

## The Mercury PhotoSensitized Reactions of Diethyl Ether

B. deB. Darwent, E. W. R. Steacie, and A. F. van Winckel

Citation: [The Journal of Chemical Physics](#) **14**, 551 (1946); doi: 10.1063/1.1724193

View online: <http://dx.doi.org/10.1063/1.1724193>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/14/9?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[The Mercury PhotoSensitized Decomposition of Methyl Chloride](#)

J. Chem. Phys. **19**, 183 (1951); 10.1063/1.1748156

[The Mercury Photosensitized Reaction of Dimethyl Ether](#)

J. Chem. Phys. **16**, 987 (1948); 10.1063/1.1746701

[On the Mercury PhotoSensitized Reactions of Ethylene](#)

J. Chem. Phys. **16**, 634 (1948); 10.1063/1.1746960

[The Mercury PhotoSensitized Reaction Between Hydrogen and Oxygen](#)

J. Chem. Phys. **14**, 707 (1946); 10.1063/1.1724090

[The Mercury PhotoSensitized Reactions of Isobutene](#)

J. Chem. Phys. **14**, 544 (1946); 10.1063/1.1724192

---



some six hundred times greater than that of a single bond. Now in isobutene there is a greater probability that quenching will occur at the paraffinic end than in propylene, and this should lead to reaction (12). On the other hand if quenching does occur at the olefinic end, reaction (13) may occur with propylene, whereas with isobutene, the increased number of degrees of freedom may cause the excitation energy of the mercury ( $^3P_1$ ) atoms to be dissipated as vibrational and rotational energy without leading to reaction. This argument is supported by the fact

that the initial quenching process seems to be only 16 percent efficient in isobutene.

#### ACKNOWLEDGMENT

It is a great pleasure to acknowledge our indebtedness to Dr. A. Keith Brewer, Chief of the Mass Spectrometry Section of the National Bureau of Standards, for his kindness in performing the mass spectrometric analyses reported in this paper.

Our thanks are also due Mr. Yves Lupien for his assistance in making the measurements.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 14, NUMBER 9 SEPTEMBER, 1946

### The Mercury Photo-Sensitized Reactions of Diethyl Ether\*

B. DEB. DARWENT, E. W. R. STEACIE, AND A. F. VAN WINCKEL  
Division of Chemistry, National Research Laboratories, Ottawa, Canada

(Received June 28, 1946)

The mercury photo-sensitized reactions of diethyl ether have been investigated in a circulatory system at 35°C and between 9- and 193-mm pressure. The principal products are hydrogen and  $C_2H_5O_2$ ; smaller amounts of CO,  $CH_4$ ,  $C_2H_6$ , and aldehydes are formed. The quantum yield for ether disappearance is about 2.0 initially but decreases with the duration of the experiment. In low pressure experiments the hydrogen produced initially is consumed in the later stages of the experiment and ultimately vanishes. The decrease in rate and the consumption of hydrogen in the late stages of the reaction are not caused by the accumulation either of polymer on the wall or to hydrogen and/or CO in the system. The nature of the reaction is altered by interrupting the experiment thus indicating the occurrence of a dark reaction. The initial stages may be explained by either a C-H split followed by "atomic cracking" or by reactions involving an active ether molecule.

#### INTRODUCTION

THE thermal decomposition of diethyl ether has been investigated extensively and the indications<sup>1</sup> are that the reaction proceeds by a mixed free radical and molecular rearrangement mechanism. The only photochemical investigation of the decomposition of diethyl ether published is that of Berthelot and Gaudechon<sup>2</sup> who report that non-condensable gas consisting of 14.5

percent CO and 85.5 percent  $H_2$ ,  $CH_4$ , and  $C_2H_6$  (ethane predominating) was formed when diethyl ether was exposed in a quartz vessel to the light of a mercury lamp. In the same investigation they found that dimethyl ether behaved similarly but report that a liquid was formed as well as the non-condensable gas. Since both dimethyl and diethyl ethers are almost completely transparent to light of wave-length longer than about 2000Å and since Berthelot and Gaudechon do not mention any precautions to remove mercury vapour from their reaction vessel and used a Hg lamp which probably gave unreversed  $\lambda 2537$ , it seems likely that they investigated the mercury photo-sensitized reaction rather than the photolysis of diethyl ether.

Although much information is available on the

\* Contribution No. 1412 from the National Research Laboratories, Ottawa, Canada.

<sup>1</sup> For comprehensive reviews see: (a) E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1946). (b) H. J. Schumacher, *Chemische Gasreaktionen* (Theodor Steinkopff, Leipzig, 1938).

<sup>2</sup> D. Berthelot and H. Gaudechon, *Comptes rendus* (Paris) **153**, 383 (1911).

photo-sensitized reactions of the simple saturated<sup>3</sup> and unsaturated<sup>4</sup> hydrocarbons, little is known about similar reactions of simple organic compounds containing oxygen. Taylor and Bates<sup>5</sup> carried out preliminary qualitative investigations of the reactions between  $\text{Hg}(^3\text{P}_1)$  atoms and a number of compounds including methyl and ethyl alcohols, acetone, and formic acid and found that those substances reacted readily; however no information was provided on which mechanisms could be assigned to those reactions. Hence it was thought that more detailed investigation of the mercury photo-sensitized reactions of some of the simple organic compounds would be of interest, and we present below the results obtained in the reaction between diethyl ether and  $\text{Hg}(^3\text{P}_1)$  atoms at 35°C and at pressures between 9 and 190 mm.

