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Decomposition of Methanol Induced by Methoxy Radicals

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Kinetical studies were made at 167°C on the decomposition of methanol induced by methoxy radicals, by pyrolyzing a small amount of dimethyl peroxide in methanol. A considerable amount of ethylene glycol was found. The following mechanism was proposed, and the kinetical equations derived therefrom could express the most part of the reaction quantitatively:

$$\begin{array}{ll}
CH_3OOCH_3 & \rightarrow 2CH_3O, \\
CH_3O+CH_3OH & \rightarrow CH_3OH+CH_2OH, \quad (a) \\
CH_3O & \rightarrow CH_2OH, \\
CH_3O+CH_2OH & \rightarrow CH_3OH+HCHO, \\
2CH_3O & \rightarrow CH_3OH+HCHO, \\
CH_3O+HCHO & \rightarrow CH_3OH+CHO, \quad (b) \\
CH_3O+CHO & \rightarrow CH_3OH+CO \quad \text{or} \quad 2CHO \rightarrow HCHO+CO, \\
2CH_2OH & \rightarrow CH_2OH-CH_2OH.
\end{array}$$

The dissociation rate constant of dimethyl peroxide is represented by $4.1\times 10^{15} \exp(-36.9\ \mathrm{kcal}/RT)\ \sec^{-1}$, and the activation heat of (a) is $3.0\sim 4.3$ kcal higher than that of (b).

INTRODUCTION

In the previous report on the methyl radical induced decomposition of methanol at 309°C,[1,2] one of the authors (Y.T.) postulated the following consecutive reactions and succeeded in a quantitative explanation of observed facts:

$$CH_3+CH_3OH \rightarrow CH_4+CH_2OH,$$

$$CH_3+CH_2OH \rightarrow CH_4+HCHO,$$

$$CH_3+HCHO \rightarrow CH_4+CHO,$$

$$CH_3+CHO \rightarrow CH_4+CO.$$

Similar mechanism would be found as to the mode of the degradation of methanol when the methyl radical is replaced with methoxy radical, for both radicals are likely to behave in the same manner as to the abstraction of hydrogen atom from molecule or radical. When dimethyl peroxide is used for the source of methoxy radicals, the formation of ethylene glycol, which is a good evidence of the presence of CH_2OH as an intermediate and accordingly may serve as a proof for the occurrence of the first dehydrogenation of methanol at C—H, might be observed, because in this case the reaction temperature can be lowered far below that of the previous case where the formation of glycol was not ascertained. Furthermore, the dissociation rate constant of dimethyl peroxide, whose numerical value, it seems, has not been given heretofore,* would be obtained in this experiment.

With these expectations the present work has been performed, and the results have met them satisfactorily.

EXPERIMENTAL

Static method was used; a small amount of dimethyl peroxide was introduced into the methanol kept at the reaction temperature, then the pressure change was pursued, and at the required moment a major part of the reaction mixture was withdrawn and analyzed.

The reaction equipment was almost the same as illustrated in the previous report.[2] A 310-cc glass bulb (surface/volume$\doteqdot$1 cm^{-1}) installed in an electric copper block furnace (temperature constancy ±0.1°C) was connected by electrically heated (*ca* 100°C) capillary tubes to mercury cutoffs and to the head of the mercury in one branch of an inclined manometer (accuracy 0.1 mm), (total dead space 0.5 cc), both of which were heated to 100°C by steam jackets to prevent ethylene glycol from condensing. The mercury vapor slowly diffusing from the cutoffs and the manometer ($\leq$0.3 mm) does not seem to affect the reaction, for, the presence of 5.4-mm mercury vapor caused by the introduction of a few drops of mercury before the reaction did not alter the features of the reaction.

The reaction mixture was withdrawn into an evacuated vessel of 500 cc (70 percent of the total reaction mixture was collected) and shaken with 15-cc water before and after it was brought to normal pressure by means of mercury, then the total gaseous products in this sampling vessel (*ca* 1 cc) were analyzed by a modified Ambler's apparatus (accuracy in reading 0.005 cc) and the quantity of formaldehyde in the aqueous solution (aliquot 5 cc) was measured according to the Clausen's method[3] by microtitration with 1/100 *N* iodine solution. On some samples colorimetric determination of formaldehyde was made with Schiff's

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[1] Kodama, Takezaki, and Yoshida, J. Chem. Soc. Japan 71, 173 (1950).

[2] Y. Takezaki, Bull. Inst. Chem. Research Kyoto Univ. 26, 1 (1951).

* The authors could not refer to the report of M. B. Neiman [Uspekhi. Khim. 7, 341 (1938)], in which the rate constant might be given.

[3] F. P. Clift and R. P. Cook, Biochem. J. 26, 1788 (1932).

reagent under strongly acid condition (H_2SO_4 15 percent by weight).

As for ethylene glycol, about a half of the reaction mixture was condensed in a small trap and the entire condensate (*ca* 0.1 cc) was treated with periodic acid solution for 1 hour at 100°C under reflux and the consumed periodic acid was measured micro-iodometrically with 1/10 N thiosulfate solution.[4]

Methanol of cp grade, free from formaldehyde and acetone, was dried with magnesium-iodine mixture[5] and rectified; the center $\frac{1}{3}$ fraction of the total distillate was used.

Dimethyl peroxide was prepared according to Rieche;[6] after the removal of hydroperoxide with saturated calcium chloride solution, it was collected in a trap at 0°C through tubes filled with calcined calcium chloride, then rectified (top temperature 13.8°C at 759 mm; Rieche, bp 13.5°C at 740 mm). The vapor pressure of the peroxide thus obtained was 433 mm at 0.0°C and 767 mm at 14.0°C. The purity of peroxide was not determined; it was absorbed in water of fivefold volume quickly and completely.[6] As shown later, the only impurity, if any, is supposed to be dimethyl ether produced in large quantities in the preparation of peroxide, which still remains owing to the insufficient distillation, and the content of ether does not seem to exceed 3 percent.

RESULTS

Table I and Fig. 1 show the results obtained under the following standard conditions: the initial pressure of methanol $(CH_3OH)_0=400\pm5$ mm; the initial pressure of dimethyl peroxide $(DMP)_0=23\pm0.5$ mm; accordingly the ratio of initial pressures (referred to as I.P.R., hereafter), $(CH_3OH)_0/(DMP)_0=17.4\pm0.6$; and the reaction temperature 166.7°C. The numerical values concerning the amount of pressure rise or of products are given by the ratio to $(DMP)_0$ throughout the paper.

