BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 1643—1650 (1966)

The Reaction of Oxygen Atoms with Dimethyl Ether*

By Yoshimasa TAKEZAKI, Sadayuki MORI and Hironobu KAWASAKI

Institute for Chemical Research, Kyoto University, Sakyo-ku, Kyoto

(Received November 6, 1965)

The gas-phase reaction of dimethyl ether with oxygen atoms produced by the mercury photosensitized decomposition of nitrous oxide has been studied by means of quantitative determinations of the reaction products. Characteristic products are water, methanol, formaldehyde, carbon monoxide, methoxy ethanol and methyl formate. The possible mechanisms of the oxygen attack on the substrate have been considered, and the following steps postulated on the basis of the relative importance of these products and their time variations:

$O + CH_3OCH_3 \xrightarrow{k_E} OH + CH_3OCH_2$, $OH + CH_3OCH_3 \longrightarrow H_2O + CH_3OCH_2$ and $CH_3OCH_2 + OH \longrightarrow CH_3O + CH_2OH$.

The rate constant, k_E, of the first step has been determined in the competitive reaction with *n*-butane as:

$$k_E = 6.3 \times 10^{10}\exp(-4700/\boldsymbol{R}T)\ \mathrm{l.\ mol^{-1}\ sec^{-1}}.$$

Rate data have been increasingly accumulated in recent years on the reactions of oxygen atoms with such saturated molecules as hydrogen and paraf-

---

* This paper was read at the International Conference on Photochemistry, Tokyo, 1965.

fins.[1-4] However, papers dealing with oxygen-containing compounds are still scant (Ref. 1f and Ref. 5), and the mode of the initial attack by oxygen seems still not to be conclusively known.

The mechanisms proposed hitherto may be classified into the following four types: hydrogen abstraction, a common type of reaction in atomic or monoradical reactions (ex., $CH_3CHO+O \rightarrow CH_3CO+OH$),[5] direct insertion into a C–H bond (ex., $CH_4+O \rightarrow CH_3OH$),[2] the displacement of one or two group(s) by O (ex., $n\text{-}C_4H_{10}+O \rightarrow CH_2O + H_2 + :CHC_2H_5$ or $H_2 + CH_3CHO + :CHCH_3$,[3] $(CH_3)_3CH+O \rightarrow (CH_3)_2CO+CH_4$ or $(CH_3)_2CO+H+CH_3$),[6] and the combination of an oxygen atom with two hydrogen atoms to form water (ex., $CH_4+O \rightarrow :CH_2+H_2O$).[7]

In all these instances, however, the methods of producing oxygen atoms vary; in the discharge in oxygen or water vapor, the formation of oxygen atoms of a single electronic energy state seems hardly to be expected, and the co-existence of oxygen molecules must obscure the proper reactions of oxygen atoms. Moreover, in high-temperature oxidation the features of the reaction may differ markedly from those prevailing in normal temperatures, further, in microwave discharge where the oxygen atom concentration is very high, the reactions of oxygen atoms with the produced radicals may complicate the discrimination of the primary action of oxygen atoms on the substrate.

In view of these facts, with the intention of determining the features of the oxygen attack on the oxygen-containing *saturated* compounds, dimethyl ether (referred to as DME hereafter) has been taken as an example, while as a source of oxygen atoms the mercury-photosensitized decomposition of nitrous oxide was used, since it has been established by Cvetanović[8] that the oxygen atoms in the ground ^3P state are produced in this reaction:

$$Hg(^1S_0) + h\nu(2537\ \text{Å}) \rightarrow Hg^*(^3P_1)$$
$$Hg^* + N_2O \rightarrow Hg(^1S_0) + N_2 + O(^3P_2).$$

The qualitative aspects of this reaction have already been reported by the present authors,[9] but in this paper a more detailed discussion based on the quantitative results will be given.

Experimental

The reaction was carried out in a static system of the usual type. A Vycor glass reactor (28φ×400 mm.,

TABLE I. G.L.C. CONDITIONS AND OTHER ANALYTICAL METHODS

Figures in the table denote the operation temperatures, °C, of g.l.c.

Column	A	B	C
H_2	35	24	
N_2, O_2			24
CO	70	24	
CO_2		107	
CH_4, C_2H_6, C_2H_4	70	107	
N_2O		107	
Column	D	E	F
N_2O	108	0	
$n\text{-}C_4H_{10}$		0	
DME	108	0	
H_2O	108/99		
CH_3OH	47		
Dimer	108		114
GTME	108		114
BMEE	108		114
$CH_3OC_2H_4OH$	99	119	82
$HCOOCH_3$	108		
$CH_3OC_2H_5$	47		
$CH_3OCH_2OCH_3$	108/47		
CH_3OOCH_3	108/47		
Ethylene oxide	108/47		
1, 4-Dioxane	108		114
$(CH_2OH)_2$			114
CH_3CHO	108		

Column		
A	Al_2O_3	2 m.
B	Active carbon	2.5 m.
C	Molecular sieve 5A	2 m.
D	D.O.P.+Polyethylene glycol 4000	2 m.
E	Dibenzyl ether	2 m.
F	Silicone oil 550	3 m.