### EXPERIMENTAL

The reaction was investigated in a circulatory system of conventional design<sup>3</sup> in which ether vapor was circulated at constant pressure, provided by the presence of liquid ether in a trap at constant temperature, over a pool of warm mercury, through a trap filled with iron pellets and kept at constant temperature to reduce the partial pressure of mercury vapor to the desired level and then through a quartz reaction vessel in which the mixture of mercury and ether was illuminated by a lamp emitting  $\lambda 2537$ . Products of low vapor pressure were removed, more or less efficiently, by circulating through a cold trap while those of high vapor pressure accumulated in the gas phase and were circulated with the ether and mercury vapor.

The volume of the reaction system was 980 cc and the circulation rate about 400 cc min.<sup>-1</sup>. The reaction vessel was a quartz annular cell of about 430-cc capacity. The lamp was of the usual low pressure type with neon as carrier gas, the emission of which is almost entirely  $\lambda 2537$ . The transmitting portion of the lamp was a quartz U which fitted into the annulus of the reaction

vessel. The intensity of  $\lambda 2537$  was measured from the rate of hydrolysis of monochloroacetic acid placed in the reactor and therefore represents the amount of  $\lambda 2537$  entering the reaction zone; allowance was made for the contribution of the dark reaction to the rate of hydrolysis of monochloroacetic acid as found by Smith, Leighton, and Leighton.<sup>6</sup> The type of lamp used emits very little light other than  $\lambda 2537$  which is active in the hydrolysis of monochloroacetic acid and the  $\lambda 2537$  emitted is narrow enough so that no great error could be introduced from the wings of the line. Since we could detect no fluorescence in our experiments, it is likely that the quantum input measured did approximate very closely to the amount of  $\lambda 2537$  entering the system, and certainly represents the upper limit of the input of useful  $\lambda 2537$ .

Stopcocks were excluded from the system because of the high solubility of ether in stopcock grease; mercury cut-offs and valves of the type described by Warwick and Fugassi<sup>7</sup> were used instead.

In preliminary experiments the reaction was carried out without the mercury saturator, depending on the contact of the gas with mercury in the circulating pump for saturation and it was found that the reproducibility was very poor. Concordant results were obtained only where the mercury saturator and desaturator were included in the system and when the desaturator was kept at a constant temperature. This was accomplished by placing the desaturator very near to the reaction vessel and immersing both in a thermostat at 35°C. The indications are that concentration of mercury in the reacting gases is critical. The thermostat was emptied and refilled with fresh distilled water and the reaction cell cleaned by flaming in an atmosphere of oxygen with an oxygen-gas flame before each experiment.

The ether used was a commercial product. It was purified by refluxing over and distilling from solid potassium hydroxide followed by freshly pressed sodium wire. The purified ether was stored over freshly cut sodium in a bulb attached to the apparatus through a mercury cut-off, and was freed from any hydrogen that might have

<sup>3</sup> (a) E. W. R. Steacie and N. W. F. Phillips, *Can. J. Research* **B16**, 303 (1938). (b) B. deB. Darwent and E. W. R. Steacie, *J. Chem. Phys.* **13**, 563 (1945).

<sup>4</sup> (a) D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.* **9**, 829 (1941). (b) H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.* **12**, 484 (1944).

<sup>5</sup> H. S. Taylor and J. R. Bates, *Proc. Nat. Acad. Sci.* **12**, 714 (1926).

<sup>6</sup> J. O. Smith, P. A. Leighton, and W. G. Leighton, *J. Am. Chem. Soc.* **61**, 2299 (1939).

<sup>7</sup> E. Warwick and P. Fugassi, *Ind. Eng. Chem. Anal. Ed.* **15**, 13 (1943).

TABLE I. Effect of time and pressure on the mercury photo-sensitized reactions of diethyl ether.

Volume of system = 980 ml  
 Volume of reaction vessel = 430 ml  
 Circulation rate = 400 ml/min.

$\lambda 2537$  absorbed =  $2.8 \times 10^{-6}$  einsteins/sec.  
 Reaction temp. =  $35.0^\circ\text{C}$   
 Hg pressure =  $4.2 \times 10^{-3}$  mm (35.0 = C)

