The Oxidation of Methane.

By Haruki FUJIMOTO.

(Received January 20, 1938.)

The isolation of the oxygenated compound formed by the direct combination of methane with oxygen is very important not only from the viewpoint of the theory of hydrocarbon combustion but also for the utilization of natural gas.

H. L. Callendar(1) has conducted an experiment by passing hexane-air mixture through a heated tube, and identified a large number of products formed, such as aldehydes, acids, unsaturated hydrocarbons, tars and carbon in addition to CO_2 and H_2O, but no trace of hydroxy compound could be isolated. It woud, therefore, appear more likely that the combustion of the hydrocarbon in air begins with the formation of peroxides by the direct incorporation of the oxygen molecule in the hydrocarbon molecule.

Although according to the view of W. A. Bone, the hydroxylation theory is correct, all efforts to isolate the corresponding alcohol from the initial products of the slow interaction of paraffins with oxygen have been unsuccessful, apparently because under ordinary conditions the further oxidation of such an alcohol to the dihydroxy stage occurs too rapidly. And recently S. G. Hill and W. A. Bone(2) have reinvestigated the slow combustion of ethane showing that the initial product is not a peroxide but either alcohol or some less oxygenated body. Also D. M. Newitt and A. E. Haffner(3) have succeeded in obtaining substantial quantities of methyl alcohol by the direct interaction of oxygen and methane at a temperature of 340° and pressures of about 100 atmospheres. Thus, it was confirmed that slow oxidation of methane proceeds throughout in accordance with the hydroxylation theory.

Although there is considerable agreement that the main course of the oxidation of hydrocarbon proceeds in accordance with the hydroxylation theory, there has been some controversy as to whether the initial product is a hydroxylated molecule or peroxide. P. Mondain-Monval and B. Quanquin(4) have reported the very interesting fact that an air mixture

---

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

(2) *Proc. Roy. Soc.* (London), A, **129** (1930), 434.

(3) *Ibid.*, A, **134** (1932), 591.

(4) *Compt. rend.*, **191** (1930), 299.

of hydrocarbon such as pentane or hexane, by passing through a tube heated to 300°C., was converted into aldehyde, CO_2 and an oily substance from which a peculiar substance was isolated which is very similar in chemical nature to peroxide CH_3OOH prepared by Rieche and Hitz by the interaction of H_2O_2 and dimethylsulphate in presence of potash.

In the investigations made heretofore, heat energy was applied for the activation of reacting substances, and in application of heat energy might give rise to some confusion in the theoretical consideration of hydrocarbon oxidation.

The present author, therefore, has studied the oxidation of methane by oxygen under influence of silent discharge, since the action of electric discharge can be controlled so as to obtain a definite initial compound in a pure state.

I. **Methane.** The sample used in this experiment is a natural gas from the Sinbara coal district, which shows after being mixed with oxygen the following compositions.

CH_4	H_2	C_nH_m	CO_2	CO	N_2	O_2
63.8	0.0	1.2	0.0	0.0	0.0	35.0

The gas was passed between two electrodes 4 mm. apart in two ozonizer discharges of 90 mm. diameter and 500 mm. long shown in Fig. 1.

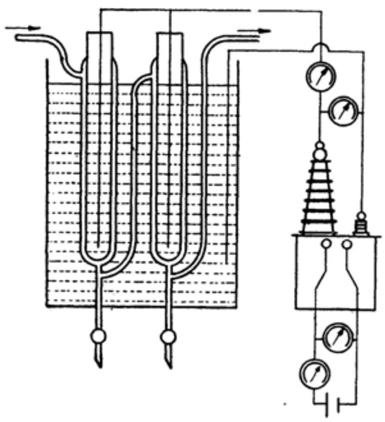


Fig. 1.

The rate of gas flow was about 30 litres per hour, and a current of 60 milliamperes at about 13000 volts was passed between the electrodes.