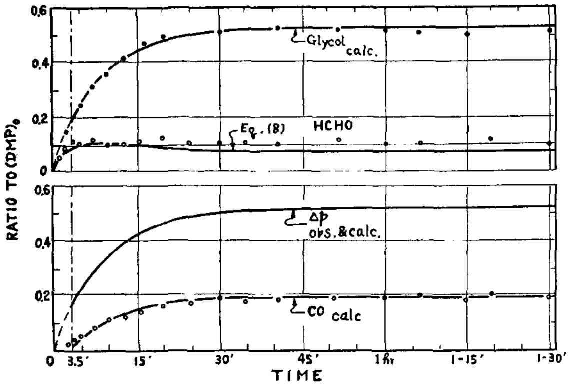

FIG. 1. Plot for the observed and calculated values of products 166.7°C, $(CH_3OH)_0=400$ mm, $(DMP)_0=23$ mm. Open and closed circles represent the observed values.

No CO_2 and olefins were found; the amount of H_2 was 0.02–0.03 between 10 min and 1.5 hr, and CH_4 was less than 0.02. Acetaldehyde was not detected by iodoform reaction. Ethylene glycol was detected by the method given Feigl,[7] *viz.*, the above-mentioned condensate was mixed with a few drops of concentrated $NaHSO_3$ solution and distilled, then the distillate was divided into two portions and the one was treated with periodic acid and the produced formaldehyde was tested with Schiff's reagent in the presence of sulfric acid. The development of color was quite remarkable, while the other, used as a control, remained almost colorless with Schiff's reagent.

Formation of glyoxal and glycolaldehyde is supposed to be negligible (0.01 or so) because of the fairly good coincidence of both aldehyde determinations shown in Table I, since it was found in the preliminary tests that glyoxal and glycolaldehyde can be measured within an error of a few percent by the Clausen method under the present analytical condition, i.e., observed "HCHO" $=HCHO+2(CHO)_2+CH_2OHCHO$ if the latter two exist, while they produce no color with Schiff's reagent under the strongly acid condition, and furthermore, that the dissolved dimethyl peroxide, a very weak oxidant,[6] does not destroy them and also formaldehyde. In the experiment in the reactor of very high surface-to-volume ratio[†] (glass-wool-filled bulb) the amount of glyoxal and glycolaldehyde was still small.

The amount of glycol decreases as $(CH_3OH)_0$ is reduced, and reaches 0.09 at I.P.R. = 0 for $(DMP)_0=23$ mm; other products in the latter case were CO (0.43), HCHO (0.02), CH_3OH (1∼2, semiquantitatively analyzed by permanganate oxidation followed by colorimetry), H_2 (0.01) and CH_4 (0.03).

The final amount of pressure rise, $\Delta p_f/(DMP)_0$, decreases as the I.P.R. is raised, in the manner shown in Fig. 2; higher $(DMP)_0$ results in somewhat lower $\Delta p_f/(DMP)_0$. In the case of I.P.R. = 0, $\Delta p_f/(DMP)_0$ was 0.93, 0.83, and 0.72, respectively, for $(DMP)_0=23$, 33, and 44 mm. But all the pressure curves obtained for the I.P.R's shown in Fig. 2 follow the first-order law exactly and have the same apparent rate constant, i.e., 1.85×10^{-3} sec^{-1} at 166.7°C.

In the range of the reaction temperature examined

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[4] M. L. Malaprade, Bull. Soc. Chim. 43, 683 (1928).

[5] N. Bjerrum and Z. Zechmeister, Ber. deut. chem. Ges. 64, 210 (1931).

[6] A. Rieche, Ber. deut. chem. Ges. 61, 951 (1928) and 62, 218 (1929).

[7] F. Feigl, *Qualitative Analyse mit Hilfe von Tüpfelreaktionen* (Akademische Verlagsgesellschaft, Leipzig, 1938), p. 383.

[†] In the bulb filled with glass-wool the decomposition of peroxide proceeded faster; the results are as follows: Peroxide alone (23 mm, 166.7°C): time of $\frac{1}{4}$ completion of pressure rise, $t_{1/4}=1'40''$, $t_{1/2}=4'25''$, $t_{3/4}=9'$, $t_{99\text{ percent}}=21'$; at the end of the reaction $\Delta p=0.90$, $CO=0.37$, $H_2=0.03$, $CH_4=0.02$, $HCHO=0.06$ (Clausen) and 0.06 (colorimetry), glycol=0.03. Methanol+peroxide (standard condition): $t_{1/4}=1'20''$, $t_{1/2}=4'00''$, $t_{3/4}=7'45''$, $t_{99\text{percent}}=21'$; at the end of the reaction $\Delta p=0.71$, $CO=0.20$, $H_2=0.05$, $CH_4=0.02$, $HCHO=0.19$ (Clausen) and 0.15 (colorimetry), hence 2 glyoxal +glycolaldehyde=0.04, glycol+glyoxal+glycolaldehyde=0.21. (Glyoxal and glycolaldehyde were found to consume one atom o of HIO_4 per molecule of each.)

TABLE I. Reaction products. 166.7°C, $(CH_3OH)_0=400$ mm, $(DMP)_0=23$ mm, surface/volume $=1\ cm^{-1}$. Numerical values are the ratios to $(DMP)_0$.

Time \ Accuracy[a]	Δp	CO	HCHO		Glycol
	±0.009	±0.012	±0.013	±0.01[b]	±0.015
1.25 min	0.063	···	0.06	···	···
2.5	0.128	0.02	0.09	0.08	0.15
3.75	0.179	0.04	0.12	···	···
5.0	0.229	0.05	0.11	0.10	0.25
7.5	0.297	0.08	0.12	···	0.32
10	0.358	0.11	0.10	0.10	0.36
13	0.412	0.12	0.10	···	0.42
16.5	0.443	0.14	0.12	···	0.48
20	0.464	0.16	0.13	0.13	0.50
25	0.493	0.17	0.11	···	···
30	0.506	0.19	0.11	···	0.51
35	0.511	0.17	0.11	0.10	···
41	0.510	0.18	0.10	···	0.53
52	0.520	0.19	0.12	···	0.52
1 hr 00	0.525	0.19	0.10	0.09	0.51
1 07	0.521	0.20	0.10	···	0.51
1 15	0.514	0.18	···	0.09	0.50
1 20	0.520	0.20	0.10	···	···
1 30	0.528	0.19	0.10	0.10	0.51

[a] Maximum possible error for each single observation, calculated from the accuracy of pressure measurement or from the accuracy of the analysis and the amount of aliquot.