Run No.	Time (min.)	Ether reacted cc	Gaseous products—cc							Liquid products			Liquid products	
			H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub>	Ald.	Et <sub>2</sub> O	Found mg	Calculated mg	cc	Formula	C <sub>2</sub> H <sub>5</sub> O <sub>2</sub>	
												X	Y	
Series (A)—Working pressure of ether = 9.3 mm														
115	1	3.2	2.0	0.2	0.0	0.2	0.3	0.78	8.0	8.0	1.4	8.6	19.0	
116	2½	6.0	4.2	0.3	0.1	0.3	0.3	0.58	7.0	16.2	2.7	8.3	17.8	
102	10	13.5	9.2	1.8	1.2	1.5	0.4	0.33	—	—	5.6	8.3	17.5	
99	30	22.3	11.7	6.8	6.3	3.6	0.3	0.18	—	—	7.6	8.5	19.0	
160(a)	30	—	14.2	5.7	5.7	—	—	—	—	—	—	—	—	
105	60	28.5	10.6	10.6	14.4	5.0	0.1	0.12	35.0	49.0	8.9	8.4	18.8	
161	60	31.1	14.0	9.6	13.0	6.1	—	0.13	—	—	—	—	—	
163	60	—	15.5	9.7	12.4	—	—	—	—	—	—	—	—	
169	60	21.7	8.8	8.5	11.4	4.1	—	0.09	—	—	—	—	—	
103	90	35.8	8.9	15.9	21.4	5.6	0.1	0.09	45.0	60.0	9.9	8.7	20.6	
165	120	48.1	11.3	15.3	26.0	8.9	—	0.10	—	—	—	—	—	
167	120	34.7	8.9	18.5	24.3	6.9	—	0.07	—	—	—	—	—	
104	150	43.6	5.6	20.8	33.0	8.3	—	0.07	56.0	67.0	11.2	8.5	20.0	
97	300	50.0	0.0	29.9	49.8	12.2	—	0.04	—	58.0	9.5	8.8	21.4	
Aldehyde—average volume = 0.26 ml														
Series (B)—Working pressure of ether = 15.0 mm														
143	10	21.3	11.4	0.6	0.2	0.7	0.3	0.51	22.5	62	10	8.0	17.8	
144	25	31.5	20.8	3.7	2.3	2.6	0.3	0.31	83.0	84	14	8.5	16.2	
139	30	40.7	23.4	3.4	2.0	3.0	0.5	0.33	43.5	112	18	8.0	17.8	
140	60	51.0	25.0	7.8	8.7	5.8	0.4	0.21	45.5	131	21	7.8	17.6	
142	80	46.0	24.5	11.1	15.3	7.4	0.2	0.14	68.5	—	—	—	—	
133	120	65.7	33.8	14.9	21.4	9.4	0.5	0.13	140.0	154	25	7.7	17.0	
150	120	58.4	23.3	14.9	25.9	9.0	0.2	0.12	80.5	132	22	7.8	17.2	
141	240	77.5	23.7	23.7	47.2	13.7	0.6	0.08	145.5	162	27	7.4	15.7	
151	240	76.1	21.9	25.6	47.9	14.5	0.2	0.08	548.5	156	26	7.4	16.2	
134	360	77.1	11.5	31.3	67.2	—	0.3	0.05	338.5	—	—	—	—	
Aldehyde—average volume = 0.35 ml														
Series (C)—Working pressure of ether = 20.0 mm														
146	30	30.2	26.6	2.0	1.1	1.7	0.4	0.24	79	84	14	8.1	17.2	
149	60	59.4	39.3	7.0	7.1	5.7	0.3	0.24	101	159	26	7.6	17.2	
147	120	75.4	38.7	13.6	18.9	10.7	0.3	0.20	121	188	31	7.7	16.7	
148	240	67.0	27.0	25.6	46.8	14.8	0.2	0.07	135	126	21	6.8	15.2	
Aldehyde—average volume = 0.31 ml														
Series (D)—Working pressure of ether = 25.0 mm														
118(B)	1	8.1	2.8	0.2	0.0	—	—	1.98	—	—	—	—	—	
120(B)	2	13.6	6.6	—	—	0.2	—	1.32	—	—	—	—	—	
119	5	20.2	10.2	0.5	0.1	0.4	—	0.98	—	—	—	—	—	
138	15	33.0	19.2	1.1	0.4	1.4	0.7	0.53	50	—	—	—	—	
136	25	49.3	—	—	—	2.3	0.4	0.48	57	—	—	—	—	
137	25	45.9	26.5	1.5	0.6	1.2	0.8	0.44	57	133	22	8.2	18.0	
132	45	54.5	39.0	3.0	1.6	2.6	0.5	0.29	96	156	26	8.0	17.2	
145	45	55.5	36.4	3.0	1.8	2.8	0.3	0.29	101	160	26	8.0	17.3	
130	120	93.5	60.2	11.0	14.9	8.9	0.8	0.19	—	—	—	—	—	
131	240	147.2	85.2	18.2	33.2	18.8	0.8	0.15	364	387	64	7.6	16.0	
127	360	—	119.2	29.2	40.1	29.9	—	—	1034	525	86	7.3	15.2	
129	360	196.0	119.6	22.8	48.0	26.1	1.3	0.13	323	—	—	—	—	
Aldehyde—average volume = 0.69 cc														
Series (E)—Working pressure of ether = 50 mm														
106	10	39	18	0.7	0.2	0.5	0.9	0.95	98	113	18	7.6	18.4	
108	30	88	41	1.6	0.7	1.1	0.7	0.70	316	261	43	8.0	18.2	
125	60	128	79	3.1	1.4	3.7	—	0.51	321	378	62	8.0	17.5	
135	84	140	87	5.0	2.7	3.6	1.2	0.39	330	415	68	8.1	17.6	
126	150	189	113	10.0	8.6	9.5	1.2	0.31	486	522	84	7.8	17.4	
128	360	316	198	28.1	28.1	24.0	0.8	0.22	728	878	144	7.8	17.2	
Aldehyde—average volume = 0.95 cc														
Series (F)—Working pressure of ether = 193 mm														
114	2.5	—	10	0.0	—	—	—	—	—	—	—	—	—	
113	5.0	37	18	0.2	0.0	0.1	0.9	1.80	80	110	18	8.2	18.2	
110	10.0	67	33	2.8	0.0	0.2	1.2	1.64	114	192	32	8.3	19.0	
112	20.0	121	64	2.1	0.0	0.8	1.9	1.46	311	354	58	8.2	18.3	

been generated by repeated freezing and melting in a vacuum. No aldehydes or other impurity could be detected by the analytical methods used. Hydrogen was taken from a cylinder of electrolytic gas and purified by passage over heated copper followed by calcium chloride, solid potassium hydroxide, and a trap in liquid air.

