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## Photolysis of Diisopropyl Peroxide<sup>1</sup>

BY G. R. McMILLAN

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Quantum yield measurements show that diisopropyl peroxide undergoes a photo-initiated, auto-inhibited chain decomposition at 26°. Chains are stopped partly by reaction of the chain carriers, isopropoxy radicals, with acetaldehyde produced by decomposition of the isopropoxy radicals. The data suggest participation of either "excited" isopropoxy radicals which inevitably decompose, or the equivalent multiple scission of bonds in the photochemical primary process. Results of the photodecomposition of diisopropyl peroxide in the presence of nitric oxide are consistent with participation of excited isopropoxy radicals. The fraction of such radicals produced as found by nitric oxide inhibition agrees with the fraction determined from the kinetics of the nitric oxide-free system. The fraction is not very dependent upon temperature. With incident radiation of  $\lambda$  2300–2900 Å., the primary quantum yield of the peroxide at 26 and 77° is close to unity.

### Introduction

Several studies of reactions of alkoxy radicals in the vapor phase have appeared recently in which simple alkyl esters and peroxides were employed as photolytic radical sources.<sup>2–4</sup>

Most attention has been centered on the primary and tertiary radicals. Wijnen has published a quantitative study of isopropoxy radicals from isopropyl propionate.<sup>2d</sup> The system was complicated, however, by a "hot radical" effect.

Diisopropyl peroxide now has been investigated in the hope of obtaining more information about the isopropoxy radical and the photochemical behavior of dialkyl peroxides.

### Experimental

Diisopropyl peroxide<sup>5</sup> was prepared according to the procedure for secondary peroxides described by Welch, Williams and Mosher<sup>6</sup> and purified by distillation at reduced pressure. The peroxide boiled (~94°) at atmospheric pressure without explosion, nor could an explosion be brought about by pounding the compound with a hammer.

A gas chromatographic purification of the peroxide was carried out immediately preceding degassing and irradiation. Even after this treatment, small amounts of acetone and isopropyl alcohol were found in blank experiments. It is believed that the decomposition of the peroxide is due to fluorescent light from the room absorbed by the liquid peroxide during preparation of the sample. With the arc unlighted, there is apparently no decomposition of the vapor in the reaction vessel in short times even at 77°. The correction is therefore constant and is important (normally <8%) only at 77° and in the experiments with added nitric oxide.

Nitric oxide, obtained from Matheson Chemical Co., was freed of other nitrogen oxides and non-condensables by repeated low temperature fractionation.

All photolyses were carried out in quartz vessels using the Hanovia type A mercury arc. The filter combination used

in quantum yield determinations consisted of a 3 mm. thickness of Corning Glass 9863 and a 12 cm. optical path of chlorine (275 mm. pressure) in a quartz vessel. The range of transmission of this filter is 2300–2900 Å. In one experiment, a 2 mm. thickness of Corning Glass 9700 was used to exclude all radiation of wave length less than 2600 Å.

Quantum yields were based on both the diethyl ketone and acetone internal actinometers, taking the quantum yield of carbon monoxide to be unity at appropriate temperatures. Fractional absorptions and lamp decay were measured with a photocell-recorder device.

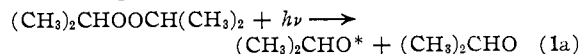
After irradiation of the peroxide, a fraction of products containing ethane, methane, carbon monoxide and oxygen (where present) was removed to the gas buret and analyzed either with the mass spectrometer or the copper-copper oxide furnace. The "liquid" products and unreacted peroxide were separated by gas chromatography. The products were trapped as they left the instrument and analyzed with the mass spectrometer.

### Results and Discussion

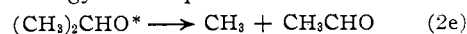
(a) **Photolysis of Diisopropyl Peroxide in the Presence of Nitric Oxide.** Table I.—When diisopropyl peroxide is decomposed in the presence of nitric oxide at 26 or 77° using radiation in the wave length region 2300–2900 Å., the products include acetaldehyde, isopropyl nitrite, methyl nitrate, acetone, nitrogen and small amounts of nitrous oxide. The quantum yields (given in Table I) for some of the products are nearly constant over the ranges of variables studied.

In a series of experiments at 26°, the acetaldehyde quantum yield fell unexpectedly from 1.1 to 0.8 to 0.3, while the yield of isopropyl nitrite was but little affected. The reaction vessel was then heated to 77° for 24 hr.; in a subsequent experiment the acetaldehyde quantum yield was 1.2. Possibly some slightly volatile substance deposited on the wall and destroyed some acetaldehyde. In any case, the cell was heated to 100° for a time before all subsequent experiments and no further "abnormal" yields have been observed.