[b] Colorimetric determination with Schiff's reagent in acid medium.

(154.8~180.0°C), $\Delta p_f/(DMP)_0$ remained constant for the same I.P.R. and $(DMP)_0$.

DISCUSSION

Elementary Reactions

These observations on the pressure rise and the shape of the curves in Fig. 1 suggest the following nonchain mechanism analogous to that which was obtained in the reaction of methyl radicals with methanol:[1,2]

Rate constant

$$CH_3OOCH_3 \rightarrow 2CH_3O, \qquad k_0 \quad (0)$$

$$CH_3O+CH_3OH \rightarrow CH_3OH+CH_2OH, \qquad k_1 \quad (1)$$

$$CH_3O+CH_2OH \rightarrow CH_3OH+HCHO, \quad \text{formation of O}-\text{H bond} \qquad k_2 \quad (2)$$

$$CH_3O+HCHO \rightarrow CH_3OH+CHO, \qquad k_3 \quad (3)$$

$$CH_3O+CHO \rightarrow CH_3OH+CO, \qquad k_4 \quad (4)$$

$$2CH_2OH \rightarrow CH_2OH-CH_2OH. \qquad k_5 \quad (5)$$

Likewise, the reactions of CH_2OH which compete with those of CH_3O,

$$CH_2OH+CH_3O \rightarrow CH_3OH+HCHO, \quad \text{formation of C}-\text{H bond} \qquad k_2' \quad (2^a)$$

$$CH_2OH+CH_2OH \rightarrow CH_3OH+HCHO, \qquad k_2'' \quad (2^b)$$

$$CH_2OH+HCHO \rightarrow CH_3OH+CHO, \qquad k_3' \quad (3^a)$$

$$CH_2OH+CHO \rightarrow CH_3OH+CO, \qquad k_4' \quad (4^a)$$

and the disproportionation of CHO

$$2CHO \rightarrow HCHO+CO \qquad k_4'' \quad (4^b)$$

may be present; the extent of their contribution will be discussed later from the kinetical viewpoint.

As for the formation of formaldehyde, the reaction

$2CH_3O \rightarrow CH_3OH+HCHO$[8] $\qquad k_2''' \quad (2^c)$

should be taken into consideration, since, as described above, methanol formation was observed in the experiment at I.P.R. = 0, though it is possible to think that all the methanol was produced by the chain decomposition of peroxide,

$$CH_3O+CH_3OOCH_3 \rightarrow CH_3OH+CH_2OOCH_3, \qquad k_0' \quad (0^a)$$

$$CH_2OOCH_3 \rightarrow CH_3O+HCHO, \qquad k_0'' \quad (0^b)$$

and the subsequent reactions of formaldehyde, (3) and (4). The reactions $CH_3O \rightarrow H+HCHO$ and $2CH_3O \rightarrow H_2 + 2HCHO$ can be entirely ruled out in the present case because of the absence of H_2 in the experiment at I.P.R. = 0, in which the concentration of CH_3O is supposed to be fairly higher than that of the present, since the amounts of methanol and formaldehyde in the former are much smaller.

The glycol must have been derived from (1) and, possibly, from the isomerization of CH_3O,

$$CH_3O \rightarrow CH_2OH, \qquad k_1' \quad (1^a)$$

followed by the dimerization of CH_2OH. The occurrence of (1) is evident, because, otherwise the over-all reaction would be independent of the presence of methanol, which is contrary to the observed variation of Δp_f with I.P.R. (Fig. 2). Thus, the presence of the H atom abstraction reaction from methanol occurring primarily at the C−H bond is confirmed. However, the relative velocity of this reaction to that of the first dehydrogena-

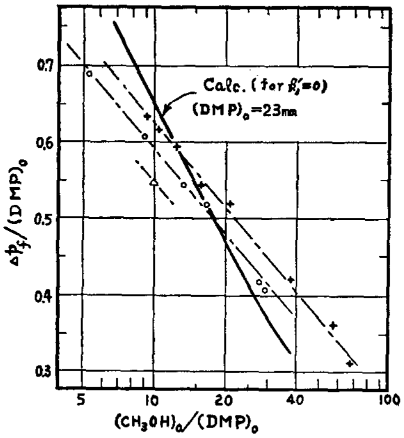

FIG. 2. Variation of final pressure rise with the initial pressure ratio. 166.7°C. △: $(DMP)_0=51$ mm. ○: $(DMP)_0=23$ mm. +: $(DMP)_0=11$ mm.

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[8] Raley, Porter, Rust, and Vaughan, J. Am. Chem. Soc. 73, 15 (1951).

tion at the O—H bond cannot be obtained from this experiment, as the intervention of the latter reaction, $CH_3O+CH_3OH \rightarrow CH_3OH+CH_3O$,[‡] a superfluous one in the present case, does not affect the features of the whole reaction.

It is very plausible that (1^a), an exothermic reaction, takes place as well as the other competing reactions of CH_3O under the present experimental condition. The presence of glycol in the products of the experiment at I.P.R. = 0, where only a small amount of methanol was present, is suggestive of the occurrence of this reaction even in the present experiment, though the relative extent to (1) must be fairly less.

It seems impossible to explain the formation of methane by the reactions between above-mentioned reactants, inclusive of glycol. Probably it was derived from the induced decomposition of dimethyl ether contained in the peroxide as an impurity.[§]

Now, besides the numbered reactions given above, assuming some hydrogen and methane formation reactions[||] and furthermore the presence of the reactions $CH_3O+CH_2OH \rightarrow CH_3OCH_2OH$ and $CH_3O+CHO \rightarrow HCOOCH_3$, we get the following relations from the material balance:

$$\Delta p=(\mathrm{HCHO})+2(\mathrm{CO})+(\mathrm{HCOOCH_3}),$$

$$(\text{Decomposed DMP})=\Delta p+(\text{glycol})+(\mathrm{HCOOCH_3}) +(\mathrm{CH_3OCH_2OH})-(\mathrm{H_2})-(\mathrm{CH_4}).$$

By the introduction of the observed values at the end of the reaction [(reacted DMP) = 0.97] we have $(HCOOCH_3)=0.02$ and $(HCOOCH_3)+(CH_3OCH_2OH)=-0.01$, hence we may say that the formation of these products is also negligible in the empty reactor.[¶]

Kinetics

As to the reaction in the unpacked reactor, two representative cases are treated mathematically at first, then the intermediate cases are considered qualitatively based on these results.

