3.

Oxidation time (t) (hours)	Corrected iodine value ($a-x$)	$k=\frac{1}{t-25}\ln\frac{a}{a-x}$	Acid value		Kinetic viscosity at 35°C	Saponification value
			Acid in oil	Acid in distillate		
0	86.6		0	0	0.463	191.8
2	—		0	0.03	0.464	192.3
4	—		0	0.04	0.464	192.8
5.5	—		0	0.05	0.466	193.2
7.5	—		0	0.05	0.466	192.9
10.0	86.5		0	0.05	0.465	192.1
15.0	86.6		0	0.05		
17.0	86.2		0	0.05		
21.0	86.1		0	0.05		
26.0	85.0	0.0296	0.20	0.07		
30.0	77.4	0.0262	1.88	0.76		
35.0	67.2	0.0252	5.44	2.59		
40 0	58.0	0.0268	11.22	4.60		
45.0	50.4	0.0276	16.62	6.54		
47.5	47.6	0 0266	19.64	7.41		
53.0	40.9	0.0268	25.94	9.40		
63.0	29.9	0.0280	36.55	12.64		
75.0	21.6	0.0277	42.87	15.44		
98.0	12.2	0.0268	53.81	20.46		
		mean 0.0271				

changes of iodine value and acid value for this case. From this figure it is seen that unsymmetrical diphenylhydrazine added to the oil acts as a strong inhibitor of the oxidation, causing the oil to remain seemingly unchanged during a period of 25 hours, *i.e.* the addition of 0.1% diphenylhydrazine causes the incubation period to be prolonged from 4 hours to 25 hours. After the incubation period of 25 hours, the oxidation proceeds as for the olive oil containing no antioxydant and the fall in iodine value resulting from the oxidation can be expressed by the equation of unimolecular reaction rate (I), in which the value of b must in this case be put equal to 25 hours. The values of k calculated by the equation for different oxidation times are found to agree well with one another as shown in Table 3. Table 4 and Fig. 5 illustrate the result of similar investigation on the oxidation of castor oil.(1) In Fig. 5, the logarithm of iodine value or log $(a-x)$ is taken as the ordinate, and

TABLE 4.

Oxidation of castor oil

Without antioxydant			0.044% unsym. diphenylhydrazine			0.10% unsym. diphenylhydrazine		
Oxidation time (hours)	Corrected iodine value $(a-x)$	$k=\frac{1}{t-2.5}\times\ln\frac{a}{a-x}$	Oxidation time (hours)	Corrected iodine value $(a-x)$	$k=\frac{1}{t-3.8}\times\ln\frac{a}{a-x}$	Oxidation time (hours)	Corrected iodine value $(a-x)$	$k=\frac{1}{t-12.0}\times\ln\frac{a}{a-x}$
0	85.83		0	85.83		0	85.83	
3.1	85 25	0.0113	3.0	85.78		7.83	85.76	
6.0	82.20	0.0123	5.0	84 59	0.0121	17.50	81.45	0.0095
9.0	79.95	0.0109	6.0	83.78	0.0110	20.58	79.46	0.0090
11.2	77.41	0.0119	11.2	79.85	0.0098	23.33	77.14	0.0094
15.0	74.43	0.0114	15.0	76.12	0.0107			mean 0.0093
		mean 0.0116			mean 0.0111			

(1) A commercial castor oil having an iodine value of 85.8 and an acid value of 2.30 has been used without special purification.

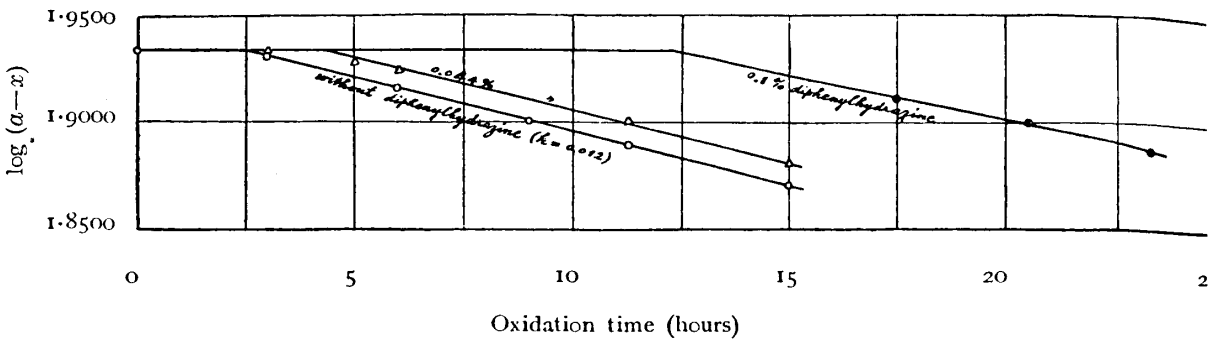


Fig. 5.

accordingly the falls in iodine value which have been found to proceed unimolecularly are represented by straight lines. Unsymmetrical diphenylhydrazine also inhibits the oxidation of castor oil, prolonging its incubation period of oxidation in a remarkable degree.

In order to examine whether or not the decomposition products of olive oil which ditill over in the condensor tube *B* in the course of oxidation may contain unsaturated substances, the determination of iodine value of such products has been carried out. The result of this determination has shown that no iodine is absorbed by the substance.

II. Effect of the Velocity of Oxygen Current.

In order to know how the rate at which oxygen is bubbled through a sample of oil affects the velocity of oxidation, two 90-grams samples have separately been oxidized for 15 hours at the respective rates of 10 liters per hour and 8 liters per hour, and the oxidized oils thus formed have been examined to compare their properties. It is seen from Table 5

Table 5.

Velocity of oxygen current (litre/hour)	Weight increase (gr.)	Amount of distilled products (gr.)	Acid value		Iodine value
			Acid in oil	Acid in distillate	
10	0·24	0·45	6·02	2·56	66·5
8	0·25	0·42	6·13	2·46	66·8

that these oils have almost no difference in properties such as iodine value, acid value and weight, giving nearly equal amounts of distilled decomposition products. This result comfirms that a small fluctuation in the velocity of oxygen current has practically no influence on the rate of oxidation.

III. Effect of Temperature.

The rate of oxidation of Olive Oil A has been determined at the temperatures of 120°, 100° and 80°C. The results are shown in Tables 6–8 and Fig. 6. The oxidation at any one of these temperatures causes iodine value of oil to decrease in an unimolecular way after corre-

TABLE 6.