Other determinations or detections:

HCHO	Colorimetry with Schiff's reagent in acid condition
H_2O_2	Coloration with KI solution
Higher *N*-oxides	Griess' test[10]
$HCOOCH_3$	Hg_2Cl_2 precipitation when boiling with $HgCl_2$ solution.

---

[1] a) E. L. Wong and A. E. Potter, Jr., *J. Chem. Phys.*, **39**, 2211 (1963) for H_2 and CH_4. b) V. V. Azatyan, A. B. Nalbandyan and Meng-Yuan Ts'ui, *Kinetika i Kataliz.*, **5**, (2) 201 (1964) for CH_4; *Dokl. Akad. Nauk SSSR*, **147**, 361 (1962) for C_2H_6; ibid., **36**, (1) 23 (1963) for C_2H_6 and C_4H_{10}. c) V. V. Azatyan, V. V. Voedodskii and A. B. Nalbandyan, *Kinetica i Kataliz.*, **2**, 340 (1961) for H_2. d) H. W. Ford and N. Endow, *J. Chem. Phys.*, **27**, 1277 (1957) for $n\text{-}C_4H_{10}$ and 3-Meheptane. e) M. A. A. Clyne, "9th Symp. on Combustion," Academic Press, New York (1963), p. 211 for H_2. f) L. I. Avramenko, "Advances in Photochemistry, II," Interscience Publishers, New York (1963), p. 57 for CH_4, C_2H_6 and $n\text{-}C_4H_{10}$.

[2] L. I. Avramenko and R. V. Kolesnikova, *Dokl. Akad. Nauk SSSR*, **91**, 107 (1953).

[3] L. I. Avramenko, R. V. Kolesnikova and G. I. Savinova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **1963**, 976.

[4] L. Elias and H. I. Schiff, *Can. J. Chem.*, **38**, 1657 (1960).

[5] R. J. Cvetanovic, ibid., **34**, 775 (1956).

[6] F. J. Wright, *J. Chem. Phys.*, **38**, 950 (1963).

[7] E. W. R. Steacie and N. A. D. Parlee, *Can. J. Research*, **B16**, 203 (1938).

[8] R. J. Cvetanović, *J. Chem. Phys.*, **23**, 1203 (1955); ibid., **30**, 19 (1959); S. Sato and R. J. Cvetanović, *Can. J. Chem.*, **36**, 970 (1958).

[9] H. Kawasaki and Y. Takezaki, *Bull. Inst. Chem. Res., Kyoto Univ.*, **42**, 378 (1964).

[10] F. D. Treadwell, "Lehrbuch der Anal. Chem. I," Fr. Deuticke, Leipzig (1935), p. 337.

210 cc.) was placed parallel to a low-pressure mercury lamp ($25\phi \times 436$ mm., Toshiba Electric Co. germicidal lamp GL-15, dc-operated, 15 W.) in an air bath furnished with heating elements in the wall and a fan at the bottom. The Vycor glass cuts off the light wavelength shorter than 2200 Å; the temperature variation in the reactor was kept within 2°C during the reaction by means of forced air circulation. The reactant mixture was saturated with mercury vapor at room temperature prior to the reaction.

At the end of the irradiation, the reactor was warmed up to 70°C in order to vaporize the heavy liquid products; almost all the products, except for a trace of the heaviest ones, were then drawn out through a liquid nitrogen trap by means of a Töpler pump; then the permanent gases and vapors, and liquids condensing at room temperature were separately analyzed, mainly by gas chromatography, as is shown in Table I, where the products were identified with the authentic samples in 2 or 3 different coulmns (the methods of preparations of some of the samples have been given in the previous paper).9)

The impurities of the reactants as measured by g.l.c. are: $O_2 < 0.00\%$, $N_2 = 0.15\%$, $CH_4 = 0.13\%$ in N_2O purified by the evacuation of the solid in a liquid nitrogen trap; $CH_3OH < 0.01\%$, $H_2O < 0.00\%$ in DME purified by repeated bulb-to-bulb distillation; the guaranteed purity of *n*-butane obtained from Takachiho Co. = 99.8%.

Results

The Mercury-photosensitized Decomposition of DME.—In order to distinguish the reaction products of oxygen-atom reactions from those of the mercury-photosensitized decomposition of DME which takes place concomitantly, we have to know about the products of the latter reaction alone. This reaction has already been studied by Marcus et al.11) in a flow system, but in order to make comparison easier, product analyses have now been performed in a static system under the conditions of the present investigation. Typical results are given in the columns 2 and 4 of Table II; the main products are H_2 and $(CH_3OCH_2)_2$ (ethylene glycol dimethyl ether; abbr. Dimer), together with small quantities of $CH_3OCH_2CH_2OCH_2CH_2OCH_3$ (bis-(β-methoxy ethyl) ether; abbr. BMEE or Trimer) and $CH_3OCH_2(OCH_3)CHCH_2OCH_3$ (glycerol trimethyl ether; abbr. GTME or Trimer). In column 4 are given those products which might exist but could not be detected, or which existed as only trace amounts.