Samples of this hydrogen were oxidized by hot copper oxide without leaving any residual gas or material volatile at  $-78^\circ\text{C}$ . Carbon monoxide was prepared by the action of concentrated sulphuric acid on formic acid and purified by passage through "ascarite," calcium chloride, and a liquid air trap. Samples of this gas were

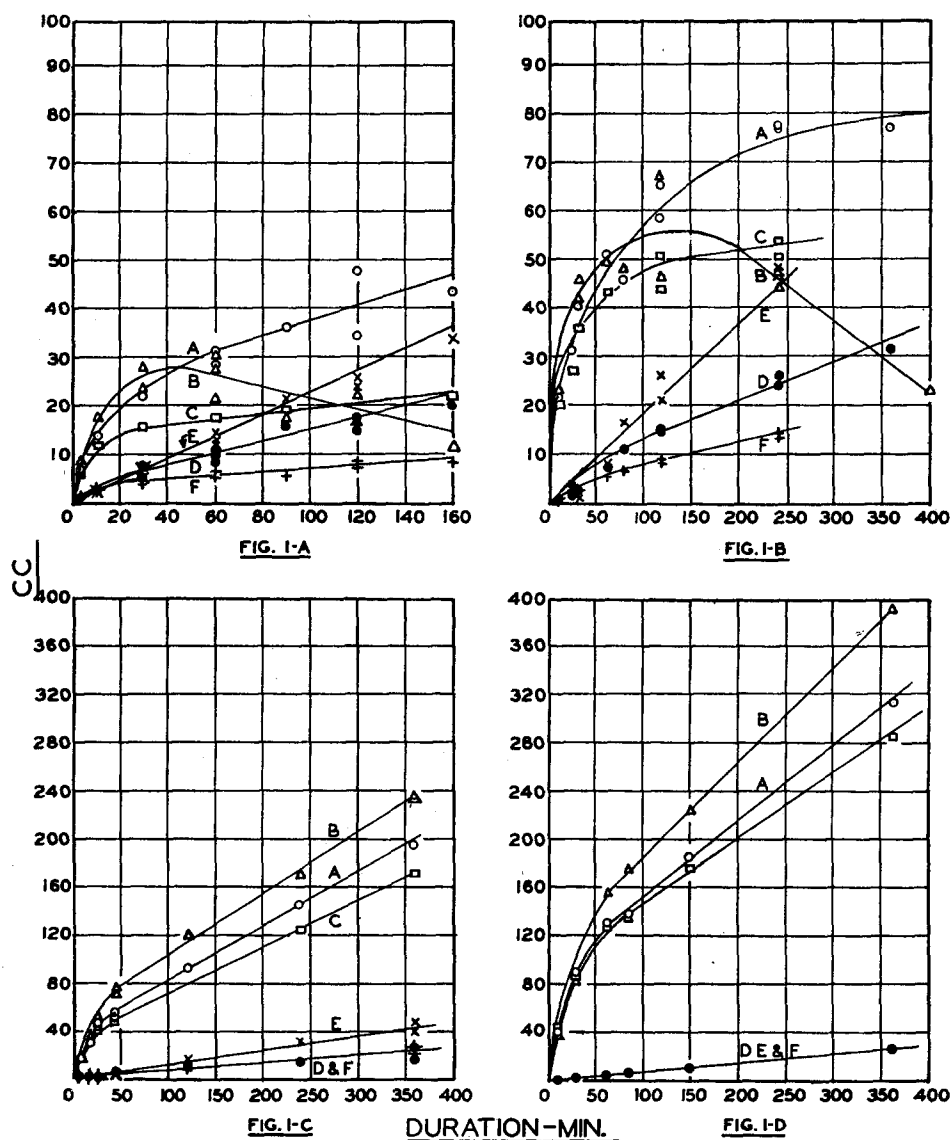


FIG. 1. Effect of time on the products.

Fig. 1-A Runs at 9.3 min.

1-B Runs at 15.0 min.

1-C Runs at 25.0 min.

1-D Runs at 50.0 min.

Curves A = cc Et<sub>2</sub>O reacted  
 B = 2 X cc H<sub>2</sub> produced  
 C = 2 X cc liquid product (as gas) produced  
 D = cc CO produced  
 E = cc CH<sub>4</sub> produced  
 F = cc C<sub>2</sub> hydrocarbons produced.

completely oxidized by CuO and the gas volatile at  $-78^{\circ}\text{C}$  was equal in volume to the samples taken.