Oxidation of olive oil without antioxydant at 100°C

Oxidation time (t) (hours)	Weight increase (gr.)	Corrected iodine value ($a-x$)	$k=\frac{1}{t-4.0}\ln\frac{a}{a-x}$
0	0	86.6	
7.5	1.25	78.5	0.0282
10.0	1.70	72.2	0.0304
15.0	2.45	61.5	0.0312
17.0	2.73	57.8	0.0311
25.0	3.76	51.8	0.0302
30.0	4.10	44.8	0.0301
			mean 0.0302

TABLE 7.

Oxidation of olive oil without antioxydant at 120°C

Oxidation time (t) (hours)	Weight increase (gr.)	Corrected iodine value ($a-x$)	$k=\frac{1}{t-0.65}\ln\frac{a}{a-x}$
0	0	86.40	
1.04	0.15	84.84	0.0453
2.40	0.61	80.03	0.0435
5.00	1.39	71.02	0.0450
10.38	2.20	56.69	0.0433
			mean 0.0443

TABLE 8.

Oxidation of olive oil without antioxydant at 80°C

Oxidation time (t) (hours)	Weight increase (gr.)	Corrected iodine value ($a-x$)	$k=\frac{1}{t-21.0}\ln\frac{a}{a-x}$
0	0	86.40	
5.0	0	86 38	
20.0	0	86.41	
22.5	0.42	83.72	0.0210
25.1	1.08	79.32	0.0208
30.0	1.93	71.70	0.0207
			mean 0.0208

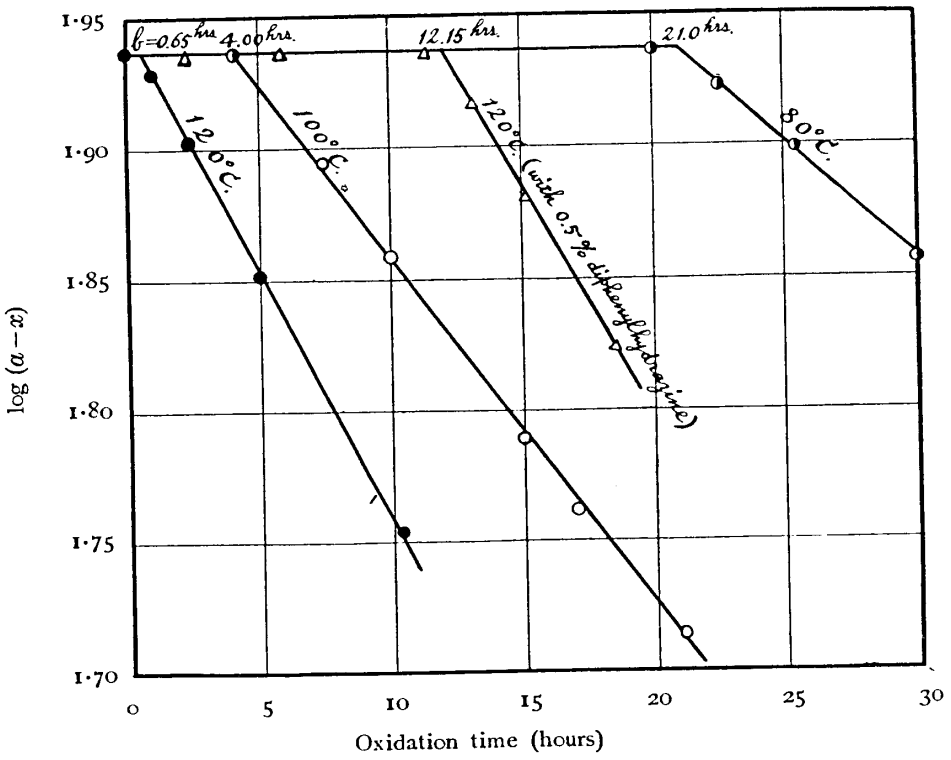


Fig. 6.

sponding incubation period as illustrated by the straight lines in Fig. 6. The incubation period decreases and the rate of oxidation increases remarkably with elevation of temperature. The periods of incubation for the oxidation temperatures of 80°, 100°, and 120°C are respectively 21.0 hours, 4.0 hours and 0.65 hour. From Fig. 7 it is seen that a

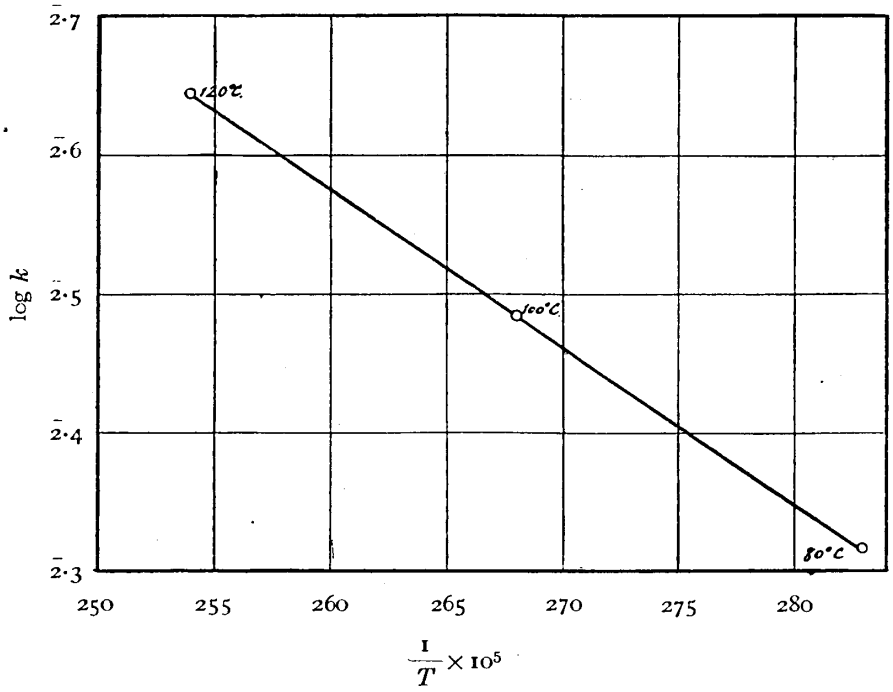


Fig. 7.

linear relation exists between the logarithm of velocity coefficient and the reciprocal of oxidation temperature expressed in the absolute unit. This relation can be expressed by the formula of Arrehnius,

$$\frac{dlnk}{dt}=\frac{Q}{RT^2} \quad \text{or} \quad lnk=C-\frac{Q}{RT}.$$

The values of C and Q in this formula have been decided from the experimental data to be: $C=3.67$, $\frac{Q}{R}=2670$ calories.