The one is the course in which the abstraction of H atom of CH_3OH, CH_3O, CH_2OH, HCHO, and CHO proceeds by the attack of CH_3O, i.e., the sequence of the reactions (0), (1), (1^a), (2), (2^c), (3), (4), and (5) (mechanism I) or (0), (1), (1^a), (2), (2^c), (3), (4^b), and (5) (mechanism II; the seventh step being the disproportionation of CHO), and the other is the course in which CH_2OH acts as the H acceptor, i.e., (0), (1), (1^a), (2^a), (2^b), (3^a), (4^a), and (5) (mechanism III) or (0), (1), (1^a), (2^a), (2^b), (3^a), (4^b), and (5) (mechanism IV).

Discussion on the presence of the chain decomposition of peroxide will be given later for both cases.

The side-reactions such as the formation of H_2, CH_4, $(CHO)_2$, etc., are ignored to get the time-variation of main products. Peroxide is assumed to be 100 percent pure for simplicity.

The differential equations derived therefrom can be solved for the reaction stage where the formaldehyde concentration can be regarded practically as constant. This stage begins at about 3.5 min after the beginning of the reaction at 166.7°C and covers the major part of the reaction period, which corresponds to the latter $\frac{2}{3}$ of the peroxide decomposition.

The origin of time t in the following rate equations is, unless otherwise stated, taken at a definite time $\bar{t}$ (from the beginning of the reaction) when $d(\mathrm{HCHO})/dt=0$ becomes available.

(A) *Case 1. Degradation by CH_3O [Mechanism I or II, (0), (1), (1^a), (2), (2^c), (3), (4)* or *(4^b), and (5)]*

From (0) it follows

$$(\mathrm{DMP})=(\mathbf{DMP})\exp(-k_0t)$$
$$=(\mathrm{DMP})_0\exp(-k_0\bar{t})\cdot\exp(-k_0t),$$

where (**DMP**), black type in parentheses, denotes the partial pressure of dimethyl peroxide at $t=0$ (and so on for (**HCHO**) etc.).

Applying the steady-state method to the concentration of radicals we get

$$(\mathrm{CH_3O})=2k_0(\mathrm{DMP})_0\exp(-k_0\bar{t})\cdot\exp(-k_0t)/ \{k_1(\mathrm{CH_3OH})+k_1'+3k_3(\mathrm{HCHO})/n +k_2'''(\mathrm{CH_3O})\}, \quad (6)$$

$$d\Delta p/dt=2d(\mathrm{CO})/dt=2k_3(\mathrm{HCHO})(\mathrm{CH_3O})/n,$$

$$d(\text{glycol})/dt=\{k_1(\mathrm{CH_3OH})+k_1'-k_3(\mathrm{HCHO})/n\} \times(\mathrm{CH_3O})/2,$$

[‡] This reaction must be far slower than (1), as discussed by Phibbs and Darwent [J. Chem. Phys. **18**, 495 (1950)], and also by us [J. Chem. Soc. Japan **73**, 440 (1952)] in the paper on the methyl radical induced decomposition of ethanol at 312°C, in which the first dehydrogenation of ethanol was concluded to occur almost exclusively at the αC—H bond, from the consideration on the steady concentration of formaldehyde and actaldehyde.

[§] The content of ether is supposed to be 3 percent from the amount of methane in the experiment at I.P.R. = 0; therefore all the numerical values about the amount of Δp or of products should be raised by 3 percent so as to be relative to the true $(DMP)_0$, but this correction and the terms which are to be introduced into the kinetical equations due to the reaction of ether and of CH_3 affect the kinetics of the proper reactions only slightly, i.e., to the magnitude less than the influence of the approximation used to integrate the rate equations.

[||] The reactions assumed here are $CHO \rightarrow H+CO$, $CH_2OH \rightarrow H+HCHO$, $2CHO \rightarrow H_2+2CO$, $2H \rightarrow H_2$, $CH_3O+CH_3OCH_3 \rightarrow CH_3OH+CH_2OCH_3 \rightarrow CH_3+HCHO$ and the H atom abstraction reactions by H or CH_3 analogous to (1)–(4).

[¶] When glyoxal and glycolaldehyde are present, the above balances become

$$\Delta p=(\mathrm{HCHO})+2(\mathrm{CO})+2(\mathrm{CHO})_2 +(\mathrm{CH_2OHCHO})+(\mathrm{HCOOCH_3}),$$

$$(\text{decomposed DMP})=\Delta p+(\text{glycol})+(\mathrm{HCOOCH_3}) +(\mathrm{CH_3OCH_2OH})+(\mathrm{CHO})_2+(\mathrm{CH_2OHCHO})-(\mathrm{H_2})-(\mathrm{CH_4}).$$

Introducing the results on the reaction in high surface/volume reactor, we get

peroxide alone: $(CH_3OCH_2OH)=0.00$, $(HCOOCH_3)=0.10$;
methanol+peroxide: $(CH_3OCH_2OH)=0.00$, $(HCOOCH_3)=0.12$.

where $n=1$ for mechanism I and $n=2$ for II, and the condition

$$d(\mathrm{HCHO})/dt=k_2'''(\mathrm{CH_3O})^2+k_2(\mathrm{CH_3O})(\mathrm{CH_2OH})$$
$$+k_4''(\mathrm{CHO})^2-k_3(\mathrm{CH_3O})(\mathrm{HCHO})=0$$

(as compared with the rate of CO formation) is used.

We now subdivide the case into two with regard to the relative velocity of two competitive reaction (2) and (2^c).

