

# Kinetic Study on the Reaction of Oxygen Atoms with Dimethyl Ether by Means of Mass Spectrometer

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Received August 23, 1966

A small quantity of dimethyl ether was added to the fast stream of oxygen which contained *ca.* 10% O atoms produced by 2450 Mc. electrodeless discharge, and the time-variations of the composition were determined by means of time-of-flight mass spectrometer furnished with the inlet pinhole situated downstream in the range of 1 to 9 msec. after the mixing.

Main products were H<sub>2</sub>O, HCHO, CO and CH<sub>3</sub>OH, and a trace amount of H<sub>2</sub>, whereas CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, CO<sub>2</sub>, (CH<sub>3</sub>OCH<sub>2</sub>)<sub>2</sub> and HCOOH could not be observed.

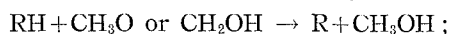
Meanwhile, similar experiments were tried in the nitrogen stream with the O atoms generated by addition of NO of an equivalent amount to the N atoms which were produced by microwave discharge. In the absence of oxygen molecules such as in this procedure, clear-cut distinctions could be observed in the products, *i. e.*, formation of H<sub>2</sub> and O<sub>2</sub> and non-appearance of water, and it has been deduced that this difference results from the choice of the reaction paths of the H atoms produced by O+OH→H+O<sub>2</sub> between H+O<sub>2</sub>+M→OH+O<sub>2</sub>+M and H+RH→H<sub>2</sub>+R.

The reaction rates in the presence of oxygen molecules can be expressed by  $-d(\text{CH}_3\text{OCH}_3)/dt = k_1\alpha(\text{CH}_3\text{OCH}_3)(\text{O})$  and  $\frac{-d(\text{O})}{dt} = k_1\beta(\text{CH}_3\text{OCH}_3)(\text{O}) + \gamma(\text{O})^2$  ( $\alpha, \beta, \gamma = \text{const.}$ ), which support the mechanism proposed by us in the same reaction caused by the O atoms produced by Hg-photosensitized reaction of N<sub>2</sub>O, *viz.*, the degradation of ether by O and OH.

The rate constant of the first step CH<sub>3</sub>OCH<sub>3</sub>+O→CH<sub>3</sub>OCH<sub>2</sub>+OH,  $k_1$ , has been determined to be  $3 \times 10^7$  l./mole sec. (30°C) in agreement with the value reported previously.

## INTRODUCTION

In the preceding paper of the similar title<sup>1)</sup> authors discriminated the elementary steps involved in the reaction of O atoms with dimethyl ether and determined the rate constant of the first step as:



$$k_1 = 2.52 \times 10^7 \text{ l./mole sec. (30°C).}$$

In that study the O atoms were produced by Hg-photosensitized reaction of N<sub>2</sub>O and accordingly the concentration was quite low. In order to test if the

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above-mentioned mechanism is valid generally for the system where the concentration of O atoms is high, investigations on the short reaction time have been made in a flow system by the technique of microwave discharge in oxygen combined with mass spectrometric determination of steady concentrations; further, to find the effect of oxygen molecules in this reaction similar experiments have been performed with O atoms produced by the reaction  $N+NO \rightarrow O+N_2$  with an equivalent amount of NO added to the discharged stream of nitrogen. One characteristic point of MW. discharge method lies in that the O atoms thus formed have been stated to be in the ground  $^3P$  state.<sup>2,5,8)</sup>

## EXPERIMENTALS

### Materials

O<sub>2</sub>: Electrolytic oxygen (N<sub>2</sub>O 0.1%, CO<sub>2</sub> 0.2%, H<sub>2</sub>O 0.3%) purified with heated CuO, soda lime and silica gel.

Dimethyl ether: Prepared by dehydrogenation of methanol, and purified by bulb-to-bulb distillations. Impurities, N<sub>2</sub>+O<sub>2</sub><0.2%, CH<sub>3</sub>OH and H<sub>2</sub>O each<0.01%.

NO<sub>2</sub> for O concentration determination: Prepared by pyrolysis of lead nitrate and purified by bulb-to-bulb distillations and refrigeration; N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O could not be detected by TOF mass spectrometer.

N<sub>2</sub>: 99.995%, obtained from Takachiho Co.

NO: Supplied by Takachiho Co., N<sub>2</sub> 1.35%, NO<sub>2</sub> 0.15%; refrigerated with liquid nitrogen and degassed.

Apparatus (Fig. 1)