IV. Effect of Antioxydants.

Owing to the exhaustive studies on auto-oxidation reactions carried out by Moureu and his co-workers,[1] it has been proved that a large number of substances belonging to hydrazines, amines, phenols and

(1) loc. cit.; Bull. Soc. Chem., **43** (1928), 942.

others act as inhibitors in auto-oxidation reactions. The author has studied the inhibiting effects of diphenylhydrazine and α-naphtylamine in the oxidation of olive oil.

(*a*) *Effect of unsymmetrical diphenylhydrazine.*

In the part of preliminary experiment, it has already been stated how 0.1% unsym. diphenylhydrazine affects the oxidation of Olive Oil A. The author has made a further study on the effect of the antioxydant, oxidizing the samples of Olive Oil B to which were added various amounts of the antioxydant. The result is given in Table 9. From Fig. 8 it is seen that the iodine value of the oil remains seemingly

TABLE 9.

Effect of unsym. diphenylhydrazine

Amount of diphenylhydrazine (%)	Oxidation time (t) (hours)	Corrected iodine value ($a-x$)	$k=\frac{1}{t-b}\ln\frac{a}{a-x}$
			(b=4.85 hours)
	0	86.20	
	5.5	84.68	0.0256
0	10.5	75.19	0.0242
	15.0	66.47	0.0256 mean
	20.0	58.12	0.0260 =0.0254
	25.0	51.73	0.0253
	28.5	46.82	0.0258
			(b=7.06 hours)
	0	86.20	
	7.50	85.25	0.0252
0 005	12.50	75.75	0.0238
	17.00	67.56	0.0245 mean
	22.00	59.11	0.0252 =0.0247
	27.00	52.82	0 0246
	30.50	48.05	0 0250
			(b=14.0 hours)
	0	86.20	
	15.00	84 07	0.0250
0.025	20 00	74.60	0.0241
	24.00	66.92	0 0253 mean
	28.00	60.03	0.0258 =0.0250
	32.10	55.25	0.0245
	36.10	49.48	0.0250

TABLE 9.—(*Continued*).

Amount of diphenyl-hydrazine (%)	Oxidation time (t) (hours)	Corrected iodine value ($a-x$)	$k=\frac{1}{t-b}\ln\frac{a}{a-x}$
			($b=18.0$ hours)
0.050	0	86.20	
	18.57	85.17	0.0241
	20.57	82.14?	?
	24.57	73.49	0.0245
	28.57	66.03	0.0253
	33.57	57.95	0.0256
	39.57	48.94	0.0263
			mean =0.0252
			($b=22.4$ hours)
0.075	0	86.20	
	23.00	84.95	0.0243
	28.00	76.43	0.0215
	32.00	70.05	0.0216
	36.00	62.99	0.0233
	40.17	58.32	0.0220
	44.17	52.55	0.0228
			mean =0.0226
			($b=28.0$ hours)
0.100	0	86.20	
	28.95	84.27	0.0238
	32.60	78.16	0.0213
	36.60	71.22	0.0222
	40.60	63.70	0.0240
	45.60	56.64	0.0238
	50.60	50.39	0.0237
			mean =0.0231

unchanged during a period corresponding to the added amount of the antioxydant, and that the oxidation (the decrease in iodine value), when once started, always proceeds unimolecularly with almost the same rate whether the reaction starts soon or has been delayed for a certain length of time by the antioxydant. The value of velocity coefficient of such an unimolecular reaction can be calculated by the Equation (I). The values of velocity coefficient calculated for different oxidation times are always in good agreement with one another as shown in Table 9. The fact that all the straight lines in Fig. 8 run almost parallel, the left-most one showing the case of the oil containing no antioxydant, means that the velocity coefficient k is practically independent of the amount of the antioxydant. The length of incubation period depends remarkably upon the amount of unsym. diphenylhydrazine and the former increases almost