Methane and oxygen react violently with violent brushy sparks, and from 584 litres (N.T.P.) of the mixed gas there were formed 240 g. of liquid and 412 litres of gaseous substances. From the composition of the gases produced, as shown below, it was judged that the reaction took place in the tube.

CO_2	C_nH_m	O_2	H_2	CO	CH_4	N_2
3.4	0.8	2.06	3.9	7.4	61.5	2.5

120 l. (N.T.P.) CH_4 and 120 l. O_2 are transformed into 9.9 l. CO_2, 16.2 l. CO, 30.4 l. H_2 and 240 g. of a liquid; in other words, when methane was oxidised 21.7% of the product was carbon dioxide and carbon monoxide, and the remainder (78.3%) was a liquid. The liquid is colourless,

d = 1.1, n = 1.38, and was assumed to be a peroxide; it is unstable when heated, decomposes gradually on standing at ordinary temperature, has a remarkable oxidising effect on acidic potassium iodide solution and hydroquinone, and contains about 9% of active oxygen. When 240 g. of the liquid was heated on the water bath until no more gas evolved, 20 litres of a gas and 235 g. of liquid residue were formed. This gas consists of 96% H_2, 0.6% CO_2 and 1.0% CH_4. The residual liquid was fractionated and the density of each fraction was determined; the results are shown in Fig. 2. The fraction with b.p. 28–40°G. is supposed to be mainly methyl formate from its odour, boiling point and density, and its content was estimated to be 75% from methoxy value by Hewett's method and its ester value. The fraction with b.p. 60–70°C. is supposed to be methyl alcohol from its density. The fraction 98–107°C. is composed of 50% of formic acid, 7% of formaldehyde and the remainder is methyl alcohol and water. From the above results, the composition of the decomposition product is represented in mol percent as follows:

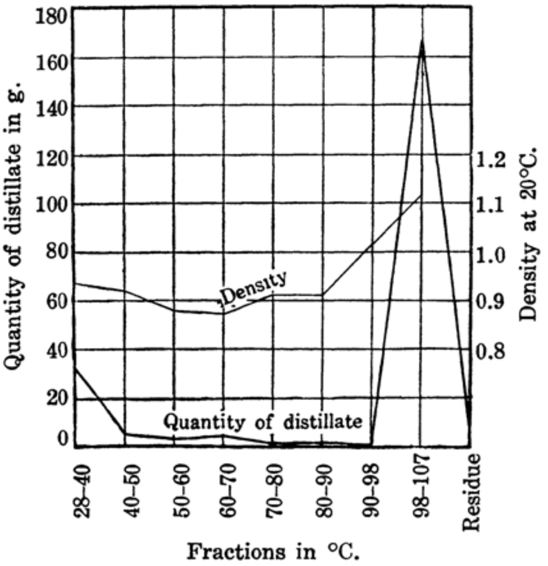


Fig. 2.

CO_2	CO	H_2	HCHO	HCOOH	$HCOOCH_3$	H_2O
8.4	13.5	41.3	7.3	33.6	14.2	74.0

In order to isolate this peroxide, the reaction product from methane and oxygen was neutralized with $MgCO_3$ under cooling with ice water and then extracted with ether. On evaporating the solvent under reduced pressure, there remained a viscous, oily residue; when cooled with ethyl alcohol brine solution to about −60°C., white crystals were deposited, filtered in a cold state and dried quickly by pressing with filter paper. The yield was 15% of the liquid product.

It melts at 62°C., and the results of elementary analysis and of molecular weight determination in benzene solution agree with those of dioxymethyl peroxide (Found: C, 25.47; H, 6.50; M.W., 108. Calc. for $C_2H_6O_4$: C, 25.53; H, 6.38%; M.W., 94; active oxygen, 17.0%). It decomposes explosively on heating, but can be kept without decomposition for a month at ordinary temperature, and shows not only oxidising action to potassium iodide solution and hydroquinone and titanium sulphate solution but reducing action to indigo solution. The active oxygen content was estimated to be 15.1%. The aqueous solution of the peroxide decomposes gradually on standing, and the reaction was accelerated by the presence of caustic alkali and also of metals such as Fe, Cu, Zn, Ni and Pt but not Al and Cr. The decomposition products are shown in Table 1.