(A-1) If $k_2(CH_3O)(CH_2OH)\gg 2k_2'''(CH_3O)^2$ almost in the entire period of the reaction.—Integration of the foregoing equations, noting

$$(\mathrm{CH_3OH})\doteqdot\text{const }(\doteqdot(\mathbf{CH_3OH})\doteqdot(\mathrm{CH_3OH})_0)$$

and $(\mathrm{HCHO})=(\mathbf{HCHO})=\text{const}$, gives

$$\Delta p/(\mathrm{DMP})_0=2(\mathrm{CO})/(\mathrm{DMP})_0=4\exp(-k_0\bar{t})$$
$$\times\{1-\exp(-k_0t)\}/(nA+3), \quad (7)$$
$$(\mathrm{glycol})/(\mathrm{DMP})_0=\exp(-k_0\bar{t})(nA-1)$$
$$\times\{1-\exp(-k_0t)\}/(nA+3),$$

where $A=\{k_1(\mathrm{CH_3OH})+k_1'\}/k_3(\mathbf{HCHO})=$ a constant for a fixed $(\mathrm{DMP})_0$ and I.P.R.

Hence, every curve should be of the first order in the reaction stage after $\bar{t}$, and its rate constant be k_0. This is well-proved in Fig. 3 with respect to Δp's at several temperatures, where every point, till 90 percent completion at least, falls within the experimental error calculated from the accuracy of pressure measurement. For 166.7°C, we get $k_0=1.87\times10^{-3}$ sec^{-1} (mean of 19 runs, average error$=0.05\times10^{-3}$ sec^{-1}) and $nA=4.82$, by the use of $\bar{t}=210$ sec and the observed value for $\Delta\bar{p}$ and Δp_f, respectively, 0.175 and 0.520. With the obtained values of k_0, nA and the final amount of CO ($=0.195$), curves for CO and glycol can be drawn. As shown in Fig. 1 (solid lines) the calculated values agree well with the observed ones.

(A-2) If $k_2(CH_3O)(CH_2OH)\gg 2k_2'''(CH_3O)^2$ does not hold.—Transformation of (6) gives as the second approximation

$$(\mathrm{CH_3O})=2k_0(\mathrm{DMP})_0\exp(-k_0\bar{t})\cdot\exp(-k_0t)/$$
$$[k_1(\mathrm{CH_3OH})+k_1'$$
$$+\{3/n+B\exp(-k_0t)\}k_3(\mathbf{HCHO})],\text{**}$$

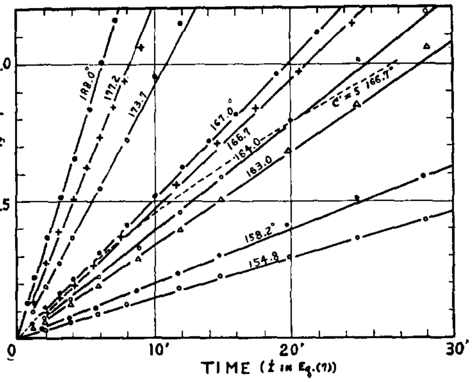

FIG. 3. First-order nature of pressure curve. $(\mathrm{CH_3OH})_0=400$ mm, $(\mathrm{DMP})_0=23$ mm.

Temp. °C	180.0	177.2	173.7	167.0	166.7	164.0	163.0	158.2	154.8
$\bar{t}$	0'50''	1'05''	2'00''	3'20''	3'30''	5'07''	5'10''	9'20''	12'10''
$k_0\times10^3$ sec^{-1}	6.20	4.72	3.51	1.96	1.88	1.49	1.29	0.779	0.565

$\bar{t}$ is taken to be the time when $\Delta p/(\mathrm{DMP})_0$ reaches 0.175 at all temperatures. $\Delta\bar{p}$ represents the pressure rise at $\bar{t}$. As for the broken line see the text.

where $B(0<B\leq1)$ is a parameter concerning the relative rate of (2^c) and (2) at $t=0$. Then we get

$$\frac{\Delta p}{(\mathrm{DMP})_0}=\frac{2(\mathrm{CO})}{(\mathrm{DMP})_0}=\frac{-4\exp(-k_0\bar{t})}{nB}\times\ln\frac{nA+3+nB\exp(-k_0t)}{nA+3+nB},$$

$$\frac{(\mathrm{glycol})}{(\mathrm{DMP})_0}=\exp(-k_0\bar{t})\left\{1-\exp(-k_0t)+\frac{4}{nB}\ln\frac{nA+3+nB\exp(-k_0t)}{nA+3+nB}\right\}.$$

Now, we know from the material balance $(\mathbf{DMP})/(\mathrm{DMP})_0=0.65$ irrespective of the mechanism assumed and it is equal to $\exp(-k_0\bar{t})$ when the chain decomposition of peroxide is absent; then on calculation using this value and $k_0=1.87\times10^{-3}$ sec^{-1} obtained before [this value is nearly the same as derived from $0.65=\exp(-k_0\bar{t})$ ($\bar{t}=210$ sec)] we see that both equations coincide, respectively, almost exactly with those of (A-1). The maximum deviations from the correct first-order expressions appear at $t=2.6$ min, and they are 0.008 for $nB=1$ and 0.012 for $nB=2$. Therefore, we may say that both mechanism I and II, with or without (2^c), can express the behaviors of Δp, CO and glycol curves

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** In this case we have

$$k_2'''(\mathrm{CH_3O})^2=k_3(\mathrm{CH_3O})(\mathbf{HCHO})/n$$
$$-k_2(\mathrm{CH_3O})(\mathrm{CH_2OH})\leq d(\mathrm{CO})/dt,$$
$$\{k_1(\mathrm{CH_3OH})+k_1'+3k_3(\mathbf{HCHO})/n\}(\mathrm{CH_3O})$$
$$\geq 2k_5(\mathrm{CH_2OH})^2+3k_3(\mathrm{HCHO})(\mathrm{CH_3O})/n$$
$$=3d(\mathrm{CO})/dt+2d(\mathrm{glycol})/dt.$$

On the other hand, we know that the observed curves are expressed formally by

$$(\mathrm{CO})/(\mathrm{DMP})_0=0.17\{1-\exp(-Kt)\}$$

and

$$(\mathrm{glycol})/(\mathrm{DMP})_0=0.33\{1-\exp(-Kt)\}.$$

Insertion of these values into the foregoing two relations gives that the last term of the denominator of (6) is at most 1/7 of the sum of the first three. Then dropping this last term from (6) we get, as the first approximation,

$$(\mathrm{CH_3O})\doteqdot 2k_0(\mathbf{DMP})\exp(-k_0t)/$$
$$\{k_1(\mathrm{CH_3OH})+k_1'+3k_3(\mathbf{HCHO})/n\}$$
$$=(\mathbf{CH_3O})\exp(-k_0t).$$

Introduction of this relation again into (6) gives the second approximation with the use of

$$k_2'''(\mathbf{CH_3O})^2=k_3(\mathbf{HCHO})(\mathbf{CH_3O})/n-k_2(\mathbf{CH_2OH})(\mathbf{CH_3O})$$
$$=k_3B(\mathbf{HCHO})(\mathbf{CH_3O}).$$

at one $(DMP)_0$ and I.P.R. As to the effect of I.P.R., we will return again to it in a later section.