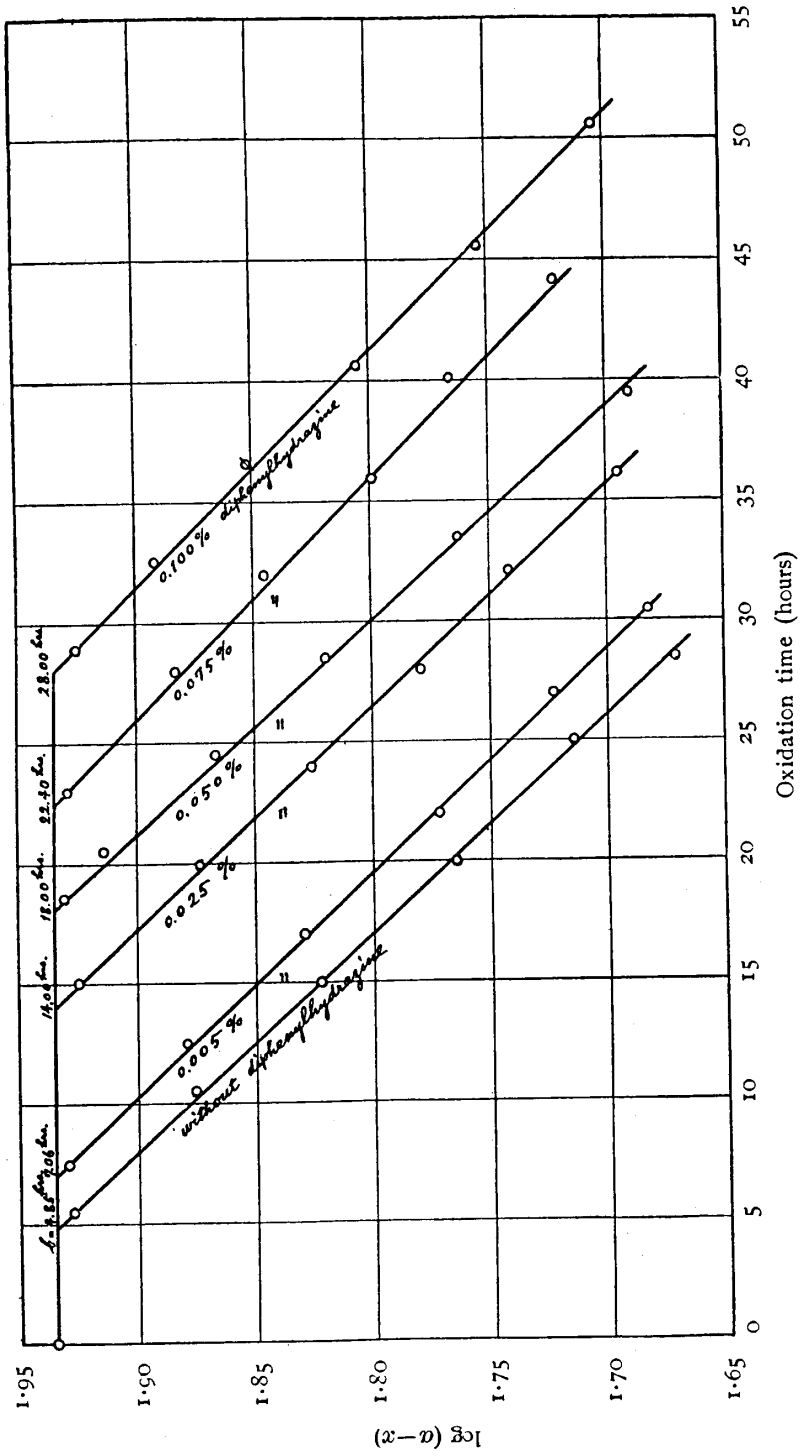


Fig. 8.

in direct proportion to the latter. Table 10 and Fig. 9 illustrate these relations. From the fact that the reaction, when once started, always proceeds at the same rate whether the oxidation starts comparatively

TABLE 10.

Amount of unsym. disphenylhydrazine (%)	$k=\frac{1}{t-b}\ln\frac{a}{a-x}$	Incubation period (hours)
0·005	0·025	7·06
0·025	0·025	14·00
0·050	0·025	18·00
0·075	0·023	22·40
0·100	0·023	28·00

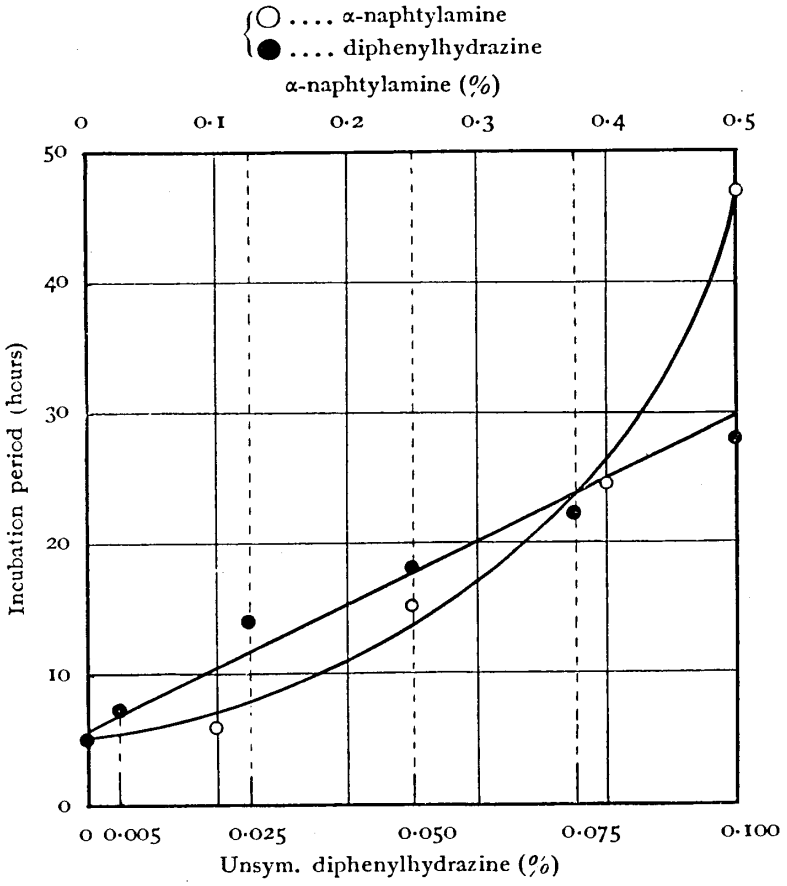
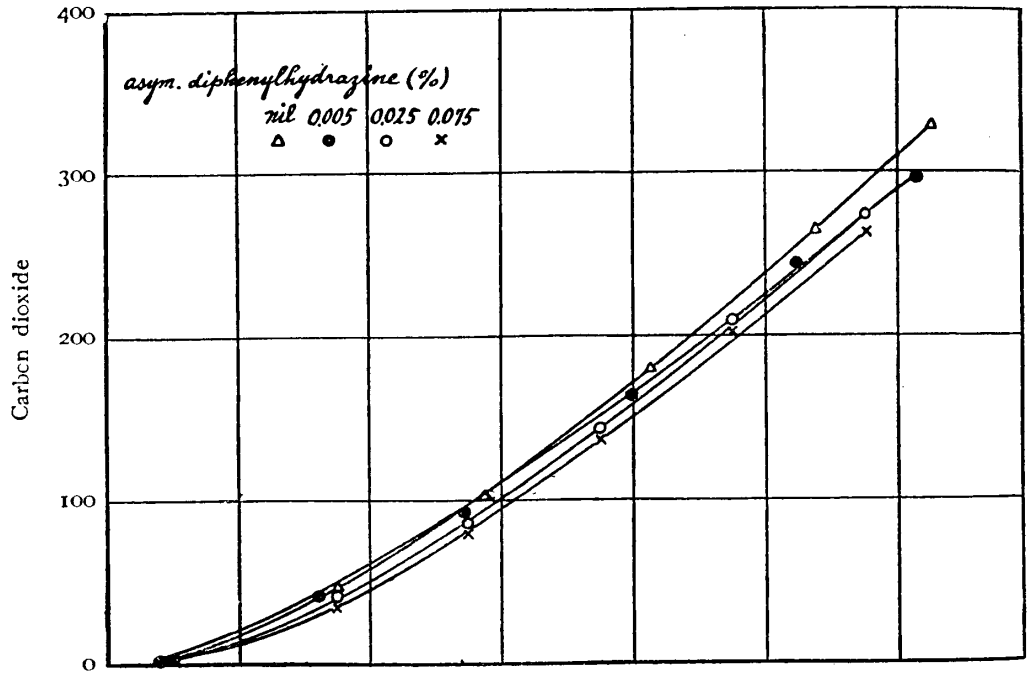