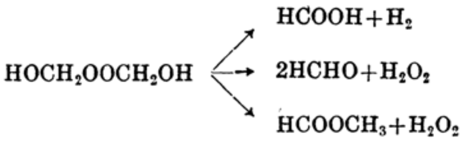
Table 1. Decomposition products in weight percentage to the peroxide.

Decomposition products	By heating	By adding NaOH	By contact with Zn	By contact with Pt-black
HCOOH	80.5	95.0	26.6	30.2
HCHO	9.3	0.0	45.7	36.3
CH_3OH	0.9	0.9	6.8	1.0
$HCOOCH_3$	0.6	0.0	1.3	10.0

The chemical properties and physical character are very like those of dioxymethyl peroxide isolated by Wieland and Wingler⁽⁵⁾ from the reaction of formaldehyde and hydrogen peroxide in an alkaline solution.

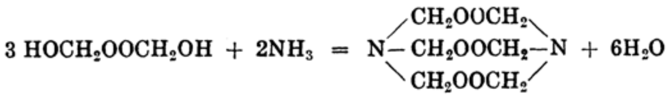
The chemical reaction of the compound will be explained easily by accepting the dioxy-methyl-peroxide formula for the peroxide but not methyl hydroperoxide CH_3OOH:

(1) The decomposition of the substance in aqueous solution described above is represented in the following scheme:



$$HOCH_2OOCH_2OH \rightarrow \begin{cases} HCOOH + H_2 \\ 2HCHO + H_2O_2 \\ HCOOCH_3 + H_2O_2 \end{cases}$$

(2) When the peroxide reacts with gaseous ammonia, a crystalline compound of explosive nature was formed, which agrees in analytical results and chemical character with hexamethylenetriperoxidediamine described by Baeyer and Villigar⁽⁶⁾ (Found: C, 34.5; H, 6.0; active oxygen, 23.35. Calc. for $C_6H_{12}O_6N_2$: C, 34.6; H, 5.8; active oxygen, 23.06%).



$$3\,HOCH_2OOCH_2OH + 2NH_3 = N\begin{cases} CH_2OOCH_2 \\ CH_2OOCH_2 \\ CH_2OOCH_2 \end{cases}N + 6H_2O$$

---

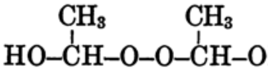
(5) *Ann.*, **431** (1923), 301.
(6) *Ber.*, **33** (1900), 2479.

II. **Ethane.** Ethane prepared from ethyl magnesium bromide and water, was mixed with oxygen in the following composition:

O_2	C_nH_m	C_2H_6	H_2
34.6	0.8	53.1	11.6

407 litres (N.T.P.) of the mixed gas were passed at a rate of 30 litres per hour into the reaction tube and produced 300 g. of the liquid product and 213 litres (N.T.P.) of gas which has the following composition:

CO_2	O_2	C_nH_m	CO	H_2	CH_4	C_2H_6	N_2
3.0	3.7	4.1	8.0	14.2	6.3	34.5	26.1

Hence, for the oxidation of ethane, conducted under conditions similar to those in the experiment with methane, it was estimated that 3 l. CO_2, 5 l. C_nH_m, 17 l. CO, 30 l. H_2, 14 l. CH_4 and 300 g. of the liquid product were yielded from 142 l. C_2H_6 and 133 l. O_2. The liquid product was supposed from its chemical behaviours to be composed of dioxyethyl peroxide  $HO-\overset{CH_3}{C}H-O-O-\overset{CH_3}{C}H-OH$,(7) but it could not be isolated in a pure state owing to the difficulty of distillation at low pressure.