TABLE II. PRODUCTS OF Hg PHOTOSENSITIZED REACTIONS

			Compds. not detected or $<0.0\%$ in both cases
Initial			
DME, mmHg	100	100	
N_2O, mmHg	0	300	
Temp., °C	30	30	
Irradiation	15 min.	1 hr.	
Product mol. % to charged DME			
DME	−20.3	−58.2	CO_2
N_2	—	30.0	O_2
H_2	13.4	3.1	CH_4
CO	0.0	2.0	C_2H_6
H_2O	0.0	27.6	C_2H_4
CH_3OH	0.0	3.8	H_2O_2
HCHO	0.0	0.7	$CH_3OC_2H_5$
Dimer*	4.8	4.6	CH_3OCH_2-OCH_3
GTME }* Trimer	0.8	1.9	CH_3OOCH_3
BMEE }	0.3	0.5	Ethylene oxide
$CH_3OCH_2CH_2$-OH	0.0	0.4	1, 4-Dioxane
$HCOOCH_3$	0.0	0.2	CH_2OHCH_2-OH
Unidentified high boil. compds.		4 kinds each ca. 0.2%	CH_3CHO
			Oxides of N

* For abbreviations see the text.

The present results generally agree with those of Marcus11) obtained at room temperature except for the additional observation of trimers; these products may be explained by:

$$\left.\begin{aligned} &CH_3OCH_3 + Hg^* \\ &\qquad \rightarrow CH_3OCH_2 + H + Hg \\ &CH_3OCH_3 + R \\ &\qquad \rightarrow CH_3OCH_2 + RH \\ &2CH_3OCH_2 \\ &\qquad \rightarrow (CH_3OCH_2)_2 \text{ Dimer} \end{aligned}\right\} \begin{array}{l} (\text{Marcus})^{11)} \\ R = H \text{ or} \\ \text{any radical} \end{array}$$

$$(CH_3OCH_2)_2 + R \begin{cases} \rightarrow CH_3OCH_2CH_2OCH_2\cdot \\ \xrightarrow{+CH_3OCH_2} CH_3OCH_2CH_2\text{-} \\ OCH_2CH_2OCH_3 \text{ (BMEE)} \\ \rightarrow CH_3OCH_2\dot{C}HOCH_3 \\ \xrightarrow{+CH_3OCH_2} CH_3OCH_2CH\text{-} \\ (OCH_3)CH_2OCH_3 \text{ (GTME)}\cdot \end{cases}$$

One point to be noticed in connection with the following discussion is the absence of carbon monoxide, methane, ethane, methanol, formaldehyde, 1, 4-dioxane and ethylene oxide, which would rule out the possibilities of the $CH_3OCH_2 \rightarrow CH_3 + CH_2O$ and $CH_3OCH_2 + R \rightarrow \cdot CH_2OCH_2\cdot + RH$ reactions at room temperature.

In this study it is necessary to know the ratio of the decomposition of DME by the excited mercury to that of N_2O; the effective quenching cross-section of N_2O decomposition (Reaction 2 in the next scheme) has been given by Cvetanović12) as 12.6 Å^2, but concerning DME the only available value is for the total quenching (7 Å^2 for (1)+(1′)13)). Therefore, a rough estimation was made, according

---

11) R. A. Marcus, B. deB. Darwent and E. W. R. Steacie, *J. Chem. Phys.*, **16**, 987 (1948).

12) R. J. Cvetanović, ibid., **23**, 1208 (1955).

13) B. deB. Darwent and M. K. Phibbs, ibid., **22**, 110 (1954).

to the following scheme, of the effective cross section for DME decomposition, (1), from the rate measurements of the hydrogen formation in DME alone and of the nitrogen formation in the mixture of DME and nitrous oxide. The results are represented in Fig. 1.

$$
\begin{array}{llll}
Hg(^1S_0)+h\nu & \rightarrow Hg^*(^3P_1) & & \text{Rate const.} \\
Hg^* & \rightarrow Hg+h\nu & & (k_0) \\
Hg^*+DME & \rightarrow Hg+CH_3OCH_2+H & (1) & (k_1) \\
 & \rightarrow Hg'(^3P_0)+DME & (1') & (k_1') \\
Hg^*+N_2O & \rightarrow Hg+N_2+O(^3P_2) & (2) & (k_2) \\
 & \rightarrow Hg'+N_2O & (2') & (k_2')
\end{array}
$$

We then have, in DME alone:

$$1(\text{rate } H_2) = (1/I_{abs})(1 + k_1'/k_1) + (k_0/k_1 I_{abs})/(DME) \qquad \text{(Fig. 1-A)}$$

and in the mixture of DME and N_2O:

$$1/(\text{rate } N_2) = (1/I_{abs})(1 + k_1'/k_1)(k_1/k_2) \times \{(k_2 + k_2')/(k_1 + k_1') + (DME)/(N_2O)\} \qquad \text{(Fig. 1-B)}$$