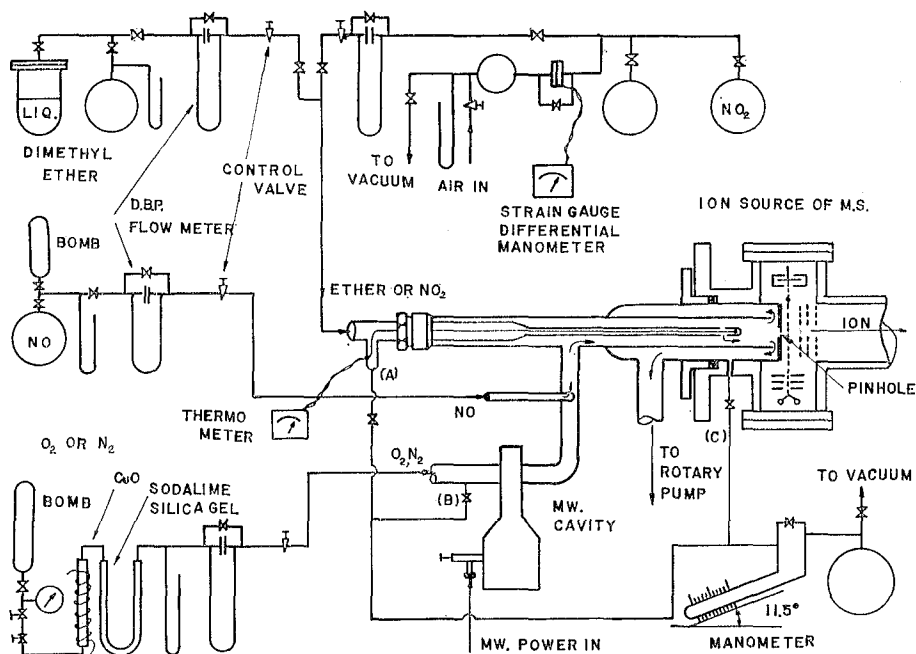


Fig. 1. Schema of experimental system.

## Reaction of Oxygen Atoms with Dimethyl Ether

Each reactant, stored once in a large vessel in order to keep the source pressure constant in each run, was drawn out through a flow meter and a fine-controlling needle valve into the reaction system. Concentric double glass pipes were introduced into the fast reaction chamber of the ion source; the inner pipe (6 mm.  $\phi$ ), being the inlet of the MW-discharged oxygen or nitrogen, had an opening for NO entrance 60 mm. apart from the position of the cavity. Inside the inner pipe a still fine pipe (2 mm.) furnished with 0.3 mm. pinholes perpendicular to the O<sub>2</sub> stream at the end was inserted to introduce ether or NO<sub>2</sub>. The position of this opening is adjustable in the range of 2 to 170 mm. from the ion source pinhole disk by sliding this fine pipe through an O ring enclosure. The entire stream turns in front of the pinhole disk (clearance 2 mm.) into the outer pipe and is pumped out by a 300 l./min. rotary pump. A fine thermocouple was, when necessary, introduced in the innermost pipe to its end. Pressure measurement was made at 3 points indicated in Fig. 1, but as shown later the pressure drop was so small that the mean pressure calculated from the observed value at B has been adopted.

The time-of-flight mass spectrometer Model 12-101 S of Hokushin Electric Co. was used, whose inlet was a gold foil with 0.05 mm.  $\phi$  pinhole. The 2450 Mc., 200 W. microwave power system was supplied by Ito MW. Co., the cavity being connected through coaxial cable.

The absolute flow rate of O atoms was determined by the consumption of added NO<sub>2</sub>, the decrease of  $m/e=46$  peak of NO<sub>2</sub> due to the fast reaction  $O+NO_2 \rightarrow O_2+NO$ , in the case of O<sub>2</sub>-discharge, and from the equivalent point of NO (peak at  $m/e=30$ ) for N<sub>2</sub>-discharge.

### Standard condition

Ambient temperature:  $20 \pm 1^\circ\text{C}$ . Observed temperature at the reaction zone:  $30 \pm 2^\circ\text{C}$ .

O<sub>2</sub> flow rate: 13.6 cc./min. ( $20^\circ\text{C}$ , 760 mmHg).

N<sub>2</sub> flow rate: 12.1 cc./min. ( $20^\circ\text{C}$ , 760 mmHg).

NO<sub>2</sub> flow rate for O concentration determination: 2.17 cc./min. ( $20^\circ\text{C}$ , 760 mm Hg, calculated as total NO<sub>2</sub> from the flow rate of NO<sub>2</sub>-N<sub>2</sub>O<sub>4</sub> equilibrium mixture at 71 mmHg reservoir pressure and  $20^\circ\text{C}$ ).

Ether flow rate: 0.68 cc./min. ( $20^\circ\text{C}$ , 760 mmHg) for O<sub>2</sub>-discharge; 0.165 to 0.62 cc./min. ( $20^\circ\text{C}$ , 760 mmHg) for N<sub>2</sub>-discharge.

Total mean pressure in reaction zone: 0.73 mmHg in O<sub>2</sub>-discharge; 0.60 mm Hg in N<sub>2</sub>-discharge.

MW. input: 150 W.

Linear velocity in reaction zone: *ca.* 900 cm./sec.

Concentration of O atom: 0.11 atom/O<sub>2</sub> molecule in O<sub>2</sub>-discharge as measured by NO<sub>2</sub> consumption; 0.0175 atom/N<sub>2</sub> molecule in N<sub>2</sub>-discharge as measured by NO titration; each independent of pressure and flow rate in the range experimented.

Reaction time: 0.7 to 10 msec.

### Operation condition of time-of-flight mass spectrometer

Ion source pressure: back ground  $5 \times 10^{-7}$  mmHg; during observation  $3 \times 10^{-6}$  mmHg.

Pulse: 10 and 40 kc.; electron beam width: 0.36  $\mu$ sec.

Trap current: 0.5  $\mu$ A.; accel. energy: 25.6 eV. (nominal).

Time constant: 0.5 sec.