300 g. of the liquid reaction product was decomposed by heating on the water bath into 1.1 l. CO_2, 0.1 l. CO, 0.41 l. CH_4, 16.14 l. H_2 and 276 g. of liquid residue. The residue was fractionated by distillation into 10° fractions. Each fraction was examined for density and content of acid, aldehyde and ester; the results are shown in Fig. 3.

The first fraction (b.p. to 30°C.) contains ester and acetaldehyde, and the latter gives semicarbazone (m.p. 163°) and dimethon (m.p. 140°). The fraction 50–60°C. consists mainly of ester which is considered to be $HCOOC_2H_5$, yielding by hydrolysis 91 percent of the theoretical amount of formic acid and a trace of acetic acid. The fraction 70–80°C. contains ethyl alcohol as is evident from its density. The fraction 100–110°C. contains mostly water, and some quantity of formic acid and acetic acid in the proportion of about 7:2, and also formaldehyde (melting point of dimethon 188.5°C.). The last fraction is composed of ester.

It was concluded that dioxyethyl peroxide is transformed by thermal decomposition into the following substances:

---

(7) Rieche, "Alkylperoxyd und Ozonid," S. 53, (1931).

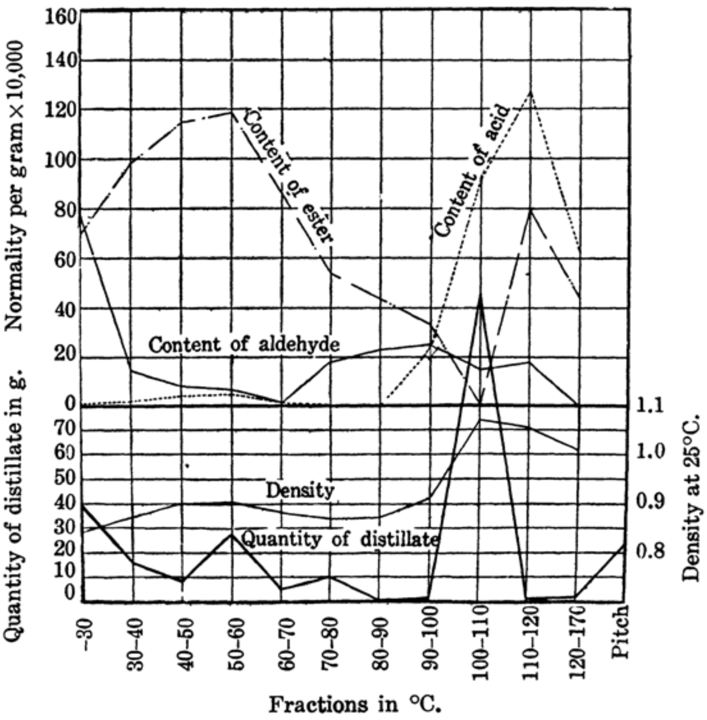
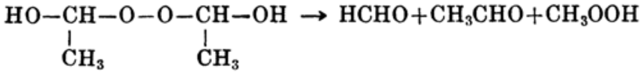


Fig. 3.

	(mol %)		(mol %)
CO_2	2.9	HCOOH	13.4
CO	12.0	CH_3COOH	4.3
H_2	32.5	Ester (mainly $HCOOC_2H_5$)	15.7
HCHO	3.1	H_2O	59.6
CH_3CHO	5.8		

These reaction products are very similar in proportion to those of oxidation of CH_3CHO by H_2O_2.⁽⁸⁾

Among these substances, formaldehyde and acetaldehyde were understood to be produced together with methylhydroperoxide by the disruption both of C–C and O–O linkings in the peroxide molecule:



$$\underset{\displaystyle CH_3}{HO-\underset{|}{CH}}-O-O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH \rightarrow HCHO+CH_3CHO+CH_3OOH$$

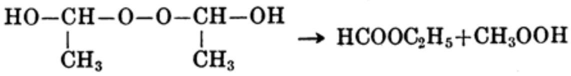
The peroxide thus liberated, gives rise to HCOOH and HCHO as reported by Rieche and Hitz.⁽⁹⁾ Formic acid ethyl ester is supposed to

---

(8) S. Bezzi, *Chem. Abstracts*, **27** (1933), 4773.