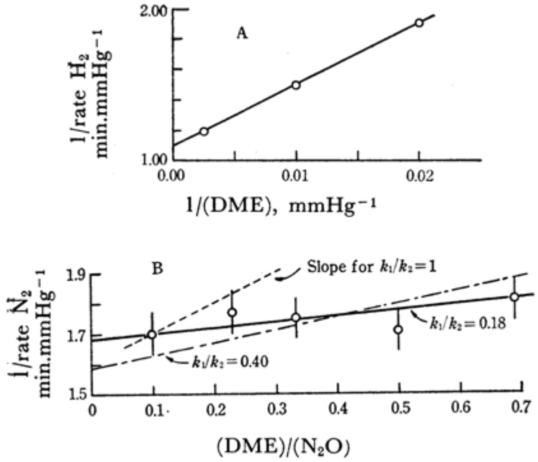

Fig. 1. Determination of cross section of DME.

	k_1/k_2	$(k_2+k_2')/(k_1+k_1')$	$k_0/(k_1+k_1')$
mean	0.18	9.55	3.83 mmHg
max.	0.40	3.92	

In this treatment we have omitted the further reactions of Hg', $Hg'+N_2O \rightarrow Hg+N_2+O$ and $Hg'+DME \rightarrow Hg+CH_3OCH_2+H$, following the argument of Cvetanović;[12] though the apparatus used here was not adequate for the exact determination, we have the cross section of $\sigma_{DME} \doteqdot 2$ Å^2 with the upper limit of 5 Å^2 for (1).

The Reaction of Oxygen Atoms with DME.—In the photo-reaction of a mixture of DME, nitrous oxide and mercury, an effort has been made to determine as many reaction products as possible in a large reactor (88ϕ × 612 mm., 2941 cc.; lamp coaxially enclosed in a Vycor sheath) and with prolonged irradiation. The results are given in Table II, columns 3 and 4, together with the conditions.

Characteristic products are water, methanol, formaldehyde, carbon monoxide, methoxy ethanol and methyl formate; moreover, though in quite small quantities, at least four kinds of peaks were observed in the gas chromatogram after the elution of the trimers. As may be seen in the last column of Table II, no lower hydrocarbons and carbon dioxide were present, and no molecular oxygen could be found, even after a long irradiation, if DME was present in an amount 1/80 of nitrous oxide at the beginning.

In Fig. 2 the variation of products with the irradiation time in a standard reactor is represented; the N_2O/DME ratio was kept high so as to reduce the mercury-photosensitized decomposition of DME (these conditions will be referred to as the standard conditions hereafter). Most of the oxygen atoms produced seem to appear as water, and from the features of the curves we see that the formation of the dimer is followed by subsequent reactions leading to trimers and other unknowns, and that carbon monoxide is produced by a sequence of steps.

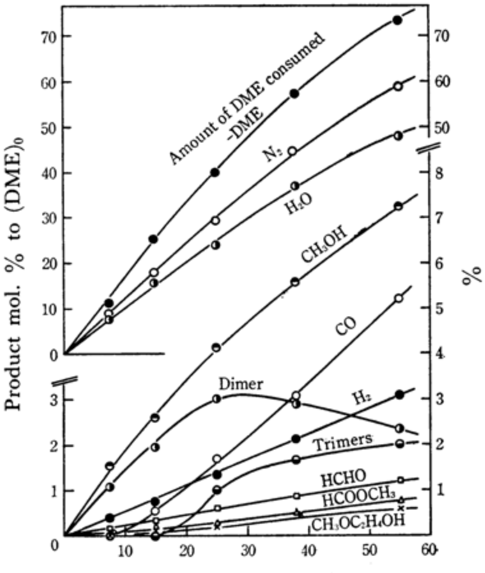

Fig. 2. Time dependence of products.
Standard condition: $(DME)_0 = 50$ mmHg, $(N_2O)_0 = 500$ mmHg, 30°C

The material balances on C, H and O in terms of the identified products are:

$$N_2 = H_2O + HCOOCH_3 + 1/2(CH_3OH + CH_3OC_2H_4OH + HCHO + CO)$$

$$\text{Obs. } N_2 = 30.0\% \text{ to } (DME)_0$$
$$\text{Calc.} \quad = 31.1\%,$$

$$\begin{aligned}\text{Consumed DME} &= 2H_2O + 3/2CH_3OH \\ &+ 1/2CH_3OC_2H_4OH + 2H_2 - (\text{Trimers} \\ &+ 1/2HCHO + 5/2CO + HCOOCH_3)\end{aligned}$$

Obs. consumed DME $=58.2\%$

Calc. $=61.0\%$,

$$\begin{aligned}H_2O &= \text{Dimer} + 2\text{Trimers} + 1/2CH_3OC_2H_4OH \\ &+ 1/2HCHO + 3/2CO - (H_2 + HCOOCH_3 \\ &+ 1/2CH_3OH)\end{aligned}$$

Obs. $H_2O=27.6\%$

Calc. 10.5% .