#### Check on the experimental condition

a. Flow pattern and pressure drop—Reynolds number of the flow is calculated to be 3.2, completely laminar, but judging from the value of random walk of  $O_2$  ( $=19 \times t^{1/2}$ (sec.) cm.) the radial distribution of concentration is supposed to be well equalized even in the shortest reaction time (0.7 msec.). The pressure drop between the nozzle opening and the pinhole disk was found to be 0.1 mmHg under the standard condition, and the volume change due to the reaction is negligible because of the low O atom concentration and of the low mole change during the reaction as becomes evident later.

b. Correction for the  $NO_2$  flow rate due to the equilibrium  $N_2O_4 \rightleftharpoons 2NO_2$ —In the storage of  $NO_2$  the equilibrium ratio  $N_2O_4/NO_2$  is 0.60 (at 71 mmHg;  $20^\circ C$  eq. const.  $=9.82 \times 10^{-2}$ )<sup>3)</sup>, so, at the point of mixing with O atoms ( $p_{NO_2}=0.14$  mmHg) the mixture is completely dissociated. Accordingly the flow rate of  $NO_2$  is 1.375 times that of the equilibrium mixture measured at 71 mmHg. The rate constant of  $N_2O_4 + M \rightarrow 2NO_2 + M$  is  $1.36 \times 10^{-6}$  l./mole sec. at  $20^\circ C$ ,<sup>4)</sup> and since the time spent between the reducing valve and the mixing point is 0.9 sec. at the total pressure 0.73 mmHg the residual amount of  $N_2O_4$  is calculated to be  $10^{21}$ th of the total.

c. Speed of  $O + NO_2 \rightarrow NO + O_2$ —The rate constant of this reaction is quite large ( $1.5 \times 10^9$  l./mole sec.,<sup>5)</sup> and that for  $NO + O \rightarrow NO_2 + h\nu$  is very small, ca.  $10^3$ )<sup>6)</sup>, and the reaction time between the encounter with O atoms and the mass spectrometer inlet is 7.1 msec., hence the residual O atoms at the inlet of spectrometer are only  $10^8$ th of the initial.

d. Speed of  $N + NO \rightarrow N_2 + O$ —The rate constant is  $1.3 \times 10^{10}$  l./mole sec.<sup>5)</sup> and the time until the mixing of ether is 17.2 msec., thus the unconverted N atoms amount to 0.9% of the original at this point.\*

e. Loss of O atoms due to wall recombination—Recombination coefficient of O atoms on the pyrex glass,  $\gamma$ , is  $2 \times 10^{-5}$ ,<sup>8)</sup> then the first order rate constant of O atom disappearance,  $k = \gamma \bar{c} / 2r$ , is calculated to be  $1.66 \text{ sec.}^{-1}$  in the present condition, thus the maximum loss of O atoms due to wall recombination becomes 1.5% for the maximum reaction time (9 msec.) and can be neglected.

\* A strange phenomenon has been found that, when the amount of O atoms thus formed is measured again by introducing  $NO_2$  downstream the consumption of  $NO_2$  is about twice that expected from the equivalent amount of NO, while the remaining N atoms are reduced to zero at the "end point" of NO titration in the absence of  $NO_2$  as measured by mass spectrometer, and the addition of  $N_2O$  to remove the vibrationally excited  $N_2$  produced by  $N + NO$  does not change the situation. There may exist something of long life which leads to the consumption of  $NO_2$  downstream in the MW. discharge. In this connection the report of S. Takahashi (*Scientific and technical report of Defence College*, 3, 359 (1966)), who has found the ever increasing afterglow in the downstream of the MW-discharged  $N_2$  flow just quenched by NO, is interesting.

Reaction of Oxygen Atoms with Dimethyl Ether

f. O atom loss due to homogeneous recombination—The rate constant of O atom disappearance due to tripple collision has been given as  $9.72 \times 10^8 \text{ l}^2/\text{mole}^2 \text{ sec.}$  (third body is Ar, but it seems equally efficient as  $\text{O}_2$ )<sup>9)</sup>, which leads to 0.2% loss at most under the standard condition.

g. O atom loss due to ozone formation—When no other reactant is present the steady state is established between the reactions  $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$  ( $k = 2.7 \times 10^8 \text{ l}^2/\text{mole}^2 \text{ sec.}$ <sup>10)</sup> for  $\text{M} = \text{O}_2$ ) and  $\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$ , which gives  $-d(\text{O})/dt = 2k(\text{O})(\text{O}_2)(\text{M})$ , hence the maximum loss is calculated to be 0.8%.

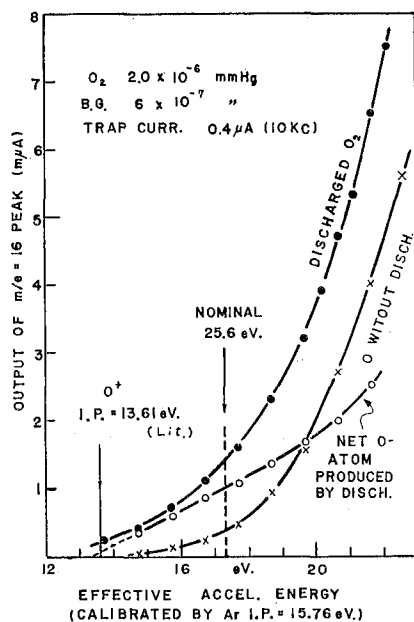


Fig. 2. Mass peak discrimination of O atom due to discharge.