(9) *Ber.*, **62** (1929), 2458.

be formed by direct decomposition of the peroxide but not by Cannizzaro's reaction of the aldehydes:



$$HO-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O-O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH \rightarrow HCOOC_2H_5+CH_3OOH$$

III. **Butane.** By the interaction of butane and oxygen under the influence of silent discharge, dioxybutyl peroxide was formed and then, by distillation, isolated in a pure state. Its physical properties and analytical results are as follows: b.p. 55–60° (2 mm.); d_4^{25} 0.9373; n_D^{25} 1.4176; C, 53.84; H, 10.32; M.W., 138; active oxygen, 10.2 ($C_8H_{18}O_4$ requires C, 53.89; H, 10.18; M.W., 178; active oxygen, 9.0%).

IV. **Ethylene.** The experimental results shown in the oxidation of ethane, were explained by assuming that oxygen will attack the C–H bond of the molecule but not the C–C linking, and ethylene was then studied to investigate this assumption.

Ethylene gas was prepared by the dehydration of ethyl alcohol with sulphuric acid and mixed with oxygen in the following proportions:

CO_2	C_nH_m	O_2	CO	H_2	C_nH_{2n+2}	(n)	N_2
0.1	53.2	33.8	0.2	0.7	3.8	(2.7)	8.3

114 litres (N.T.P.) of the mixed gas were passed at the rate of 15 litres per hour into the reaction tube, and 59 g. of liquid reaction product and 66.7 litres of gas of the following composition resulted:

CO_2	C_nH_m	O_2	CO	H_2	C_nH_{2n+2}	(n)	N_2
4.4	43.1	12.2	12.2	7.8	4.8	(2.6)	15.5

From these data it appears that 31.8 l. (N.T.P.) ethylene by oxidation with 30.4 l. oxygen gave 2.8 l. CO_2, 7.9 l. CO, 4.4 l. H_2, and 59 g. of a peroxide. 246 g. of the impure peroxide (d_4^{25} 1.064, active oxygen 3.8%) yield by heating, 237 g. of liquid residue and gas of the composition 6.11 l. (N.T.P.) H_2, 0.2 l. CO_2, 0.04 l. CO, 0.25 l. C_nH_{2n+2}. The residue was fractionated and the distillates were examined for density and composition with the results shown in Fig. 4.

The fraction 40°C. consists of acetaldehyde (semicarbazone m.p. 163°C. and dimethon m.p. 140°C.) and ester. The fraction 50–60°C. consists mainly of $HCOOC_2H_5$, since by hydrolysis 94% formic acid was formed together with a trace of acetic acid. The fraction 100–110°C. is largely water with some formic acid and acetic acid in the proportion 7: 2.3, and formaldehyde (dimethon m.p. 189°C.).