Fig. 9.

soon as in the case for the oil containing no antioxydant or has been delayed for a certain length of time by the antioxydant, we arrive at the conception that the antioxydant must have been lost completely from the oil before the oxidation apparently starts and even a very small amount of the antioxydant can inhibit the oxidation very efficiently as long as it remains in the oil. The antioxydant may be removed from the oil by evaporation or may be destroyed by oxidation, losing the inhibitory power.(1)



Diphenyl-								
hydrazine 0% ...	3·5	7·5	11·5	15·5	19·5	23·5	27·5	31·5
„ 0·005% ...	6	10	14	18	22	26	30	34
„ 0·025% ...	13	17	21	25	29	33	37	41
„ 0·075% ...	21	25	29	33	37	41	45	49

Oxidation time (hours)

Fig. 10.

(1) The amount of antioxydant contained in the oil decreases with time of oxidation owing to various causes. The substance may be (1) oxidized and thus lose its inhibitory power; (2) evaporated directly without being subject to oxidation; (3) destroyed by the action of heat alone; (4) partly destroyed by oxidation, partly removed by evaporation—i.e., a combination of (1) and (2). As has been shown by Halsam and Frölich (Jour. Ind. Eng. Chem. 19, 292, 1927), unsym. diphenylhydrazine is a typical example of an antioxydant that is partly destroyed by oxidation and partly removed by evaporation.

Fig. 10 shows how equally the olive oils containing various amounts of unsym. diphenylhydrazine evolve carbon dioxide after their respective periods of incubation when the oils are oxidized at 100°C. In this figure the ordinate denotes the number of c.c. of $\frac{N}{10}$ alkali solution needed to neutralize the evolved carbon dioxide.

Similarly at a temperature of 120°C, unsym. diphenylhydrazine can inhibit the oxidation, delaying it in a remarkable degree, and the oxidation, when once started, proceeds unimolecularly. The result given in Table 11 and Fig. 6 shows the effect of 0.5% unsym. diphenylhydrazine at this temperature.

TABLE 11.

Effect of 0.5% unsym. diphenylhydrazine at 120°C. (Olive oil A)

Oxidation time (t) (hours)	Corrected iodine value ($a-x$)	$k=\frac{1}{t-12.15}\ln\frac{a}{a-x}$
0	86.20	
2.37	86.21	
5.90	86.25	
11.40	86.12	
13.15	82.68	0.0416
15.15	75.99	0.0420
18.48	66.49	0.0410
		mean 0.0415

(*b*) *Effect of α-naphtylamine.*

The results of the investigation on the effects of various amounts of α-naphtylamine on the oxidation of Olive Oil B are given in Table 12. Fig. 11 shows the results for the two cases in which the effects of 0.25% and 0.40% α-naphtylamine have been studied. From this figure it is seen that α-naphtylamine does not inhibit the oxidation so completely for a certain length of time as diphenylhydrazine does: in the other words, the period of incubation is not altered by the antioxydant, although the initial rate of the oxidation is exceedingly lowered by it.

TABLE 12.

Effect of α-naphtylamine

0·10% α-naphtylamine			0·25% α-naphtylamine			
Oxidation time (t) (hours)	Corrected iodine value ($a-x$)	$k=\frac{1}{t-5\cdot85}\ln\frac{a}{a-x}$	Oxidation time (t) (hours)	Corrected iodine value ($a-x$)	$k=\frac{1}{t-15\cdot2}\ln\frac{a}{a\ \ x}$	Caluculated iodine value
			0			
0	86.20		7·00	85·21		85·88
6·50	84·43		11·80	84·83		84·84
9·00	79·85	0·0243	14·67	83·68		83·84
11·67	75·00	0·0239	16·67	82·39		82·62
14·17	69·90	0·0252	18·17	80·26	0·0240	80·77
18·85	61.49	0·0260	21·17	73·82	0·0259	74·22*
23·38	54·17	0·0264	25·67	65·65	0·0259	66·33*
28·93	46·81	0·0265	30·17	59·10	0·0252	59·25*
		mean 0·0254			mean 0·0253	

0·40% α-naphtylamine				0·50% α-naphtylamine		
Oxidation time (t) (hours)	Corrected iodine value ($a-x$)	$k=\frac{1}{t-24\cdot5}\ln\frac{a}{a-x}$	Caluculated iodine value	Oxidation time (t) (hours)	Corrected iodine value ($a-x$)	$k=\frac{1}{t-47}\ln\frac{a}{a-x}$
0				0		
21·00	84·44		83·81	41·00	84·90	
23·87	83·40		82·80	45·00	83·79	
25·87	82·21		81·62	50·00	80·39	
27·37	80·45	0·0240	79·79	55·00	71·33	0·0232
30·37	74·76	0·0243	74·51*	59·50	63·84	0·0237
34·87	65·93	0·0259	66·77*	65·00	57·64	0·0240
39·37	60·15	0·0242	59·77*			0·0224
		mean 0·0246				mean 0·0232

The oxidation of the oil containing any amount of α-naphtylamine always starts just after the same length of time as the incubation period for the oil without antioxydant and proceeds initially with a very small rate. The rate, however, increases gradually with time of oxidation till a point