In these equations the balances not involving dimer are fairly good, but the last one is far from sufficient, probably due to a number of missing higher products small in quantity.

Discussion of the Mechanism

The Mode of the O Attack on DME.—Following elementary steps may be conceivable in the initial attack of oxygen atoms according to the classification given in the introduction:

$O + DME \rightarrow$:

1. $\rightarrow OH + CH_3OCH_2$,

$OH + CH_3OCH_3 \rightarrow H_2O + CH_3OCH_2$,

2. $$\left.\begin{array}{l}\xrightarrow{\qquad\qquad\qquad} \\ \rightarrow CH_3OOCH_3 \rightarrow\end{array}\right\} 2CH_3O, \qquad (a)$$

$$\rightarrow CH_3OCH_2OH \rightarrow \left\{\begin{array}{ll}CH_3O + CH_2OH & (b) \\ CH_3OCH_2 + OH, & (c)\end{array}\right.$$

3. $\rightarrow HCOOCH_3 + H_2$ or $2H$, (a)

$\rightarrow CH_3O + CH_2O + H$, (b)

4. $\rightarrow CH_3OCH\!: + H_2O$,

$\rightarrow \cdot CH_2OCH_2\cdot + H_2O$.

Case 1 is quite attractive to account for the production of a large amount of water, an amount which is close to that of the oxygen atoms produced, which in turn corresponds to about a half of the DME consumed. However, other possibilities leading to the water formation should be considered here; in the present study the following three processes can conceivably account for the origins of OH:

$$H + O + M \rightarrow OH + M, \quad H + N_2O \rightarrow OH + N_2 \text{ and } H_2 + O \rightarrow OH + H.$$

However, since these hydrogens can all originate from the photosensitized decomposition of DME, calculation has been made on the rate of hydrogen atom formation in the competitive quenching of Hg* in the mixture of DME and nitrous oxide under the standard experimental conditions ($(N_2O)_0=500$ mmHg, $(DME)_0=50$ mmHg, 30°C) using the effective cross section, σ_{DME}, obtained in the preceding section. Then, by comparing the calculated rate of hydrogen atom production (0.023 mmHg/min.) with the observed rate of water formation (0.47 mmHg/min. in Fig. 2), it could be concluded that the photosensitized decomposition of DME contributes at most 5% to the total water formation. (It is of interest to note that the observed rate of hydrogen production (0.027 mmHg/min.) is close to the calculated rate of hydrogen atom production.)

Case 2 involves direct double decomposition into two radicals or insertion into a C–H or O–C bond; but since the insertion reactions are highly exothermic, since the O–O bond energy is only 36.9 kcal. in dimethyl peroxide,[14] and since the hemiacetal is known to be too unstable to exist in a free state, the inserted molecules will eventually decompose into the radicals shown in the scheme. We could not prove the presence of dimethyl peroxide.

The two steps, 2 (a) and 2 (b), cannot be the main courses of the oxygen attack, however, since they fail to explain the formation of a large amount of water, and the sum of methanol (resulting from $RH+CH_3O$ or $RH+CH_2OH$) and its decomposition products, formaldehyde and carbon monoxide and methoxy ethanol (assuming the reaction $CH_2OH+CH_2OCH_3$), is much less than the amount of oxygen produced. Further, ethylene glycol (by $2CH_2OH$) and formal (by $CH_2OCH_3+CH_3O$) could not be detected; they may be supposed to be produced if these mechanisms are predominantly operative. Case 2 (c) is not distinguished from Case 1. However, in any case, it should be admitted that for these insertion reactions to take place, spin conservation rule has to be violated, because the oxygen atom participating here is in the triplet state.

In Case 3, (a) would contribute at most a small portion of the total oxygen attack, as judged from the minuteness of methyl formate which, according to the result of Thynne's experiments,[15] has the usual reactivity towards the subsequent radical attack. Further, as will be shown later, there is evidence that methyl formate can be produced by the reaction of OH+DME in the absence of oxygen atoms. The fact that the total amount of $1/2H_2O+H_2$ is by far greater than that of $CH_3OH+HCHO+CO+CH_3OC_2H_4OH$ excludes 3-(b) as the main course of oxygen atom reaction.

As for Case 4, none of the recombination products expected from this mechanism (ethylene oxide, 1, 4-dioxane and $(CH_3OCH\!:)_2$) were found. Although this does not lead to the complete exclusion of this mechanism, the elementary reactions involving biradical formation in one process do not seem to proceed so easily as to compete with monoradical formation steps, even for the

---

14) Y. Takezaki and C. Takeuchi, ibid., **22**, 1527 (1954).

15) C. J. Thynne and P. Gray, *Trans. Faraday Soc.*, **59**, 1140 (1963); C. J. Thynne, ibid., **58**, 676 (1962).

exothermic reaction, at least to an extent enough to account for a large amount of water.