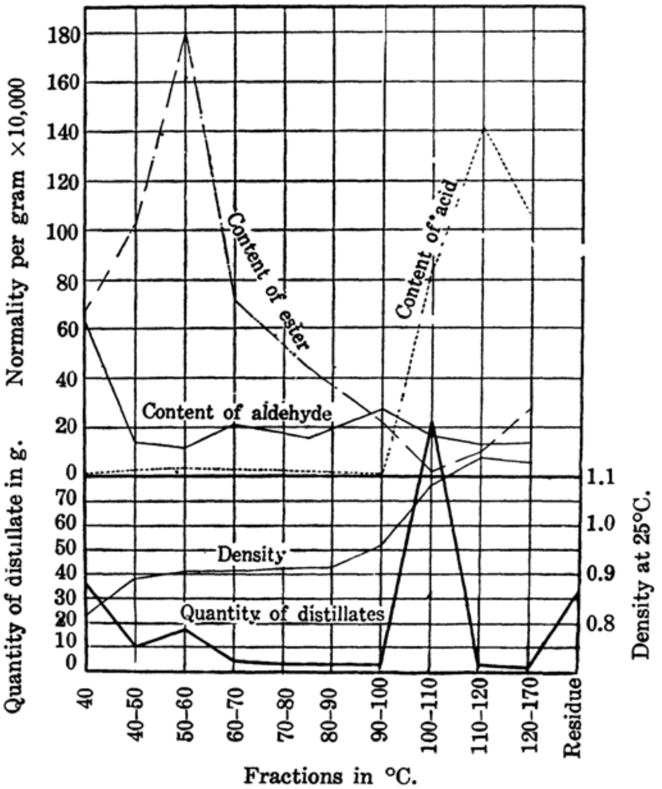
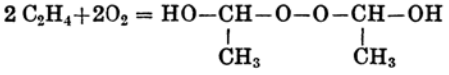
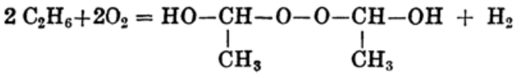


Fig. 4.

The peroxide obtained in an impure state from ethylene and oxygen will decompose by heating into the compounds which are shown below in comparison with those from ethane (Table 2). Since the results show slight difference in proportion of hydrogen and CO, it was concluded that the same dioxymethyl peroxide is formed both from ethane and ethylene: oxygen, as we expected, will combine with the C–H linking of the molecule.



$$2\,C_2H_4+2O_2 = HO-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O-O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH$$



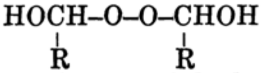
$$2\,C_2H_6+2O_2 = HO-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O-O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH + H_2$$

The peroxide which was predicated by P. Mondain-Monval and B. Quanquin⁽⁴⁾ as the first oxidation product from hydrocarbon by air, was actually isolated in some abundance by the author by the interaction of methane and oxygen under the influence of silent discharge, and the

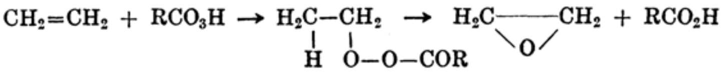
Table 2.

Decomposition products	From ethylene	From ethane
CO_2	8.8%	2.9%
CO	24.8	12.0
H_2	17.0	32.5
HCHO	3.7	3.1
CH_3CHO	4.2	5.8
HCOOH	10.9	13.4
CH_3COOH	3.8	4.3
$HCOOC_2H_5$	14.7	15.7
H_2O	50.6	59.6

molecular structure was found to be $HOCH_2OOCH_2OH$ by a precise investigation of its physical and chemical properties.

Ethane, ethylene and butane gave the peroxide of chemical structure  $HO\underset{R}{C}H-O-O-\underset{R}{C}HOH$ by similar treatment in the electrical discharge of a mixture of hydrocarbon and oxygen, and the peroxides decomposed spontaneously into alcohol, aldehyde, acid and ester.

This fact emphasizes that the initial stage of the reaction is the excitation of the C–H bond of hydrocarbon but not of oxygen, since when an activated oxygen is present with an ethylenic compound, as in the case of ethylene and oxygen, a peroxide of another type should be formed, as postulated by S. Tanaka:(10)



Theoretically, however, as to the mechanism of the formation of the peroxide from methane and oxygen, it may be considered that the initial step involves an excitation of either methane or oxygen molecules in the system.