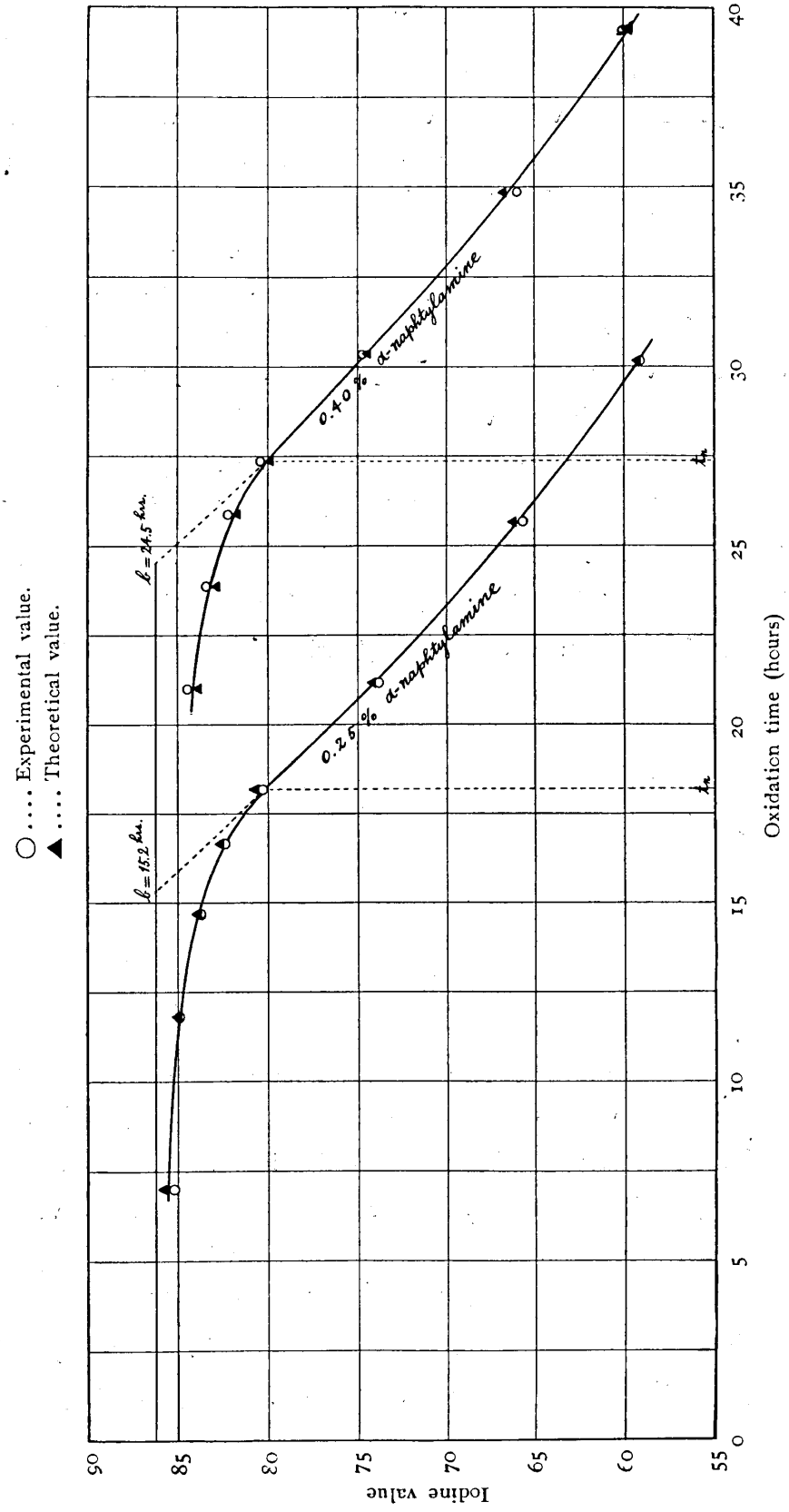


Fig. 11.

of time t_n after which the reaction is found to proceed completely unimolecularly. All the values of velocity coefficient which have been calculated by Equation (I) for different times of oxidation greater than t_n are found always consistent as shown in Table 12, and the mean value of them is found almost equal to the velocity coefficient of oxidation of the oil containing no antioxydant. The values of b which must be introduced in these calculations can be easily determined. For, as the fall of iodine value after t_n is always expressed by a straight line when the logarithm of iodine value is plotted against time of oxidation, so the intersection between the prolongation of the straight line and the horizontal line which represents the initial iodine value of the oil decides the required value of b. Of course b in this case does not mean a true period of incubation. The values of b thus decided for the oils to which were added various amounts of α-naphtylamine are shown in Table 13

TABLE 13.

Amount of α-naphtylamine %	$k=\frac{1}{t-b}\ln\frac{a}{a-x}$	b (hours)
0·10	0·025	5·85
0·25	0·025	15·20
0·40	0·025	24·50
0·50	0·023	47·00

and also in the expression of k given in Table 12. Fig. 9 illustrates the relation between the value of b and the amount of α-naphtylamine.

From the fact that the unimolecular oxidation which the oil containing α-naphtylamine undergoes after t_n has almost the same velocity coefficient as that of the oxidation of the oil without antioxydant, we can conceive that t_n must be the time at which α-naphtylamine has just been lost completely from the oil. α-naphtylamine is not only partly removed by evaporation, partly destroyed by

oxidation[1] but also lessened in activity as a result of reactions with the decomposition products of oil due to oxidation such as some organic acids.

The length of time from the starting point of the oxidation, namely from the end point of the true incubation period to the point of time t_n depends, as might be anticipated, upon the amount of the antioxydant. (This length of time will be denoted simply by t_n hereafter in this paper. $t_n=13.17$ hours for 0.25% α-naphtylamine; $t_n=22.37$ hours for 0.40% α-naphtylamine).

The inhibitory power of unsym. diphenylhydrazine is much superior to that of α-naphtylamine. This is evidently seen from the experimental fact that the incubation period for the oil containing 0.1% unsym. diphenylhydrazine is 28 hours while the value of b for the oil containing 0.1% α-naphtylamine is less than 6 hours.

Theoretical.

In the part of introduction the author has already stated that among all the theories concerning the mechanism of inhibition in auto-oxidation reactions, Christiansen's theory of chain mechanism is most favorable at present time to account for all the experimental facts which have ever been known in connection with the phenomenon of inhibition. Indeed not only the mechanism of the inhibitory action of α-naphtylamine and unsym. diphenylhydrazine in the oxidation of olive oil can be explained by the theory of chain mechanism, but also it is ascertained that the rate of such an inhibited reaction can be exactly expressed by the equation which has been established on the basis of Christiansen's theory.

(1) Prolonged heating in nitrogen atmosphere of an oil sample containing α-naphtylamine at 100°C before oxidation has made no change in the susceptibility of the oil to oxidation, thus indicating that α-naphtylamine contained in the oil is not destroyed by heat alone. Experimental runs in which nitrogen has been substituted for oxygen and later again superseded by oxygen has made possible the conclusion that α-naphtylamine is partly removed by evaporation, partly destroyed by oxidation and partly lessed in activity as a result of some reaction with the decomposition products of oil due to oxidation.