Thus the abstraction of the hydrogen atom (Case 1) may be concluded to be the most predominant process, although the minor contributions of other modes cannot be entirely ruled out.

Another oxygen atom reaction to be considered is $CH_3OCH_2+O \rightarrow CH_3OCH_2O$ or $CH_3O+HCHO$; the former must have a large rate constant and has been taken into account in the argument of Wright on the reaction of oxygen atoms with isobutane.⁶⁾ However, both these reactions can be shown to be negligible under the present experimental conditions by the following considerations.

Consider the following scheme which is simplified but sufficient to get the upper limit values necessary for the present discussion:

$$Hg+h\nu \rightarrow Hg^*$$

		Rate const.
$N_2O+Hg^* \rightarrow N_2+O+Hg$		
$O+DME \rightarrow CH_3OCH_2+OH$	(E)	k_E
$OH+DME \rightarrow CH_3OCH_2+H_2O$	(E′)	k_E'
$2CH_3OCH_2 \rightarrow (CH_3OCH_2)_2$	(3)	k_3
$O+CH_3OCH_2 \rightarrow CH_3OCH_2O \rightarrow \cdots$	(4)	k_4
$\rightarrow CH_3O + CH_2O\cdot$	(4′)	k_4' .

The steady concentration of the O atom is:

$$(O) = \frac{I_{abs}}{k_E(DME) + k_4'(CH_3OCH_2) + \cdots}$$
$$\leq \frac{d(N_2)/dt}{k_E(DME)} .$$

Therefore, under the standard conditions (rate N_2(obs.)$=0.65$ mmHg/min. $=5.8\times10^{-7}$ mol./l. sec. at 30°C, (DME)$=50$ mmHg$=2.68\times10^{-3}$ mol./l.), we have $(O)\lesssim 7.7\times10^{-12}$ g.-atom/l. and $\beta\equiv (DME)/(O) \gtrsim 3.5\times10^8$.

Now, k_3 and k_4 should be close to the collision numbers, i. e., $k_4' < k_3 \fallingdotseq k_4 \fallingdotseq 10^{11}$ l./mol.sec. and $k_E=2.8\times10^7$ l./mol.sec. at 30°C, as will be established later; then, dropping unimportant terms in numerical calculation, we have $(CH_3OCH_2) \fallingdotseq \{(O)(DME)k_E/k_3\}^{1/2}$ within an accuracy of 0.2%; finally the following expressions are obtained:

$$\frac{\text{rate }(4')}{\text{rate }(3)} < \frac{\text{rate }(4)}{\text{rate }(3)} \fallingdotseq \left(\frac{k_3}{2k_E\beta}\right)^{1/2}$$
$$\lesssim 1.6\times10^{-3} \text{ and}$$
$$\frac{\text{rate }(4')}{\text{rate }(E)} < \frac{\text{rate }(4)}{\text{rate }(E)} \fallingdotseq \left(\frac{k_4}{k_E\beta}\right)^{1/2}$$
$$\lesssim 3.2\times10^{-3}.$$

Thus the reactions between the oxygen atom and CH_3OCH_2 can well be ignored with respect to both reactants.

The Origin of Methanol and Methoxy Ethanol.—Since the $CH_3OCH_2 \rightarrow CH_3+CH_2O$ decomposition has been proved to be unlikely in the preceding section, combination of CH_3 and OH cannot be the source of methanol. Hence, the steps responsible for the formation of methanol are probably the C–O bond fission of DME or derived radicals to produce CH_3O or CH_2OH; however, $CH_3OCH_2 \rightarrow CH_3O+:CH_2$ is too endothermic to occur at normal temperatures, and the elementary steps, $O+DME \rightarrow 2CH_3O$, CH_3O+CH_2OH, or CH_3O+CH_2O+H and $O+CH_3OCH_2 \rightarrow CH_3O+CH_2O$, have already been ruled out. Therefore, we would like to propose here:

$$CH_3OCH_2 + OH \rightarrow (CH_3OCH_2\cdots OH)$$
$$\rightarrow CH_3O+CH_2OH+21 \text{ kcal./mol.} \quad (5)^*$$

The assumption that the transient complex of the hemiacetal type decomposes instantly at the weakest methyl C–O bond would be reasonable because of the extreme instability of hemiacetal just mentioned. Moreover, since OH and $CH_3 \cdot OCH_2$ are the most abundant radicals during the reaction, this inter-radical process may explain the medium amount of methanol and also the minute amount of methoxy ethanol* which have resulted from

$$CH_2OH \text{ or } CH_3O + RH \rightarrow CH_3OH + R$$
$$CH_3OH + R \rightarrow CH_2OH + RH$$
$$CH_2OH + CH_3OCH_2 \rightarrow CH_3OCH_2CH_2OH.$$

However, no positive evidence was obtained on the presence of the products to be expected from the following equations when CH_3O and CH_2OH were present:

$$2CH_2OH \rightarrow (CH_2OH)_2 \quad \text{(trace?)}$$
$$CH_3O + CH_2OCH_3 \rightarrow CH_3OCH_2OCH_3$$
$$\text{(rather unstable?)}$$

Further, the possibility of the $OH+CH_3OCH_2 \rightarrow CH_3OH+HCHO$ reaction cannot be entirely ruled out, though this cannot be the main source of methanol since the observed methanol /(HCHO +CO) ratio is less than unity.