According to the investigation by Sponer(11) methane exhibits absorption spectra of fundamental frequencies of 3022 cm.$^{-1}$ and 1304 cm.$^{-1}$ due to the oscillations of bonds shown in Fig. 5, and the electronic affinity of

---

(10) *J. Chem. Soc. Japan*, **53** (1932), 668.

(11) H. Sponer, "Molekülspektren," **I**, 82.

the oxygen molecule was assumed by Bradburg(12) and by Weiss(13) to be 1.6 volts and 2.7 volts respectively. When silent discharge operated on the mixture of methane and oxygen, the primary action might be dissociation of the electron pair forming the C–H bond of methane molecule, giving rise to partial ionisation. The activated molecule will then traverse the tube, picking up oxygen, forming a compound as a sort of dative peroxide of Milas(14):

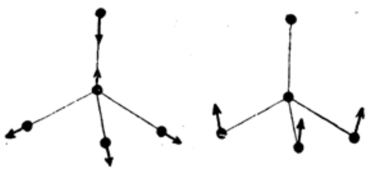
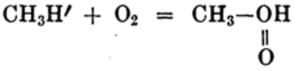
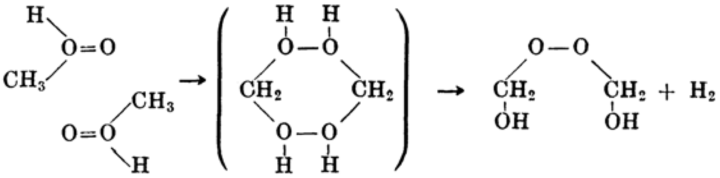


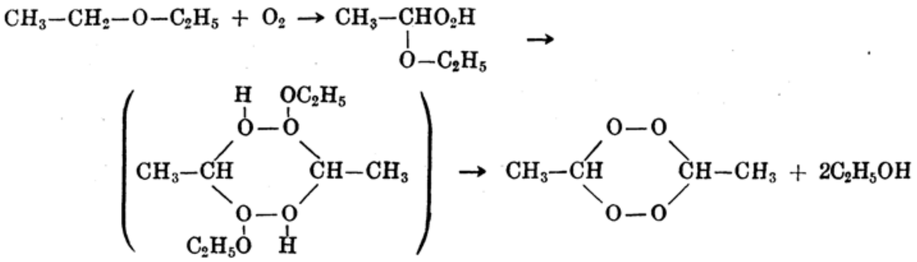
Fig. 5.



$$CH_3H' + O_2 = CH_3{-}\underset{\underset{\textstyle O}{\|}}{OH}$$

The dative peroxide being of a polar nature will then transform by the halochromic action into the stabler peroxide form as explained in a manner similar to the autoxidation of diethyl-ether.(15)





Since Berthelot's classical work on the silent discharge in methane gas appeared, many investigators have used the silent discharge for transformation of the hydrocarbons into other substances, and also for the interaction of hydrocarbon and oxygen.

---

(12) *Phys. Rev.*, **44** (1933), 883.

(13) *Trans. Faraday Soc.*, **31** (1935), 966.

(14) *J. Phys. Chem.*, **38** (1934), 411.

(15) Rieche, "Alkylperoxyd und Ozonid," S. 74, (1931).

The most striking characteristic of the action of silent discharge on paraffin or on a mixture of paraffin and oxygen is the attack on the linkage of C–H of hydrocarbon molecule, and the result is similar in some respects to that which follows applying of heat energy.

In conclusion, the author wishes to express his sincere thanks to Rear Admiral Viscount M. Kawase, Rear Admiral R. Kinashi and Rear Admiral S. Nomura, the former and present Chiefs of the Scientific Research and Experimental Branch, for their kindness of enabling him to take part in this work, and also to Prof. S. Komatsu of Kyoto Imperial University whose advice and encouragement was valuable, and also to Mr. M. Mihara and Mr. T. Iwamoto, whose kind assistance enabled him to complete the experiment.