Table 1. Cracking patterns and relative sensitivities at 25.6 eV. (nominal)

$m/e$	$\text{CH}_3\text{OCH}_3$	$\text{CH}_3\text{OH}$	$\text{HCHO}$	$\text{CO}$	$\text{H}_2\text{O}$	$\text{H}_2$
2						100 p.*
15	13.5	18.7				
17					7.55	
18					100 p.	
28			7.1	100 p.		
29	25.5	25.1	70.5			
30	1.35	5.2	100 p.			
31	4.95	100				
32		79.5 p.				
45	100					
46	36.0 p.					
Sensitivity**	1.00	0.87	0.87	0.68	0.34	0.30

\* parent peak

\*\* Sensitivity of each maximum peak relative to  $m/e=45$  of  $\text{CH}_3\text{OCH}_3$

h. Calibration for the mass spectrometer peaks—In order to avoid the disturbance on the peaks due to the fragmentation of the parents, low acceleration potential of electron (25.6 eV. nominal) was used, which is especially necessary for the exact determination of O atoms using  $m/e=16$  peak in the large excess of oxygen as shown in Fig. 2.

The cracking patterns and the relative sensitivities are given in Table 1; the actual output was 8-17  $m\mu A.$  as to ether and 0-4  $m\mu A.$  for other species, and the sensitivities were sufficient for the present study (mean fluctuation was *ca.* 10% during the observation) and the linear relationship between the output and the reaction chamber pressure was also satisfactory.

### RESULTS

In Fig. 3 are given the time dependences of the reactants and of the products in the  $O_2$ -discharge experiment of standard condition, *i. e.*, initially  $p_{O_2}=0.62$  mm Hg,  $p_O=0.072$  mmHg,  $p_E=0.033$  mmHg (E denotes ether hereafter). Here, the reaction time is given by the volume-mean residence time (= (distance between

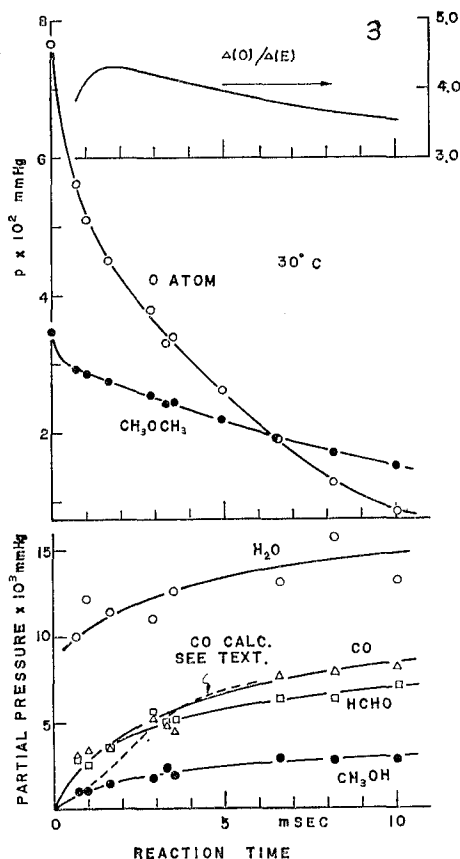


Fig. 3. Features of the reaction in the presence of  $O_2$  at  $30^\circ C.$   
 Initial condition:  $p_E=0.033$  mmHg  $p_O=0.072$  mmHg  
 $p_{O_2}=0.62$  mmHg

Reaction of Oxygen Atoms with Dimethyl Ether

mixing point and pinhole)/(linear velocity)) each calculated from respective measurement.

The observed products are H<sub>2</sub>O, CO, HCHO and CH<sub>3</sub>OH, whereas, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, (CH<sub>3</sub>OCH<sub>2</sub>)<sub>2</sub>, HCCOH, species of *m/e*>60, H<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>OOCH<sub>3</sub> and, noticeably, CO<sub>2</sub> could not be observed. Hydrogen was produced to a trace amount. The material balance on carbon amounts to only 50%, and as to the missing species no information could be obtained except for the above-mentioned non-existent products.

In the reaction of O atoms produced indirectly in the N<sub>2</sub>-discharge (*in the absence of O<sub>2</sub>*) the absolute concentration of O atom was *ca.* 20% of that in the O<sub>2</sub>-discharge, therefore the ether charge was also reduced concomitantly. In this case the initial (E)/(O) ratio was varied between 0.75 and 2.76, the features of the curves being similar to each other, of which the ones for initial (E)/(O) = 0.62, similar ratio to that in the O<sub>2</sub>-discharge, are given in Fig. 4.

A remarkable alteration can be seen that, in this case water formation is reduced to so small an amount that it is masked by the peak of the back ground water in mass spectrometer, and instead corresponding amount of H<sub>2</sub> is produced; moreover, the formation of O<sub>2</sub>, which could not be proved in the former case be-

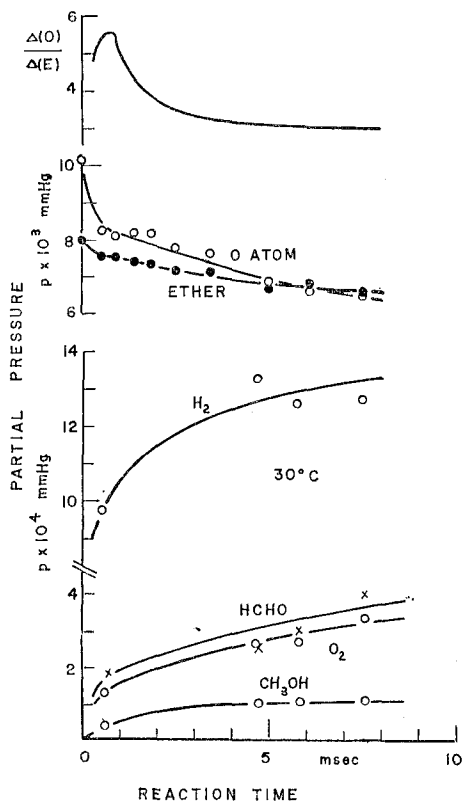


Fig. 4. Features of the reaction in the absence of O<sub>2</sub> at 30°C.