These mechanisms, however, are not complete in that they intrinsically give the expression for formaldehyde that decreases again through a maximum point. For instance, in the case of (A-1), the differential equation for formaldehyde is approximately represented by

$$d(\mathrm{HCHO})/dt=\{k_2(\mathrm{CH_2OH})-k_3(\mathrm{HCHO})/n\}(\mathrm{CH_3O})$$

$$\doteqdot\frac{2(\mathrm{HCHO})k_0\exp(-k_0t_m)\cdot\exp(-k_0\Delta t)}{nA'+3(\mathrm{HCHO})}\cdot\left[\frac{(\mathrm{HCHO})_m}{(\mathrm{HCHO})}\left\{\frac{nA'+3(\mathrm{HCHO})_m}{nA'+3(\mathrm{HCHO})}\right\}^{\frac{1}{2}}\times\exp(-\tfrac{1}{2}k_0\Delta t)-1\right],\quad(8)$$

where

$$(\mathrm{CH_2OH})=[-k_2(\mathrm{CH_3O})+\{k_2^2(\mathrm{CH_3O})^2+8k_5[k_1(\mathrm{CH_3OH})+k_1'](\mathrm{CH_3O})\}^{\frac{1}{2}}]/4k_5$$

$$\doteqdot[\{k_1(\mathrm{CH_3OH})+k_1'\}/2k_5]^{\frac{1}{2}}(\mathrm{CH_3O})^{\frac{1}{2}}\dagger\dagger\quad(9)$$

is used, and $A'=\{k_1(\mathrm{CH_3OH})+k_1'\}/k_3$, $(\mathrm{HCHO})_m$ = maximum value of formaldehyde, t_m = time (from the beginning of the reaction) when $(\mathrm{HCHO})_m$ is reached, and Δt = time from t_m.

This equation is sufficiently accurate for the period after t_m ($\Delta t>0$), but less so for $\Delta t<0$, especially for $\Delta t\approx -t_m$. The result of numerical integration is represented by the curve denoted by "Eq. (8)" in Fig. 1 (the same curve for both mechanisms); it has the maximum point (assumed to be 0.11) at 8.5 min and decreases to 0.08 at $\Delta t=40$ min, whereas no decrease is actually recognized in the amount of formaldehyde.

If (2^c) is predominant in the neighborhood of $\bar{t}$, a steeper decline of formaldehyde curve would be seen after the maximum point (t_m shifts to the smaller value; this is favorable for the observed $\bar{t}$); therefore this reaction must be predominant, if at all, only in the very beginning of the reaction (before $\bar{t}$).

First-order rate equations are not obtained in the case where (4) and (4^b) take place concurrently, though it cannot be determined if the deviation from the first-order law attains to the recognizable amount under the present experimental conditions.

(B) *Case 2. Degradation by CH_2OH [Mechanism III or IV, (0), (1), (1^a), (2^a), (2^b), (3^a), (4^a) or (4^b), and (5)]*

In this case we have

$$(\mathrm{CH_3O})=2k_0(\mathbf{DMP})\exp(-k_0t)/\{k_1(\mathrm{CH_3OH})+k_1'\},$$

$$d\Delta p/dt=2d(\mathrm{CO})/dt=2k_3(\mathbf{HCHO})(\mathrm{CH_2OH})/m,$$

$$d(\mathrm{glycol})/dt=k_5(\mathrm{CH_2OH})^2,$$

$$(\mathrm{CH_2OH})=\frac{-k_2'(\mathrm{CH_3O})-2k_3'(\mathbf{HCHO})/m+\{[k_2'(\mathrm{CH_3O})+2k_3'(\mathbf{HCHO})/m]^2+8(k_2''+k_5)[k_1(\mathrm{CH_3OH})+k_1'](\mathrm{CH_3O})\}^{\frac{1}{2}}}{4(k_2''+k_5)},\quad(9a)$$

where $m=1$ for mechanism III and $m=2$ for IV.

The last equation is transformed into

$$(\mathrm{CH_2OH})=\varphi_{(t)}\left[\frac{k_1(\mathrm{CH_3OH})+k_1'}{2(k_2''+k_5)}\right]^{\frac{1}{2}}(\mathrm{CH_3O})^{\frac{1}{2}}$$

$$=\varphi_{(t)}\left[\frac{k_0(\mathrm{DMP})_0\exp(-k_0\bar{t})}{k_2''+k_5}\right]^{\frac{1}{2}}\exp(-\tfrac{1}{2}k_0t),$$

$\varphi_{(t)}=0.85$, practically constant for

$$k_2''(\mathrm{CH_2OH})^2\gg k_2'(\mathrm{CH_3O})(\mathrm{CH_2OH}),\ddagger\ddagger$$

$\varphi_{(t)}=0.71$, practically constant for

$$k_2''(\dot{\mathrm{C}}\mathrm{H_2OH})^2\ll k_2'(\mathrm{CH_3O})(\mathrm{CH_2OH}),$$

$0.85>\varphi_{(t)}>0.71$, varies with t for the cases between above two extremes, if these mechanisms agree with the truth.

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†† The right side of (9) is derived by the use of

$$k_2^2(\mathrm{CH_3O})^2(\mathrm{CH_2OH})^2/8k_5(\mathrm{CH_2OH})^2\cdot\{k_1(\mathrm{CH_3OH})+k_1'\}(\mathrm{CH_3O})=1/120$$

calculated as in reference (**).