The products of the reaction were analyzed by separation into four fractions and further analysis of these fractions. The fractions obtained were as

follows: (1) *Non-condensable gas*—volatile at liquid air temperatures; analyzed by oxidation over copper oxide at  $220^{\circ}\text{C}$  and measurement of the  $\text{CO}_2$  formed. The residue was characterized as  $\text{CH}_4$  by combustion with excess oxygen on a glowing platinum wire. (2) *Volatile at  $-103^{\circ}\text{C}$* —

obtained by pumping down to 0.1 mm from traps at  $-80^{\circ}\text{C}$  and  $-103^{\circ}\text{C}$  (melting cyclohexene); analysis of this fraction by micro fractionation has shown that it consists almost entirely of  $\text{C}_2$  hydrocarbon. (3) *Residual ether*—a fraction volatile at  $-70^{\circ}\text{C}$ ; this fraction was measured in as small a volume as possible to minimize inaccuracies caused by the possible presence of small amounts of heavy products and was analyzed for aldehydes by bisulphite titration.<sup>8</sup> (The volume of the residual ether was obtained by subtracting from this volume the volume of aldehyde found and by correcting the pressure for the presence of heavy products.) (4) *Residue non-volatile at  $-70^{\circ}\text{C}$* —this consisted of a heavy liquid with a vapor pressure of about 7 mm at  $25^{\circ}\text{C}$  and was weighed in a removable trap. The heavy products were also analyzed for aldehydes by bisulphite titration.

The  $\text{C}_2$  fraction, residual ether, and the heavy product were analyzed for compounds of the ethylene oxide type by a reaction which depended on the formation of the chlorhydrin<sup>9</sup> and for unsaturates by bromine titration. Neither of these types of compounds was detected.

The procedure adopted for a typical experiment was as follows: Ether was condensed from the storage bulb into a calibrated volume of convenient size and the pressure measured at room temperature with a constant volume manometer. This amount of ether was then condensed in a liquid air trap in the reaction system. This trap was warmed with dry ice-acetone to the desired temperature. The lamp was turned on but separated from the reaction vessel by a cylindrical copper shutter, until the lamp and reaction system, with the circulating pump on, had attained equilibrium. The reaction vessel was illuminated, by dropping the copper shutter, for

TABLE II. Composition of "dimer" and related compounds.

Compound	Formula	% C	% H	% O
"Dimer"	—	65.11	11.89	23.00
$(\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{C}_2\text{H}_4)_2$	$\text{C}_8\text{H}_{18}\text{O}_2$	65.8	12.3	21.9
$(\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{CH}_2)_2$	$\text{C}_8\text{H}_{14}\text{O}_2$	61.0	11.8	22.2
Ethyl ether	$\text{C}_4\text{H}_{10}\text{O}$	64.9	13.5	21.6

<sup>8</sup> A. Zahorka and K. Weiman, *Monats. f. Chemie* **71**, 229 (1938).

<sup>9</sup> (a) O. F. Lubatte, *Trans. Soc. Chem. Ind.*, 361T (1932). (b) F. W. Kerchow, *Zeits. f. anal. Chemie* **108**, 249 (1937).

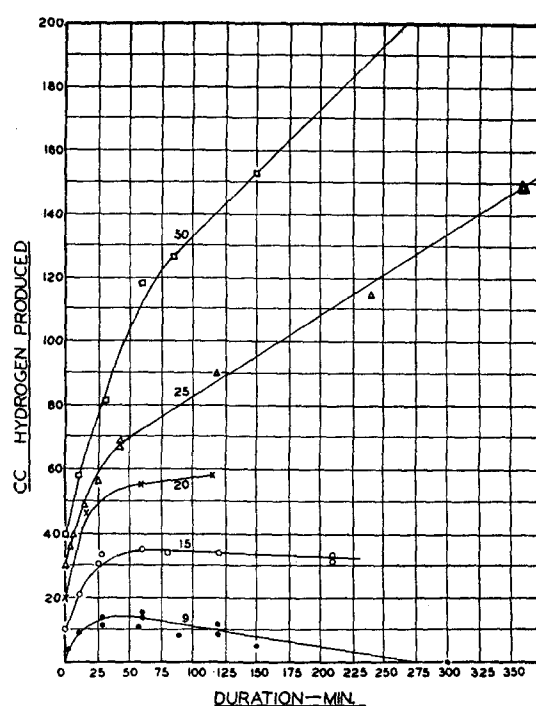


FIG. 2. Effect of time and pressure on the production of hydrogen. Working pressure of ether as indicated on graph.

a definite period, and the lamp was turned off and the products analyzed as described above.

## RESULTS

The effect of working pressure of ether and of the duration of the experiment at constant ether pressure on the nature of the products of the reaction are shown in Table I and Figs. 1 and 2. In Table I we have given a material balance for each experiment; the amounts of C, H, and O found in the products, assuming the aldehyde to be  $\text{CH}_3\text{CHO}$ , were subtracted from the amount of C, H, and O in the ether reacted, the weight of liquid product necessary for a perfect material balance was obtained on the assumption that, on the average, each molecule of liquid product contained two atoms of oxygen. With regard to the above assumption: the aldehyde was found almost entirely in the residual ether fraction and is therefore probably acetaldehyde; the analysis of the liquid product\* was:—65.11 percent C, 11.89 percent H, 23.00 percent O, which is close

\* We are indebted to Dr. Léo Marion of this Laboratory for the micro C—H analysis.

to that of  $C_8H_{18}O_2$ ; the analysis of liquid product is compared in Table II to that of other compounds which may be produced in the reaction and which would be found in the heavy products. From these results it would seem not unreasonable to assume that the liquid product consisted of the "dimer"  $(C_2H_5 \cdot O \cdot C_2H_5)_2$  of diethyl ether probably contaminated with small amounts of the other compounds shown in Table II. The analysis of the portion of the products unaccounted for in the gas corresponds rather closely to  $C_8H_{18}O_2$  in agreement with the analysis of the liquid product, and the weight of liquid product found is, on the average, about 70 percent of the calculated figure. This is considered reasonable in view of the uncertainties attendant on the estimation of small amounts of volatile liquids.