Initial condition:  $p_E = 0.0064$  mmHg  
 $p_{O_2} = 0.010$  mmHg  $p_{N_2} = 0.58$  mmHg

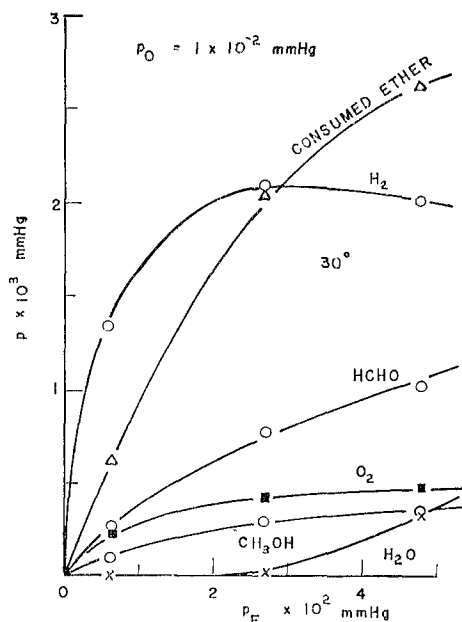


Fig. 5. Variation of products with the amount of ether in the absence of O<sub>2</sub> at 4.7 msec., 30°C.

cause of the presence of a large amount of oxygen, can be clearly observed. On the other hand, the formation of CO could not be discriminated because of the interference of  $m/e=28$  of  $N_2^+$ .

In Fig. 5 is given the variation of the products with increasing ether charge at constant reaction time (=4.7 msec.) without addition of  $O_2$ ; this shows that water becomes to appear as the amount of ether increases and at the same time the formation of  $H_2$  becomes suppressed even in the absence of  $O_2$ . Similar trend, though only slight, was also observed in the case of low ether charge when the reaction time was much prolonged.

Finally, qualitative observation was made on the effect of added  $O_2$  in the NO-titrated stream of discharged  $N_2$ , condition being  $p_E=5.6 \times 10^{-3}$  mmHg,  $p_{O_2}=5.6 \times 10^{-2}$ ,  $p_O=1 \times 10^{-2}$  and 4.7 msec. When the amount of  $O_2$  reached ten times that of O, the water formation (about  $7 \times 10^{-4}$  mmHg) began to be recognized, but the depression of  $H_2$  was not clear.

## DISCUSSION

In the experiments *with the discharged  $O_2$*  the consumption of O is seen to be much more than that of ether, *viz.*  $\Delta(O)/\Delta(E)$  is more than 4 in the major part of the reaction (Fig. 3), while as is evident from the schemes  $CH_3OCH_3 + 2O \rightarrow 2HCHO + H_2O$  and  $CH_3OCH_3 + 4O \rightarrow 2CO + 3H_2O$ ,  $\Delta(O)/\Delta(E)$  should not exceed 4 unless  $CO_2$  is formed as is actually so in the present experiment, and should be less if  $O_2$  participates in the decomposition or oxidation; moreover, in the case of Fig. 3 where equal amounts of CO and HCHO are produced this value must be less than 3. This fact suggests that O atoms are consumed by some processes other than the reaction with ether and its derivatives, but as stated in the preceding section these cannot be  $2O \rightarrow O_2$  or  $O + O_2 \rightarrow O_3$ . On the other hand, it has been recognized that O atoms quickly disappear in the presence of OH, and Petersen<sup>11)</sup> has proposed the sequence  $O + OH + M \rightarrow HO_2 + M$  and  $HO_2 + O \rightarrow HO + O_2$ , while Kaufman<sup>12)</sup>  $O + OH \xrightarrow{k_{21}} O_2 + H$ ,  $H + O_2 + M \xrightarrow{k_{22}} HO_2 + M$  and  $HO_2 + O \xrightarrow{k_{23}} HO + O_2$ . The presence of water as a main product in the present case and also in the previous experiment<sup>1)</sup> with O atoms from  $N_2O + Hg^*$  in the absence of oxygen clearly shows the presence of OH as an important intermediate.

Now, the observed facts may be summarized as:

	$O_2$	(E) to (O)	Products
A)	(ref. 1) absent	large excess	$H_2O$ , no $O_2$ , $H_2$ trace
B)	(Fig. 5) absent	ca. 4-fold	$H_2O$ (small amount), $O_2$ , $H_2$
C)	(Fig. 4) absent	ca. 1/2	no $H_2O$ , $O_2$ , $H_2$
D)	$10 \times (O)$	ca. 1/2	$H_2O$ (small amount), $O_2$ ?, $H_2$
E)	(Fig. 3) large excess	ca. 1/2	$H_2O$ , $O_2$ ?, $H_2$ trace.