‡‡ The following relations are obtained as to the relative amount of the two terms in the root sign of (9a) by the use of the observed velocities of CO and glycol formation as before and with the condition $d(\mathrm{HCHO})/dt=0$:

$$\frac{\text{First term}}{\text{Second term}}\begin{cases}=\left\{\dfrac{d(\mathrm{CO})}{dt}\right\}^2\Big/2\left\{\dfrac{d(\mathrm{CO})}{dt}+\dfrac{d(\mathrm{glycol})}{dt}\right\}\times\left\{4\dfrac{d(\mathrm{CO})}{dt}+2\dfrac{d(\mathrm{glycol})}{dt}\right\}=\dfrac{1}{46} & \text{for the first case,}\\ =\left\{3\dfrac{d(\mathrm{CO})}{dt}\right\}^2\Big/8\left\{\dfrac{d(\mathrm{glycol})}{dt}\right\}\times\left\{3\dfrac{d(\mathrm{CO})}{dt}+2\dfrac{d(\mathrm{glycol})}{dt}\right\}=\dfrac{1}{12} & \text{for the second case,}\\ <\left\{3\dfrac{d(\mathrm{CO})}{dt}\right\}^2\Big/8\left\{\dfrac{d(\mathrm{glycol})}{dt}\right\}\times\left\{3\dfrac{d(\mathrm{CO})}{dt}+2\dfrac{d(\mathrm{glycol})}{dt}\right\}=\dfrac{1}{12} & \text{for the third case.}\end{cases}$$

That is, (CH_2OH) is (or almost is, at worst) proportional to $(CH_3O)^{\frac{1}{2}}$; hence we get

$$d\Delta p/dt = \text{constant}\cdot\exp(-\tfrac{1}{2}k_0t)$$
$$d(\text{glycol})/dt = \text{constant}\cdot\exp(-k_0t).$$

This result conflicts strongly with the observed fact that both curves have a same first-order rate constant, even if we allow the slight deviation from the first-order law which may arise in some cases.

(C) *Intermediate Cases*

(*C*-1).—Mechanisms constructed by replacing any one or two of (2^c), (3), and (4) by (2^b), (3^a), and (4^a), respectively [e.g., {(0), (1), (1^a), (2), (2^b), (3), (4) or (4^b), (5)}, etc.], seem improbable, because if $k_2''(CH_2OH) \gg k_2'''(CH_3O)$ as assumed in this example, $k_3'(CH_2OH) \gg k_3(CH_3O)$ and $k_4'(CH_2OH) \gg k_4(CH_3O)$ are also expected to hold simultaneously, since the value of the ratio of k's, for two H acceptors CH_3O and CH_2OH, of the same H abstraction reaction from one common molecule or radical, i.e., k_2''/k_2''', k_3/k_3', or k_4/k_4', must not reciprocate remarkably one after the other in these three pairs (these are all exothermic).

(*C*-2): The possibility that the reaction passes through the stage where all the above elementary reactions take place to the comparable extents seems improbable from the next consideration.

We have seen $(CH_2OH) \propto (CH_3O)^{\frac{1}{2}}$ in two extreme cases; the same expression can be shown to hold near the point where all the reactions have the same velocities. Therefore, if $k(CH_3O)(M)$ is not much greater than $k'(CH_2OH)(M)$ (M = radicals and HCHO) at $\bar{t}$ the change of mechanism from somewhat like I (or II) to somewhat like III (or IV) would appear in the meantime of the reaction and this would cause an appreciable deviation of Δp curve from the first order. If $k(CH_3O)(M) \approx k'(CH_2OH)(M)$ at $\bar{t}$ the reaction would assume more and more the mechanism III (or IV) as the time elapses and the inconsistency between pressure and glycol curves would be seen.

(D) *Chain Decomposition of Peroxide*

The presence of the chain decomposition of peroxide, (0^a), (0^b), and $CH_2OH + CH_3OOCH_3 = CH_3OH + CH_2OOCH_3$ k_0''' (0^c), can be excluded as calculated below.

When (0^a) and (0^b) are added to the mechanism I or II [(2^c) being dropped for simplicity; the conclusion is the same since the contribution of (2^c) is only slight in the expression of CH_3O as shown before], we get

$$(\mathbf{DMP})/(\mathrm{DMP})_0 = \exp(-k_0\bar{t})/[1+C\{1-\exp(-k_0\bar{t})\}],$$

$$\frac{2k_0'(\mathrm{DMP})_0}{k_1(CH_3OH)+k_1'} > C > \frac{2k_0'(\mathrm{DMP})_0}{k_1(CH_3OH)+k_1'+3k_3(\mathbf{HCHO})/n} > \frac{k_0'(\mathrm{DMP})_0}{2\{k_1(CH_3OH)+k_1'\}},$$

$$\Delta p = 4(\mathbf{DMP})\ln[1+C'\{1-\exp(-k_0t)\}]/C'(nA+3),$$

$$C' = 2k_0'(\mathbf{DMP})/\{k_1(CH_3OH)+k_1'+3k_3(\mathbf{HCHO})/n\}.$$

By C or C' we can express the relative rate of (0^a) to those of other competing reactions at the respective origin of time. As shown in Fig. 3 (broken line, at 166.7°C) the deviation of this equation from the first order can be recognized sufficiently well if the extent of the contribution of (0^a) is corresponding to $C' \geq 5$ under the present experimental condition (166.7°C and I.P.R. = 17.4) and the accuracy of pressure measurement. Also we get $k_0 \doteqdot 1\times10^{-3}$ sec^{-1} for $C'=5$ as the lower limit of the true k_0 which is to be used in the above equation so that the calculated pressure curve coincides approximately with the observed one in the aerly stage.

On the other hand, we known $(\mathbf{DMP})/(\mathrm{DMP})_0 = 0.65$ from the material balance, then introducing this value and the lower limit of k_0 $(=10^{-3})$ into the first relation we get $C=0.02$, that is, the rate of (0^a) is less than 4 percent of the sum of the rates of (1) and (1^a) even at the beginning of the reaction.

Similar equations are obtained for the mechanism composed of III (or IV) and (0^c) and (0^b),§§ and the ratio [rate of (0^c)]/2[rate of $(2^b)+(5)$] is less than 0.03 at the beginning of the reaction, therefore we cannot expect by assuming the presence of the chain decomposition of peroxide to get the equations for pressure rise and glycol which are consistent with the observed fact.

From the arguments so far it seems the most probable that the mechanism I or II, with or without (1^a) and (2^c), is operative in the most part of the reaction period after $\bar{t}$; near the end of the reaction the relative concentration of CH_2OH to CH_3O becomes high and (2^a), (2^b), (3^a), and (4^a) may contribute to some extent or more, but they would affect the whole reaction only slightly as judged from the constancy of the rate constant in the range of 0–90 percent completion.