The author assumes that the oxidation of auto-oxidable substances such as unsaturated fatty oils occurs by a chain mechanism as represented by the following equations:—

(i) $A+(O_2+\epsilon) \longrightarrow \underline{AO_2'}$

(ii) $\underline{AO_2'}+\underline{\underline{A}}+\underline{\underline{O_2}} \longrightarrow \underline{AO_2}+\underline{\underline{AO_2'}}$

A: auto-oxidable substance.
O_2: oxygen molecule.

AO_2'[1] is an unstable, activated peroxide of the auto-oxidable substance A and as compared with AO_2 contains not only the energy of activation (represented by ϵ), but also the ordinary heat of reaction. Among all the molecules of oxygen introduced into the substance A, only those whose energy exceeds the activation energy ϵ can react with the molecules of A to form unstable activated peroxides in the manner of the equation (i). Now these very active peroxides have sufficient energy to activate molecules of the reactants at the first encounter, and when they react, the resultants in their turn are again able to act as activators and so on. Consequently, it is possible that the occurrence of one elementary reaction will give rise to a whole series of such reactions. In order to explain the phenomena of inhibition, it is assumed that the inhibitors are the substances that have the power of breaking the reaction chains thus set up by taking up the energy from the active peroxides or reacting with them in some way or another. The equation for the rate of such an inhibited chain reaction can be established theoretically, as has been done by Christiansen,[2] in the following manner.

Let the number of reactions started per unit time be N[3] and the number of links in each chain, namely the number of the molecules of

(1) This may be considered as one kind of the so-called "unatable primary peroxide" or "dative peroxide."

(2) Trans. Faraday Soc. 24 (1928), 596.

(3) Among all the molecules of oxygen introduced into the substance A, only those whose energy exceeds ε can react with molecules of A. Therefore, if the rate of formation of such activated molecules is assumed to be much slower than that of the primary reaction represented by the equation (i), the number N will be a constant independent of the concentration of the substance A and time of oxidation when the velocity of oxygen current through the substance A is held constant, because the number depends only upon the amount of activated oxygen. The author assumes that N is relatively a very small constant in the case of oxidation of olive oil.

reactant A which react in each chain be L, then the velocity of the reaction must be

$$v=N\cdot L \qquad \text{(II)}$$

if the chains do not interfere with each other. The latter assumption will be true, when the chains are not excessively long and we shall assume it as a first approximation. Now let us assume that the probability that one elementary reaction shall induce another is P. Then obviously the number of links will be

$$L=1+P+P^2+\cdots\cdots$$

which sum is equal to $1/(1-P)$ if $P<1$.

The active resultant AO_2' which is formed by one elementary reaction activates molecules of the reactants or it becomes de-activated. This de-activation may occur either independently on the inhibitor or by some reaction (transfer of energy or chemical reaction) with it. We may classify these two probabilities as "spontaneous" and "induced" de-activation. Consequently

$$P=\frac{k_r c_r}{k_r c_r+k_i c_i+k_s}$$

where index r refers to reaction, i and s to induced and spontaneous de-activation respectively. We thus get

$$v=NL=N\frac{k_r c_r+k_i c_i+k_s}{k_i c_i+k_s} \qquad \text{(III)}$$

When the chain is very long (N assumed to be very small), the expression reduces to

$$v=N\frac{k_r c_r}{k_i c_i+k_s} \qquad \text{(IV)}$$

If the inhibitor is not present ($c_i=0$), then the equation becomes

$$v=N\frac{k_r c_r}{k_s}=k\cdot c_r \qquad \text{(V)}$$

where $k=\frac{k_r N}{k_s}$.

Since we have already found that the rate of oxidation of pure olive oil can be expressed by the equation of unimolecular reaction [Equation (I)], the above equation (V) must be equivalent to Equation (I) and accordingly, N must be considered to be a constant independent of time of oxidation. The consideration that N is independent on time of oxidation can be justifield when we assume that the rate of activation of oxygen molecules is much slower than that of the primary reaction (i) (see the foot-note on the preceding page).

Nextly, in order to consider the velocity of oxidation of olive oil containing an inhibitor, let the initial iodine value of the oil or the number of unsaturated linkages contained in unit amount of the oil be a, and the decrease of iodine value or the decrease of unsaturated linkages in time t be x, then Equation (IV) is transformed into the following form.

$$v=\frac{dx}{dt}=\frac{N\cdot k_r}{k_i c_i+k_s}(a-x)$$

$$=\frac{\frac{N\cdot k_r}{k_s}}{1+\frac{k_i}{k_s}c_i}(a-x)=\frac{k}{1+k'c_i}(a-x) \qquad \text{(VI)}$$

where $k=\frac{N\cdot k_r}{k_s}$, $k'=\frac{k_i}{k_s}$

The amount of antioxydant contained in the oil (c_i) decreases with time of oxidation. As has already been stated, α-naphtylamine which was added to the oil as an inhibitor must have just been lost completely from the oil at the time t_n, since the velocity coefficient of the unimolecular reaction which the oil containing α-naphtylamine undergoes after t_n is found equal to that of the oxidation of the oil without inhibitor. Furthermore, the decrease of α-naphtylamine with time of oxidation is caused not only by oxidation and evaporation, but also by some reaction

with the decomposition products of oil resulting from oxidation: the rate of the decrease of α-naphtylamine due to this latter cause increases with time of oxidation, while the rate of decrease due to the other causes probably decreases with time of oxidation. It is, therefore, simply assumed that α-naphtylamine added to the oil is lost approximately in proportion to time of oxidation and vanishes completely at the time t_n.

Thus $$c_i = k''(t_n - t)$$

where t_n represents the point of time at which α-naphtylamine has just completely been removed.

Equation (VI) therefore becomes

$$\frac{dx}{dt} = \frac{k}{1 + k'''(t_n - t)} \cdot (a - x) \qquad \text{(VII)}$$

where $k''' = k' \cdot k''$.