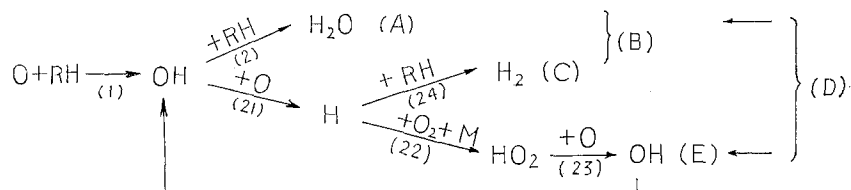
This trend may be explained consistently by the following argument:

According to the mechanism given in the Introduction of this paper, at first O atom attacks ether to produce OH by (1), then ether and O atom compete the produced OH, and if ether is present in large excess against O atom in the

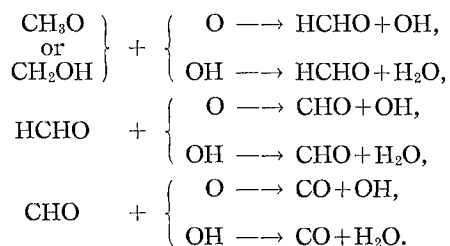


Reaction of Oxygen Atoms with Dimethyl Ether

absence of  $O_2$ , OH will react with ether and its derivatives exclusively to form water (case A), but even in the absence of  $O_2$  when the amount of ether is reduced to about a half of O atom the O atom will preferentially react with OH and produce  $O_2$  and H according to the Kaufman's scheme ( $k_{21}=5 \times 10^{10}$  l./mole sec.<sup>13)</sup>;  $k_2$  may be about  $10^8$  l./mole sec. as estimated later), then the abstraction of H of the substrate by this H atom leads to  $H_2$  formation where  $O+H+M \rightarrow OH+M$ ,  $H+OH+M \rightarrow H_2O+M$  and  $H+OH \rightarrow H_2+O$  are slow processes as shown later (case C). The intermediate condition of (E)/(O) corresponds to the case B. When oxygen molecules are accumulated or added previously, at first OH will react with O atom to produce H atom as before, but the reaction  $OH+O_2 \rightarrow HO_2+O$  cannot take place because of high endothermicity. And, in this case some of the H atom thus formed must be consumed by the fast termolecular reaction  $H+O_2+M \xrightarrow{k_{22}} HO_2+M$  along with the competitive reaction  $H+RH \xrightarrow{k_{24}} H_2+R$  ( $k_{22}=5 \times 10^{11}$  l<sup>2</sup>./mole<sup>2</sup> sec.,  $M=O_2$ <sup>14)</sup> and  $k_{24}$  must be of the order of magnitude of  $10^6$  l./mole sec. for methyl ether where pre-exponential factor is assumed to be  $1.5 \times 10^{14}$  l./mole sec.<sup>15)</sup> and activation heat as 7 kcal<sup>16)</sup>, therefore this is well conceivable), and the  $HO_2$  produces again OH and  $O_2$  as proposed by Kaufman, thus the concentration of OH increases and some of the originally produced OH will begin to be converted into water (case D). If  $O_2$  is present in large excess all the H atom will be used to reproduce OH and no  $H_2$  formation is observed (Case E). From the present argument the Petersen's scheme must be abandoned since it does not afford  $H_2$  formation. The whole feature may be represented schematically by



Turning to the experiment in the  $O_2$ -discharge system, the observed formation of water, HCHO, CO and methanol can be explained by the above-mentioned scheme together with the degradation of  $CH_2OH$  and  $CH_3O$  by O and OH and the secondary decomposition of HCHO, e. g.,

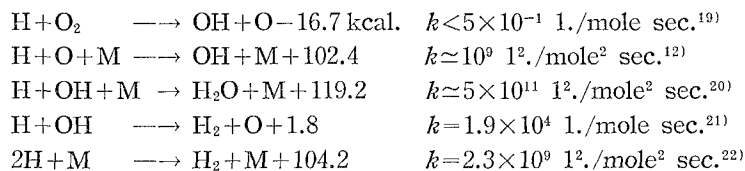


The absence of  $CO_2$  shows the non-occurrence of the reactions such as  $CO+O+M \rightarrow CO_2+M$  (quite slow because of the violation of spin conservation rule,  $k \ll 5 \times 10^8$  l<sup>2</sup>./mole<sup>2</sup> sec.<sup>12)</sup>) and of the processes leading to  $CO_2$  formation which involve the reaction of  $O_2$  with ether or the derived radicals. This conclusion is contrary to those of Wong<sup>17)</sup> and Wright<sup>18)</sup> given in the similar experiment; supposingly, their

results must have arisen from the secondary oxidation of CO during the long reaction time adopted (10-60 times that of us).

According to the mechanism given above, CO is produced only *via* HCHO; meanwhile the rate of CO formation by HCHO+O measured by the same method under similar concentration has given  $d(\text{CO})/dt=9.85(\text{HCHO})(\text{O})\text{mmHg/sec.}$ , and the calculated CO curve using this value and the observed amount of O and HCHO, dotted line in Fig. 3, does not reproduce the fact that CO is produced early in the beginning of the reaction. In the previous paper<sup>1)</sup> authors pointed out that the reaction  $\text{CH}_3\text{OCH}_2+\text{O}\rightarrow\text{CH}_3\text{O}+\text{HCHO}$  is not actually the main step in spite of its high possibility; however, it may be reasonable to consider that this reaction, 84.4 kcal. exothermic, does not stop at the stage of HCHO formation, and proceeds to the formation of H+CHO (net 7.4 kcal exothermic). If we accept this step as operating, direct formation of CO without intermediation of HCHO can be explained.