In Fig. 1 we have plotted the volumes of ether reacted and of the various products against the duration of the experiment. The sections of Fig. 1 refer to experiments carried out at different working pressures of ether. In Fig. 2 we have replotted the volumes of hydrogen produced against time so as to make easier the comparison of the effects of time and pressure on the production of hydrogen.

From the results shown in Table I and Fig. 1 it is evident that the volume of ether reacted and of  $H_2$ , CO,  $CH_4$ ,  $C_2$  and liquid products (calculated) varies in a rather regular manner with the duration of the experiment, the volume of aldehyde produced is reasonably constant at constant ether pressure and we have given the average "steady-state" concentration of aldehyde in Table I, Section A to E.

The decrease in the rate of reaction (cc of ether reacted per minute) and of the production of hydrogen and liquid product as well as the consumption of hydrogen produced initially in the runs at low pressures, with the duration of the experiment (Fig. 1) is an important point in deciding on the mechanism of the mercury photosensitized reactions of ether. The effect of time on these rates may be caused either by the accumulation of liquid product on the incident face of the reactor, leading to the formation of "polymer" by subsequent reaction at the wall and so to a decrease in light intensity, or by the accumulation of some product which inhibits the reaction. The results of experiments carried out

to obtain information on this point are given in Table III. These experiments were carried out with ether at 9.3 mm, since the above-mentioned effects are most pronounced at low pressures. To determine the possible effects of the accumulation of polymer on the wall, the reaction was conducted in the normal way for 60 minutes at 9.3 mm pressure; the non-condensable gases,  $C_2$  hydrocarbons and residual ether were removed and measured as usual and the liquid products removed by sealing off a small bulb at the bottom of the cold trap. Fresh ether was then measured, introduced in the reaction system and reacted for 60 minutes at 9.3 mm pressure (Run No. 169(b)). In this way no air was admitted to the system between experiments, and it is likely that most of the polymer formed in the first experiment would remain on the wall for the second reaction. The results do not indicate that the accumulation of polymer has any appreciable effect on the nature of the reaction.

Information on the effect of hydrogen and carbon monoxide on the rate of the reaction is obtained from the results of runs 158 and 159 in which  $H_2$  and  $H_2 + CO$  were added at the start of 30-minute runs in the amounts in which they are present at the end of the first 30 minutes of the reaction. The volumes of ether reacted and of products in these runs therefore should be the same as found during the second thirty minutes of reaction if  $H_2$  and/or CO were responsible for altering the nature of the reaction. From experiment 158 it may be seen that the only effect of hydrogen is to reduce the initial rate of production of hydrogen from 13 to 9 cc in the first 30 minutes and that neither the rate of reaction nor the rate of formation of other products is affected significantly. The additional effect of CO (Run 159) is negligible. The rates found in these experiments do not correspond to those expected in the second half of a 60-minute run. A similar experiment of 60-minute duration (Run No. 162) confirmed that the addition of  $H_2$  reduces only the rate of production of  $H_2$  but not to the extent necessary to explain the disappearance of that product in the 9.3-mm runs and that the rates of disappearance of ether and of the production of CO,  $CH_4$ , and  $C_2$  hydrocarbons are unaffected. Hence the presence of some other products as well as hydrogen and/or CO must be responsible for the re-

TABLE III. Effect of H<sub>2</sub>, CO, and polymer on the reaction at 9.3 mm. Conditions as in Table I.

Run No.	Duration min.	Ether reacted cc	Products—cc				Remarks
			H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub>	
A	30	22	13±1	6±1	6±1	4	Average of "normal" 30-min. runs 99 and 160(a).
B	60	27±4	12±4	10±1	13±1	5±1	Average of "normal" 60-min. runs 105, 161, 163, 169.
C	120	41±7	10±2	17±1	25±1	8±1	Average of "normal" 120-min. runs 165, 167.
D	—	5	0	4	5	1	Production during second 30 min.
E	—	14	0	7	14	3	Production during second 60 min.
158	30	19	9	5	6	4	12.0 cc H <sub>2</sub> added at start.
159	30	20	8	5	7	4	12.0 cc H <sub>2</sub> +7 cc CO added at start.
160(b)	30	—	6	4	6	6	12.0 cc H <sub>2</sub> +7 cc CO added to condensible residue from "normal" 30-min. run (160(a)).
169(b)	60	31	21	8	10	5	Experiment carried out after a "normal" 60-min. run (169) without cleaning cell.
162	60	26	5	8	14	4	15 cc H <sub>2</sub> +6 cc CO added at start.
163(b)	60	—	6	7	13	10	14 cc H <sub>2</sub> +6 cc CO to condensible residue from a "normal" 60-min. run (163).
166	120	46	17	18	24	10	Runs stopped after 60 min.; non-conds. removed from liquid air trap and experiment resumed after 60-min. interruption.
168	120	45	17	17	24	9	
170	120	54	19	13	16	9	