In order to test above-mentioned postulate—methanol formation without the participation of the oxygen atom, a supplementary study was made on the reaction of DME with the OH radicals produced by the photolysis of hydrogen peroxide. It has been well established that H_2O_2 produces

---

* The heat of reaction is calculated using the data given by Gray¹⁶⁾ and Field¹⁷⁾. The approximate calculation as before has given the lower limit of rate(5)/rate(E′) or rate(5)/rate(3) as ca. 0.02 when $kE'=10^{11}\exp(-6000/\boldsymbol{RT})$ l./mol.sec., which is assumed, by referring to other OH reactions¹⁸⁾, to be the highest value for this reaction.

16) P. Gray, *Chem. Revs.*, **59**, 239 (1959).

17) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York (1957), p. 137.

18) Ref. 1f, p. 32.

2OH by 2537 Å light,[19] and the decomposition into $O+H_2O$ has been stated to be implausible at least in the gas phase.[19] The results are as follows:

DME 93 mmHg, H_2O_2 (87% concn.), 70°C, 2537 Å, 1 hr.;

CH_3OH 3.7%, HCHO 0.3%, $CH_3OC_2H_4OH$ 0.2%, Dimer 4.0%, GTME 1.0%, BMEE 0.2%, CO 1.2%, $HCOOCH_3$ 0.7%, relative to $(DME)_0$ respectively.

Of course, no methanol, formaldehyde or carbon monoxide could be found, either when the mixture of DME and hydrogen peroxide was merely kept at 70°C, or when the mixture of DME and oxygen, the latter being a product on the heating of hydrogen peroxide, were irradiated by a 2537 Å light. The presence of the expected products supports the proposed mechanism strongly; furthermore, the methyl formate found here suggests that the presence of this compound in the reaction of the oxygen atom cannot be evidence for Case 3-(a) in the preceding section.

The Rate Constant of $O+CH_3OCH_3 \rightarrow OH + CH_3OCH_2$.—With the aim of determining the absolute rate constant of the first attack of oxygen on DME, the rate of the consumption of each substrate has been measured in the competetive reaction of oxygen atoms with DME and *n*-butane; the rate for the latter had been determined to be $k_B=(3.01\pm0.96)\times10^{10}\exp(-4200\mp200)/\boldsymbol{R}T$ l./mol.sec. by Elias and Schiff.[4]

According to the discussion above, we take:

	Rate const.
$O + CH_3OCH_3 \rightarrow OH + CH_3OCH_2$	k_E
$OH + CH_3OCH_3 \rightarrow H_2O + CH_3OCH_2$	k_E'
$O + n\text{-}C_4H_{10} \rightarrow OH + C_4H_9$	k_B
$OH + n\text{-}C_4H_{10} \rightarrow H_2O + C_4H_9$	k_B'

as the sole substrate-consuming steps. This scheme should hold only for the early stage of the reaction; further, it implies the neglect of the following cross reaction:

$$C_4H_9 + CH_3OCH_3 \rightleftarrows C_4H_{10} + CH_3OCH_2 - 0.6 \text{ kcal.}^{**} \quad k_E'' \text{ and } k_B'',$$

that is, we are to assume *tentatively* that the net extent of this reaction (second term) is negligible as compared with the main substrate-consuming reactions (first term) in

$$\frac{-d(DME)}{dt} = \{k_E(O) + k_E'(OH)\}(DME) + \{k_E''(C_4H_9)(DME) - k_B''(C_4H_{10})(CH_3OCH_2)\},$$

$$\frac{-d(C_4H_{10})}{dt} = \{k_B(O) + k_B'(OH)\}(C_4H_{10}) - \{k_E''(C_4H_9)(DME) - k_B''(C_4H_{10})(CH_3OCH_2)\}.$$

Therefore, we have

$$\alpha \equiv \frac{\ln[(DME)_0/(DME)_t]}{\ln[(C_4H_{10})_0/(C_4H_{10})_t]} = \frac{\int_o^t (O)dt + (k_E'/k_E)\int_o^t (OH)dt}{\int_o^t (O)dt + (k_B'/k_B)\int_o^t (OH)dt} \cdot \frac{k_E}{k_B}.$$

In solving this, a further assumption is made that the ratios of the reaction rates between O and OH are the same for both substrates, i. e., $k_E'/k_E=k_B'/k_B$; then we get a simple relation $\alpha=k_E/k_B$. In order for this assumption to hold over the entire range of temperature, however, the next two conditions must be satisfied:

$$\frac{Z_E'/Z_E}{Z_B'/Z_B} \cdot \frac{P_E'/P_E}{P_B'/P_B} = 1$$

$$\text{and } E_E - E_E' = E_B - E_B'.$$

(*Z*, *P* and *E* have the usual meanings.)