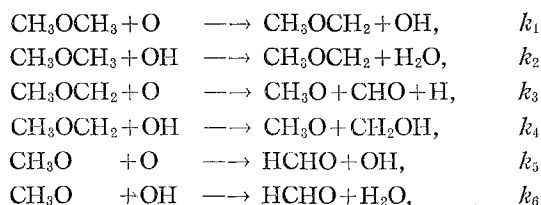
As described before, H atoms must be solely consumed by  $\text{H}+\text{O}_2+\text{M}\xrightarrow{k_{22}}\text{HO}_2+\text{M}$ ,  $k_{22}=5\times 10^{11}$  l<sup>2</sup>./mole<sup>2</sup> sec.,<sup>14)</sup> in the O<sub>2</sub>-discharge system, and as compared with this step the following steps can be neglected from the view-point of concentration or rate constant:



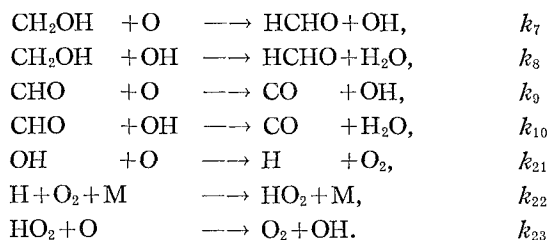
Absence of a) CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, b) C<sub>2</sub>H<sub>4</sub> and c) H<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>OOCH<sub>3</sub>,  $m/e > 60$ , may be taken as evidences for the non-occurrence of a) processes which produce CH<sub>3</sub>, b)  $2\text{CH}_3\text{OCH}_2\rightarrow\text{C}_2\text{H}_4+2\text{CH}_3\text{O}$  and c) the recombination of radicals such as OH, CH<sub>3</sub>O, CH<sub>2</sub>OH, CH<sub>3</sub>OCH<sub>2</sub> *etc.*, respectively.

It is impossible to solve the kinetics composed of the remaining possible processes after the screening discussed so far; however, in order to find out the overall rate equation which fits the present observation and the rate constant of the first step  $\text{O}+\text{CH}_3\text{OCH}_3\rightarrow\text{OH}+\text{CH}_3\text{OCH}_2$ , following simplification has been assumed *in the O<sub>2</sub>-discharge experiment*: Degradation of ether skeleton proceeds solely by the abundant O atom and the primary radical OH, and as compared with these processes the reactions of organic radicals with O<sub>2</sub> and with ether (*e. g.*, methanol formation) and also the recombinations of such radicals are negligible, and further, only to the initial stage of the reaction attention is to be paid where the decomposition of the intermediate HCHO may be disregarded.

One of the sets of elementary steps assumed here is:



## Reaction of Oxygen Atoms with Dimethyl Ether



In this scheme we have,

$$(\text{OH}) = K(\text{O}), \quad (K \text{ is a constant, composed of } k\text{'s only})$$

$$(\text{CH}_3\text{OCH}_2) = \left( \frac{k_1 + k_2 K}{k_3 + k_4 K} \right) (\text{E}),$$

$$(\text{CH}_3\text{O}) = \left( \frac{k_3 + k_4 K}{k_5 + k_6 K} \right) \left( \frac{k_1 + k_2 K}{k_3 + k_4 K} \right) (\text{E}),$$

$$(\text{CH}_2\text{OH}) = \left( \frac{k_4 K}{k_7 + k_8 K} \right) \left( \frac{k_1 + k_2 K}{k_3 + k_4 K} \right) (\text{E}),$$

$$(\text{CHO}) = \left( \frac{k_3}{k_9 + k_{10} K} \right) \left( \frac{k_1 + k_2 K}{k_3 + k_4 K} \right) (\text{E});$$

$$\frac{-d(\text{E})}{dt} = k_1(\text{E})(\text{O}) \left\{ 1 + \frac{k_2}{k_1} K \right\} \equiv k_1 \alpha (\text{E})(\text{O}), \quad (\text{I})$$

$$\begin{aligned} \frac{-d(\text{O})}{dt} = k_1(\text{E})(\text{O}) & \left[ 1 + \left\{ \frac{2k_3}{k_1} + \frac{k_3}{k_1} \left( \frac{k_3 + k_4 K}{k_5 + k_6 K} \right) + \frac{k_7}{k_1} \left( \frac{k_4 K}{k_7 + k_8 K} \right) + \right. \right. \\ & \left. \left. \frac{k_9 k_3}{k_1 (k_9 + k_{10} K)} \right\} \left( \frac{k_1 + k_2 K}{k_3 + k_4 K} \right) \right] + 2k_{21} K (\text{O})^2 \equiv k_1 \beta (\text{E})(\text{O}) + 2k_{21} K (\text{O})^2 \end{aligned} \quad (\text{II})$$

( $\alpha$  or  $\beta$  is a constant, respectively).

Result of the numerical integration of (I) is shown in Fig. 6. A fairly good linear relation is seen for the first 4 msec. (decrease in O atom is 60% and reacted ether amounts to 23%); the steep rise in the initial 0.2 msec. must be due to the establishment of steady state, and as for the deviation from the linearity in the later stage some consideration will be given later. From the slope of the straight line we have  $k_1 \alpha = 3.1 \times 10^7$  l./mole sec.