moval of hydrogen from the later stages of the reaction at 9.3 mm. This possibility was tested by adding the requisite amounts of hydrogen and CO to the condensible products, after removal of the non-condensable gases, from experiments of 30-minutes (Run 160(b)) and 60-minutes (Run 163(b)) duration. Again it was found that the rate of production of hydrogen was reduced to about the same extent as when H<sub>2</sub> and CO were added at the start of the experiment. Hence, if some product, other than hydrogen and CO, is responsible for the consumption of hydrogen in the runs at low pressures, it is either removed or changed during the period in which the condensible gases were being frozen out in liquid air. To test this possibility experiments were conducted in which (a) the products after 60-min. reaction at 9.3 mm were frozen out in liquid air for 45 min. and the reaction resumed for a further period of 60 min. after readjusting the trap temperature (Runs 166, 168) and (b) same as (a) but instead of freezing out the products the trap was allowed to warm up to atmospheric temperature while the experiment was interrupted for 45 min. (Run 170). Both experiments

(a) and (b) showed similar trends but the effect in (b) is more marked. By interrupting a 120-min. experiment after 60 min. (Run 170) the volume of ether reacted was increased from 41(±7) to 54 cc and the volume of hydrogen produced increased from 10±2 to 19 cc whereas significant decreases were noted in the volumes of CO and CH<sub>4</sub> produced. These effects can only be explained by the disappearance of some relatively unstable intermediate during the interval between the two halves of the experiment.

#### DISCUSSION

The following facts brought out by this investigation are of importance in devising a mechanism to account for the observed results of the mercury photo-sensitized reactions of diethyl ether:

- (1) The initial products of the reaction are principally hydrogen and the "dimer" of ether with minor amounts of CH<sub>4</sub>, CO, C<sub>2</sub> hydrocarbons and acetaldehyde.
- (2) Initially half a mole each of hydrogen and "dimer" are produced per mole of ether reacted.
- (3) The rates of production of CO, CH<sub>4</sub>, and



C<sub>2</sub> hydrocarbons are equal in the early stages of the reaction.

(4) The rate of production of methane is independent of time but decreases with increasing ether pressure.

(5) The rates of production of CO and C<sub>2</sub> hydrocarbons decrease with time and with increasing ether pressure; the time dependence of these rates is more pronounced in the experiments at low ether pressure.

(6) The volume of acetaldehyde found in the products is independent of time, indicating that the "stationary" concentration is rapidly attained, but increases with increased working pressure of ether.

(7) The rate of decomposition of diethyl ether decreases with time and eventually attains a constant value. The initial rate of ether decomposition is independent of pressure but the constant rate eventually attained increases with increasing ether pressure.

(8) The rates of production of hydrogen and "dimer" also decrease with time and, at high ether pressures, reach constant values. In experiments at low pressures (9.5 and 15 mm) the hydrogen produced in the early stages is consumed in the later stages of the experiment and, at 9.5 mm, actually disappears entirely from the products.

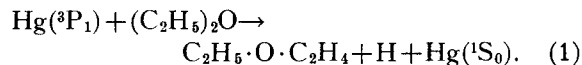
(9) The decrease in the reaction rate and in the rate of production of hydrogen with time is not caused by the accumulation of polymer on the incident face of the reactor.

(10) The addition of hydrogen either to pure ether at the start of the reaction or to a mixture of ether and the condensable products of the reaction decreases the rate of production of hydrogen but does not lead either to the consumption of hydrogen nor does it affect significantly the rates of either the decomposition of ether or of the production of the other products of the reaction.

(11) By interrupting the experiments at low pressures the consumption of hydrogen in the later stages is prevented and the rate of decomposition of ether increased.

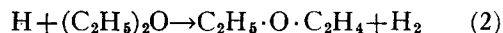
The fact that approximately  $\frac{1}{2}$  mole each of hydrogen and "dimer" (C<sub>8</sub>H<sub>18</sub>O<sub>2</sub>) are produced per mole of ether reacted indicates that the

principal primary act is:



This reaction is in complete accord with the primary step proposed for the similar reactions of the lower paraffin hydrocarbons.<sup>3</sup>

Since the quantum yield for ether decomposition approaches 2.0 at zero time the reaction,

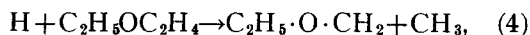


probably occurs with relatively high efficiency. The production of "dimer" is explained satisfactorily by recombination of the radicals produced in reactions (1) and (2),

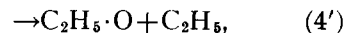


The recombination of the radicals in reaction (3) is probably fast and occurs without real activation energy.