As to the collision numbers, this ratio has been shown to be unity by calculation, but, strictly speaking, there is no such intrinsic necessity for the remaining two factors. However, the thermodynamical situations are almost the same in these two sets of exothermic reactions,

$$\Delta H_E = -8.4 \text{ kcal./mol.} \quad \Delta H_B = -7.8^{**}$$

$$\Delta H_E' = -25.2 \quad \Delta H_B' = -24.6,$$

and the reaction center in the configuration of the activated complex is, in all these cases, thought to be the same, $-O\cdots H\cdots C\equiv$. Such being the case, the approximation of the equality of the ratios of steric factors and of the differences in activation heats may be accepted as being fairly reasonable.

Moreover, the correction factor by which the observed α should be multiplied to obtain k_E/k_B when the above-mentioned ratio deviates from unity is only 2 or so against a tenfold deviation of that ratio in both directions, as is seen in the next table calculated using the values obtained with the present approximation.

---

[19] D. H. Volman, "Advances in Photochemistry, I," Interscience Publishers, New York (1963), p. 69.

** Calculated from
$OH + H \rightarrow H_2O + 119.2$ kcal./mol.
$O + H \rightarrow HO + 102.4$
$n\text{-}C_4H_{10} \rightarrow H + C_4H_9 - 94.6$[20]
$CH_3OCH_3 \rightarrow H + CH_3OCH_2 - 94$[21]

[20] G. C. Fettis and A. F. Trotman-Dickenson, *J. Chem. Soc.*, **1961**, 3037.

[21] S. W. Benson and D. V. S. Jain, *J. Chem. Phys.*, **31**, 1008 (1959).

$\frac{k_E'/k_E}{k_B'/k_B}$	0.1	0.2	0.5	1	2	5	0
C for $\frac{k_E}{k_B}=C\alpha$	2.4	2.0	1.4	1.0	0.71	0.50	0.46

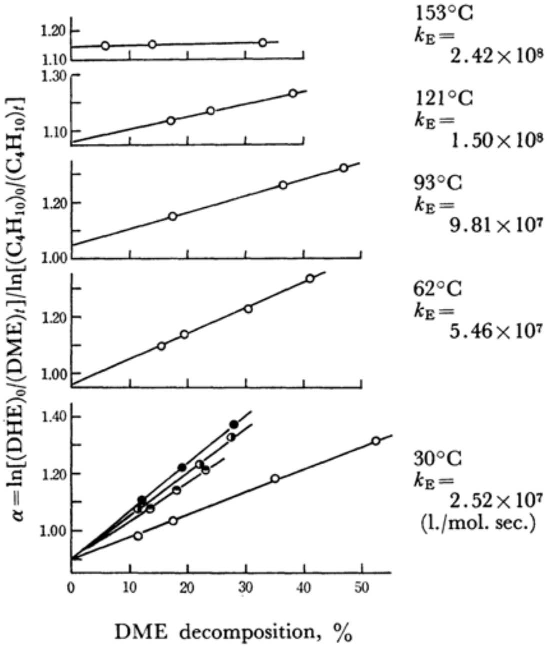

Fig. 3. Determination of α at various temperatures.

Initial pressures of reactants (mmHg)

	DME	n-C_4H_{10}	N_2O
○	24	24	405
●	43	22	419
◑	24	45	415
◓	42	44	395

As may be seen in Fig. 3, the α's lie near unity in the temperature range examined, but tend to increase as the decomposition proceeds, probably as a result of the accumulation of the primary products which would produce other radicals which replace the rôle of oxygen atom. Though the slopes differ according to the amounts of the reactants, the curves converge to one point at zero conversion, so the extrapolated values at zero conversion have been adopted. From the Arrhenius plot (Fig. 4), we find the activation heat to be 4.7 kcal./mol.; finally, the rate expression is given as:

$$k_E = (6.3\pm3.5)\times10^{10}\exp(-4710\mp400)/\boldsymbol{RT} \quad \text{l./mol.sec.}$$

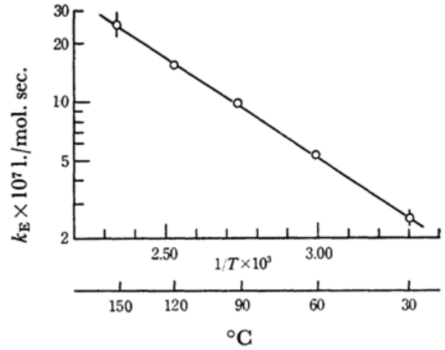

Fig. 4. Arrhenius plot of k_E.

Although the experimental error is less than about 5%, the combined allowance is rather large, and if the afore-mentioned two assumptions do not hold, the error in k_E will become still larger. However, the frequency factor found here seems to be of the usual order of magnitude for the abstraction reactions of atoms.