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§§ In this case we get

$$\{(\mathbf{DMP})/(\mathrm{DMP})_0\}^{\frac{1}{2}} \doteqdot \exp(-\tfrac{1}{2}k_0\bar{t})/[1+D(\mathrm{DMP})_0^{\frac{1}{2}}\{1-\exp(-\tfrac{1}{2}k_0\bar{t})\}],$$

$$\Delta p = 4k_3'(\mathbf{HCHO})\ln[1+D(\mathbf{DMP})^{\frac{1}{2}}\{1-\exp(-\tfrac{1}{2}k_0t)\}]/mk_0''',$$

where

$$D = \varphi_{(t)}k_0'''/\{k_0(k_2''+k_5)\}^{\frac{1}{2}}.$$

(E) *Isomerization of CH_3O, and the Activation Heats*

To see the variation of Δp_f with I.P.R, the following approximations are adopted in the mechanism I or II of (A-1):

(i) $(\mathbf{HCHO})=(\text{HCHO})_m$
(ii) t_m is assumed to be the same for all I.P.R.'s.
(iii) Equation (7) is applicable from the beginning of the reaction; this may be reasonable since the extrapolation of (7) to $t<0$ coincides with the observed curve quite well, and as described before pressure curves for all I.P.R.'s are of the first order from the beginning of the reaction.

Then, from (8), using (6) and (9), we get

$$\frac{(\mathbf{HCHO})}{(\text{DMP})_0}=\frac{nk_2}{k_3}\left\{\frac{k_0\exp(-k_0t_m)}{k_5(\text{DMP})_0}\right\}^{\frac{1}{2}}\left\{\frac{k_1(\text{I.P.R.})/k_3+k_1'/k_3(\text{DMP})_0}{k_1(\text{I.P.R.})/k_3+k_1'/k_3(\text{DMP})_0+3(\mathbf{HCHO})/n(\text{DMP})_0}\right\}^{\frac{1}{2}},$$

and from (7)

$$\frac{\Delta p_f}{(\text{DMP})_0}=\frac{4(\mathbf{HCHO})/(\text{DMP})_0}{k_1(\text{I.P.R.})/k_3+k_1'/k_3(\text{DMP})_0+3(\mathbf{HCHO})/n(\text{DMP})_0}.$$

At first the absence of (1^a) is assumed, then on calculation using $nk_1/k_3=0.030$ (given later) the change in (**HCHO**) is found to be quite small for the wide variation of I.P.R. [e.g., 0.086 (observed 0.08 ± 0.01) for I.P.R.$=5$, and 0.119 for 30, both at $(\text{DMP})_0=23$ mm]. The result on Δp_f is shown in Fig. 2 by the thick line for the case of $(\text{DMP})_0=23$ mm. (The same line is obtained for both mechanisms.)

The slope of this line differs somewhat from that of the observed one, presumably because of the omission of (1^a) and/or the assumption (ii) on t_m. If the discrepancy of slope is assumed to be caused solely by the omission of (1^a), good coincidence of both lines can be attained by the assignment of proper values to nk_1/k_3 and nk_1'/k_3, respectively, 0.021 and 3.5 mm ($=1.3\times10^{-7}$ mole/cc) at 166.7°C, that is, 29 percent of total CH_2OH is produced by (1^a) at I.P.R.$=17.4$. This value 29 percent is considered to be the upper limit of the contribution of (1^a) in the present case, as it can be shown that the slope of the calculated line for $k_1'=0$ approaches the observed one to some extent when the change of t_m with I.P.R. is taken into account.

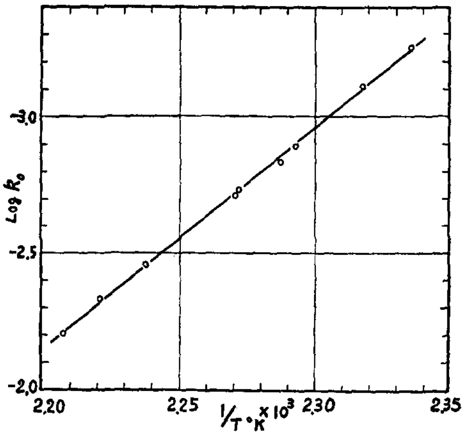

FIG. 4. Activation heat plot for the dissociation of dimethyl peroxide.

From the value of nA given before, in which $(\mathbf{HCHO})/(\text{DMP})_0=0.11$ and $(\mathbf{CH_3OH})/(\text{DMP})_0=17.6$, we get $nk_1/k_3=0.030$ for the case of $k_1'=0$ [$+0.004\sim-0.008$ with sufficient allowance for the change of (CH_3OH) during the reaction, fluctuation of I.P.R. in each run, precision of pressure measurement and HCHO analysis, and the presence of glyoxal and glycolaldehyde amounting to 0.02 which might be involved in $(\mathbf{HCHO})=0.11$], hence the difference of the activation heats, E_1-E_3, is obtained to be $3.1\left\{\begin{matrix}+0.3\\-0.1\end{matrix}\right\}$ kcal for the mechanism I, or $3.7\left\{\begin{matrix}+0.3\\-0.1\end{matrix}\right\}$ kcal for II [each value is raised by 0.3 kcal when (1^a) takes place to the maximum], assuming that the collision numbers and the steric factors of these two reactions are respectively the same.

Also, we get $k_0'/k_1<0.7$ or <1.0 at 166.7°C, respectively, for $k_1'=0$ or $nk_1'/k_3=3.5$ mm, from the value of C obtained before.

From the plot of $\log k_0$ *vs* $1/T$ (Fig. 4), the activation heat for (0) is found as 36.9 kcal (accurate within ±1.1 kcal), and finally we have $k_0=4.1\times10^{15}\exp(-36.9\ \text{kcal}/RT)$ sec^{-1}, and the entropy of activation$=+10.2$ eu at 166.7°C.

We may regard the value 36.9 kcal as a good approximation of the dissociation heat of the O−O bond in dimethyl peroxide. It is of interest to note that this value is close to those of di-*t*-butyl peroxide [39.1 kcal, frequency factor$=3.2\times10^{16}$;[9] 36 kcal, $(4\sim7)\times10^{14}$ [10]] and di-*t*-amyl peroxide ($37\sim41$ kcal[9]), and *not less* than that of dipropyl (~35 kcal[11,12]) or diethyl (31.7 kcal, 2.1×10^{13} [11]) peroxide.

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