Concerning the decrease of O, we get  $d(\text{O})/d(\text{E})$  from (I) and (II) instead of solving (II),

$$\frac{d(\text{O})}{d(\text{E})} \equiv \frac{d(\text{O}/\text{E})}{d(\text{E})} (\text{E}) + \frac{(\text{O})}{(\text{E})} = \frac{\beta}{\alpha} + \frac{2k_{21} K}{k_1 \alpha} \frac{(\text{O})}{(\text{E})}, \quad (\text{III})$$

therefore  $d(\text{O})/d(\text{E})$  should be linear against  $(\text{O})/(\text{E})$ ; as shown in Fig. 7 the line curves slightly, but the maximum change of the slope is 20%, and the line can be regarded as straight for the first 3.2 msec. From this slope and the intercept we have  $\beta/\alpha = 1.15$  and  $2k_{21} K/k_1 \alpha = 1.64$ , and these three values, together with  $k_{21} = 5 \times 10^{10}$  l./mole sec.<sup>13)</sup>, give  $K \equiv (\text{OH})/(\text{O}) = 2.5 \times 10^{-3}$ . Although no determination has been reported on  $k_2$ , the rate of H-abstraction reaction by OH seems about ten times faster than that of O at room temperature as estimated from the analogous reactions for  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$  and  $\text{CH}_3\text{CHO}$ .<sup>23)</sup> Then we may put  $k_2 K/k_1 < 0.01$ , or  $1 \leq \alpha \leq 1.1$  with sufficient allowance, hence  $k_1 = (3.1 \sim 2.8) \times 10^7$  l./mole sec. is derived, which is in agreement with  $2.52 \times 10^7$  (30°C) given previously.<sup>1)</sup> Since  $\beta/\alpha = 1.15$ , we have  $\beta \approx 1$ , and this means, referring to (II), that the reactions of

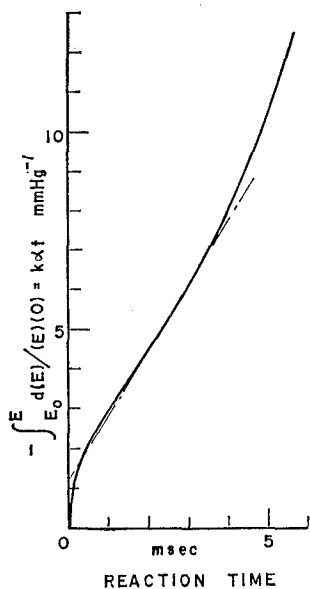


Fig. 6. Graphical integration of Eq. (I).

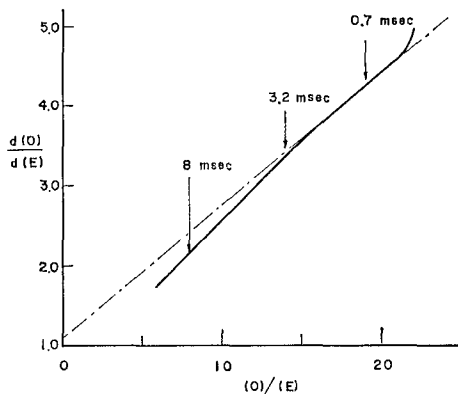


Fig. 7. Representation of Eq. (II).

organic radicals with O is almost nil as compared with the reaction of ether with O, and the subsequent degradation proceeds practically by OH, consistent with the discussion given before in this section.

One of the reasons for the deviation of curves from being straight in Figs. 6 and 7 must lie in the neglect of the subsequent decomposition of HCHO. If we add  $\text{HCHO} + \text{O} \rightarrow \text{OH} + \text{CHO}$  and  $\text{HCHO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CHO}$  to the above mechanism,  $K(\equiv (\text{OH})/(\text{O}))$  now becomes the function,  $F$ , of  $k$ 's and  $(\text{HCHO})/(\text{E})$  only, which, on approximate calculation, will increase slightly according as  $(\text{HCHO})/(\text{E})$  ascends. Further, the rate equations are expressed by

$$\begin{aligned} -\frac{d(\text{E})}{dt} &= k_1(\text{E})(\text{O}) \left\{ 1 + \frac{k_2}{k_1} F_{(\text{HCHO}/\text{E})} \right\} \equiv k_1 \alpha'(\text{E})(\text{O}), \\ \frac{d(\text{O})}{d(\text{E})} &= \frac{\beta'}{\alpha'} + \frac{2k_2 F_{(\text{HCHO}/\text{E})}}{\alpha'} \frac{(\text{O})}{(\text{E})}, \end{aligned}$$

where  $\beta'$  is a constant which is determined mainly by  $k$ 's and varies only slightly with  $(\text{HCHO})/(\text{E})$ . Accordingly it can be seen qualitatively that  $\int -d(\text{E})/(\text{E})(\text{O})$  will run apart from the straight line as the time elapses and the slope will increase slightly as the  $(\text{O})/(\text{E})$  drops, or  $(\text{HCHO})/(\text{E})$  increases.

Finally, the value  $3 \times 10^7$  l./mole sec. should give the upper limit for the step (1) if the processes omitted in the assumption given before are actually operative. However, it is shown, though quite roughly, that even when these steps intervene, the shape of  $\int \frac{-d(\text{E})}{(\text{O})(\text{E})}$  would not change appreciably, and the correction needed for the value of  $k_1$  may be only minute.

## Reaction of Oxygen Atoms with Dimethyl Ether

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