Integrating the equation, we have

$$\log \frac{a}{a-x} = \frac{k}{k'''} \log \frac{1 + k'''t_n}{1 + k'''(t_n - t)} . \qquad \text{(VIII)}$$

In the case of the oxidation of olive oil at 100°C, the value of k, which is equal to $\frac{Nk_r}{k_s}$, representing the velocity coefficient of the unimolecular oxidation which occurs in the absence of antioxydant (see Equation (V)), has been found equal to 0.025, and the initial iodine value a is equal to 86.20.[1]

Therefore

$$\log \frac{86.20}{86.20 - x} = \frac{0.025}{k'''} \log \frac{1 + k'''t_n}{1 + k'''(t_n - t)} . \qquad \text{(VIII)}'$$

(1) This is the inital iodine value of the olive oil containing no antioxydant. The initial iodine value of the oil containing α-naphtylamine is slightly different from 86.20 since the antioxydant reacts with iodine and has its own iodine value, but when the amount of the antioxydant added to the oil is very small, this difference of iodine value can be neglected. Even when the difference is not neglegible, we have almost no objection to put a=86.20 in Equation (VIII), for the sensible fall in iodine value of the olive oil itself due to oxidation starts only after the greater part of the antioxydant added has been removed by evaporation and the above-said difference of iodine value has become neglegible.

Here it must be noted that t and t_n in this equation are times measured from the point at which, if the oil contained no antioxydant, the oxidation would have to start, *i.e.*, times measured from the end point of the incubation period for the oil containing no antioxydant, and are not times measured from the point at which the bubbling of oxygen through the oil has been started. The former times are about 5 hours less than the latter ones.

The value of t_n is easily decided, since the point of time at which the reaction just begin to take an unimolecular course can be graphically determined by means of the oxidation curve such as Fig. 11. (The diagram in which the logarithm of iodine value is plotted against time of oxidation is more convenient for this object, because the unimolecular course is, in this case, represented by a straight line). In this way we obtain

$t_n=13\cdot17$ hours for 0·25% α-naphtylamine,
$t_n=22\cdot37$ hours for 0·40% α-naphtylamine.

Lastly, the value of k''' must be decided. It has been determined in the following manner. As t_n is known and the iodine value at t_n can be calculated from Equation (I), the left-hand side of Equation (VIII)′ is evaluated if the iodine value thus calculated is introduced in the equation. Then the value of k''' by whose introduction the right-hand side of Equation (VIII)′ must become equal to that value of the left-hand side can be easily determined by a graphical method. In this way the value of k''' has been decided to be 0·90 in the case of 0·25% α-naphtylamine and 1·15 in the case of 0·40% α-naphtylamine, the mean of the two values being 1·03.

Equation (VIII)′ thus becomes

$$\log\frac{86\cdot20}{86\cdot20-x}=\frac{0\cdot025}{1\cdot03}\log\frac{1+1\cdot03\times t_n}{1+1\cdot03(t_n-t)} \qquad \text{(IX)}$$

where $t_n=13\cdot17$ hours for 0·25% α-naphtylamine,
$t_n=22\cdot37$ hours for 0·40% α-naphtylamine.

By means of this equation the iodine value at any time of oxidation ($t<t_n$) can be calculated. The calculated iodine values, as shown in Table 12 and Fig. 11 are in good agreement with the experimental values. The values marked with * in the table are the values calculated by Equation (I). The results of experiments for unsym. diphenylhydrazine whose inhibitory power is much superior to that of α-naphtylamine can also be explained, if we assume that unsym. diphenylhydrazine has a very strong power to break the chain of reaction, *i.e.*, that the specific inhibitory power represented by k_i in Equation (III) is enormously great. If k_i is so sufficiently great that the relation, $k_ic_i+k_s \gg k_rc_r$ holds even for a very small value of c_i, Equation (III) reduces to

$$v = N.$$

If N is very small, the velocity of oxidation will possibly be so extremely slow that the oil will remain seemingly unchanged untill the antioxydant will have been almost completely removed by evaporation and oxidation. This conclusion is in agreement with the result of actual experiment.

Now it remains to explain why the phenomenon of an incubation period occurs even when oil is oxidized without an antioxydant. One possible explanation of it is to assume that oil contains originally some natural antioxydant whose inhibitory property is similar to that of diphenylhydrazine. It has, however, not yet been decided whether the assumption may be true or not. The author who is now studying on the oxidation of pure triolein and on the action of accelerators in the oxidation of olive oil believes that the results of these studies will give some decicive answer to the question. Further, the author are now carrying out the investigations on the action of other inhibitors such as diphenylamine, hydroquinone and β-naphtol in the oxidation of olive oil, the result of which will shortly be reported.

Summary.

(1) For the determination of the rate of oxidation of unsaturated fatty oils, it is most preferable to measure the decrease in iodine value resulting from the oxidation.

(2) The oxidation of olive oil and castor oil does not practically start at once at 100°C, *i.e.*, oil remains apparently unchanged during a period of incubation. When the oxidation has once started after the incubation period, the reaction, however, proceeds unimolecularly with an appreciable rate. The decrease of iodine value resulting from the oxidation can be expressed by the equation

$$ln\frac{a}{a-x}=k(t-b)\,.$$

(3) The rate of oxidation increases with elevation of temperature and the relation between the velocity coefficient and temperature can be expressed by the formula of Arrehnius.

(4) Diphenylhydrazine (unsymmetrical) has been found to act as a strong inhibitor of the oxidation, prolonging the incubation period in a remakable degree. The length of the period thus prolonged depends directly upon the amount of diphenylhydrazine added. After the incubation period the oxidation proceeds unimolecularly as for the oil containing no antioxydant.

(5) α-naphtylamine does not inhibit the oxidation so completely for a certain length of time as diphenylhydrazine does; in the other words, the incubation period apparently is not altered by the antioxydant, although the initial rate of the oxidation is exceedingly lowered by it. The oxidation of the olive oil containing a small amount of α-naphtylamine starts initially with a very small but sensible rate just after the same length of time as the period of incubation for the oil containing no antioxydant. The rate, however, increases slowly as the antioxydant is gradually removed by evaporation and destroyed by oxidation. After the antioxydant has been completely lost, the reaction now proceeds

unimolecularly as for the oil containing no antioxydant, and the value of velocity coefficient of the unimolecular reaction is almost equal to the value obtained for the pure olive oil.

(6) The mechanism of the inhibitory action of α-naphtylamine and diphenylhydrazine can be explained fairly on the assumtion that the oxidation of fatty oils occur by the chain mechanism of Christiansen. It has been shown that the actual rate of the inhibited oxidation can be expressed exactly by the equation which has been established on the basis of the theory of chain mechanism.

In conclusion the author wishes to express his cordial thanks to Prof. M. Katayama for his valuable advices during the work and also to Mr. Gengo Nara for his earnest assistance.

March, 1930.