The formation of CO, CH<sub>4</sub>, C<sub>2</sub> hydrocarbons and acetaldehyde indicates that C—C bonds are broken and it has been customary in these reactions to explain C—C splitting as the result of "atomic cracking" reactions first suggested by Rice and Teller.<sup>10</sup> According to the Rice-Teller principle, atomic cracking will occur by the following process:



or



depending on whether the structure of the radical in question was C<sub>2</sub>H<sub>5</sub>·O·CH<sub>2</sub>·CH<sub>2</sub> (leading to (4)) or C<sub>2</sub>H<sub>5</sub>·O·CH·CH<sub>3</sub> (leading to (4')). Since the secondary<sup>11</sup> and tertiary<sup>12</sup> hydrogen atoms are removed more easily than the primary in these reactions, it is likely that the radical would be C<sub>2</sub>H<sub>5</sub>·O·CH·CH<sub>3</sub> and so reaction (4') is likely to be the first stage in the atomic cracking chain. The activation energy of reactions of this type is probably small and may be zero<sup>3(b)</sup> so atomic cracking may be responsible for the early formation of C<sub>2</sub> hydrocarbons and methane. For a rapid formation of acetaldehyde the reaction

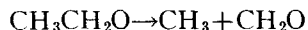


<sup>10</sup> F. O. Rice and E. Teller, J. Chem. Phys. 6, 489 (1938).

<sup>11</sup> E. W. R. Steacie and D. J. Dewar, J. Chem. Phys. 8, 571 (1940).

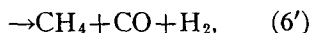
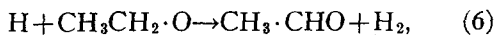
<sup>12</sup> B. deB. Darwent and C. A. Winkler, J. Phys. Chem. 49, 150 (1945).

may be postulated. There is no information available about the speed of this reaction but the reaction



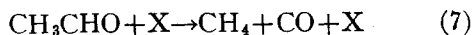
has been estimated to have an activation energy of 28–34 kcal.<sup>13</sup> So by analogy it is likely that the activation energy for reaction (5) is high and therefore this reaction will not be noticeable at 35°C in a system such as the present.

The decomposition of  $\text{C}_2\text{H}_5\text{O}$  by further reaction with H,



may be the source of aldehyde CO and  $\text{CH}_4$  if reactions (5) and/or (4') are responsible for  $\text{CH}_4$  and  $\text{C}_2$  hydrocarbons.

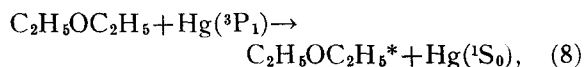
The stationary concentration of acetaldehyde has been found to be a direct linear function of the working pressure of ether, hence acetaldehyde probably disappears by a second-order process in which it is in competition with ether for the second reactant. The decomposition of acetaldehyde has been shown to lead to the formation of CO and  $\text{CH}_4$  and the following reaction:



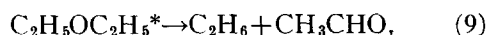
preceded by reactions (4') and (6) can account for the products obtained initially and for the pressure dependence of the rates of production of CO,  $\text{CH}_4$ ,  $\text{C}_2$  hydrocarbons and stationary concentration of acetaldehyde. In the above reaction X may be H or  $\text{Hg}(^3\text{P}_1)$ . If the acetaldehyde disappeared by direct photolysis involving  $\lambda 2537$ , then the stationary concentration of acetaldehyde would not depend on the ether pressure since the aldehyde would be in competition only with  $\text{Hg}(^1\text{S}_0)$  for  $\lambda 2537$  and, since a large excess of mercury was used, the concentration of  $\text{Hg}(^1\text{S}_0)$  is not dependent on the pressure of ether in the reaction vessel under conditions where quenching is reasonably complete. The ratio of the pressure of aldehyde to the working pressure of ether is constant at  $0.020 \pm 0.004$ , hence X must react

considerably faster with acetaldehyde than with ether.

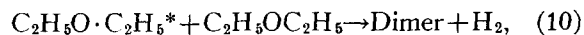
The above mechanism accounts for some of the characteristics of the reaction and is in accord with the mechanisms postulated for the similar reactions of the lower paraffin hydrocarbons,<sup>3(a), 11, 12</sup> however it seems likely that the unsaturated hydrocarbons<sup>4</sup> and even the saturated hydrocarbons<sup>3(b)</sup> react at least in part by the formation of an active molecule and the reactions



and



followed by further rapid reaction of acetaldehyde by reaction (7) could also account for the formation of the minor products of the reaction. The possibility that the "dimer" and hydrogen are also formed by second-order reactions of active ether,



cannot be discredited by our results and would explain the high quantum yield as well as the pressure dependence of the rates of production of CO,  $\text{CH}_4$ , and  $\text{C}_2\text{H}_6$ .

The secondary effects, such as the decrease in rate and consumption of hydrogen with time are indicative of complications in the later stages of the reaction. We have shown that these effects are not caused by the accumulation of hydrogen and carbon monoxide in the system, and, since the aldehyde and the "dimer" must rapidly attain their steady-state concentrations in the gas phase they cannot be responsible for those effects which occur over a considerable period. The experiments in which the runs were interrupted show that a dark reaction occurs and it is likely that this is connected in some way with the removal of hydrogen in the later stages of the experiments. It seems impossible to account for the above phenomena at the present stage of this problem but it is hoped that investigations of similar reactions of simpler compounds of the same type now in progress will throw some light on the subject.

<sup>13</sup> F. O. Rice and E. L. Rodowskas, J. Am. Chem. Soc. 57, 350 (1935).