The high quantum yield of acetaldehyde formation in the presence of an efficient free radical scavenger, nitric oxide, requires a primary photochemical process such as



where  $(\text{CH}_3)_2\text{CHO}^*$  is an excited or "hot" isopropoxy radical which inevitably decomposes due to the excess energy of the quantum.



An equivalent description (for present purposes) is a combination of primary processes in which

(1) Presented in part at the 138th National Meeting of the American Chemical Society, New York, N. Y., September, 1960.

(2) M. H. J. Wijnen, *J. Chem. Phys.*, **27**, 710 (1957); (b) **28**, 271 (1958); (c) *J. Am. Chem. Soc.*, **80**, 2394 (1958); (d) **82**, 1847 (1960); (e) **82**, 3034 (1960).

(3) G. R. McMillan and M. H. J. Wijnen, *Can. J. Chem.*, **36**, 1227 (1958).

(4) G. R. McMillan, *J. Am. Chem. Soc.*, **82**, 2422 (1960).

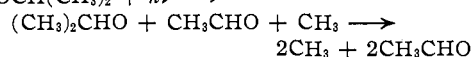
(5) Diisopropyl peroxide is mentioned often in the literature. Gray and Williams (*Chem. Revs.*, **59**, 239 (1959)) and Tobolsky and Mesrobian ("Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, p. 164) give references to the peroxide in their reviews, but the compounds described in the original reports are di-*n*-propyl and methyl isopropyl peroxide, respectively. Milas ("Encyclopedia of Chemical Technology," Vol. X, edited by R. E. Kirk and D. F. Othmer, Interscience Encyclopedia, Inc., New York, N. Y., 1953, p. 65) claims the peroxide can be prepared but offers no reference.

(6) F. Welch, H. R. Williams and H. A. Mosher, *J. Am. Chem. Soc.*, **77**, 551 (1955).

TABLE I  
 PHOTOLYSIS OF DIISOPROPYL PEROXIDE IN THE PRESENCE OF NITRIC OXIDE,  $\lambda$  2300–2900 Å.

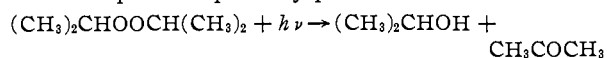
$10^{-17}$ [Peroxide] molecules/ ml.	$10^{-17}$ [NO] molecules/ ml.	$10^{-12}$ $I_a$ , quanta/ ml./sec.	Time, sec.	$\Phi_{\text{CH}_3\text{CHO}}$	$\Phi_{(\text{CH}_3)_2\text{CHONO}}$	$\Phi_{\text{CH}_3\text{COCH}_3}$	$\Phi_{\text{CH}_3\text{ONO}_2}$	$\alpha$	$\varphi$	$k_{16}/k_{17}$
$T = 26^\circ$										
6.8	2.9	2.17	1320	1.13	0.57	0.08	0.45	0.63	0.89	7.1
7.1	6.2	2.15	2220	1.24	.51	.07	.42	.68	.91	7.3
9.7	10.7	2.51	2100	1.21	.61	.09	.51	.63	.96	6.8
10.4	3.2	3.03	1500	(0.8)	.53	.10	.17	...	...	5.3
11.0	6.5	3.33	1620	1.20	.61	.10	.42	.63	.96	6.1
12.5	4.2	3.65	1560	(0.3)	.40	.06	.19	...	...	6.7
$T = 77^\circ$										
6.1	3.6	2.02	1920	1.32	.45	.08	.45	.71	.93	5.6
6.2	5.5	2.08	1440	1.34	.48	.10	.46	.70	.96	4.8
8.7	3.6	2.52	1260	1.36	.56	.13	.51	.66	1.03	4.3
9.9	5.8	3.12	1440	1.34	.54	.09	.56	.68	0.99	6.0

more than one bond is broken in the photolytic act

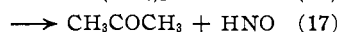
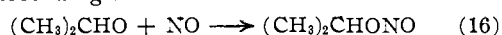
$$(\text{CH}_3)_2\text{CHOOCH}(\text{CH}_3)_2 + h\nu \longrightarrow$$


The description developed will use process 1a, and it will be assumed that the fraction of excited radicals produced, to be called  $\alpha$ , is independent of pressure but not necessarily independent of temperature and of wave length of the absorbed radiation.

The absence of isopropyl alcohol in the products indicates that there is no appreciable contribution from the possible primary process

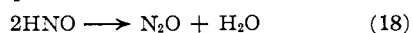


A few mm. of nitric oxide scavenges all the *t*-butoxy radicals produced in the thermal decomposition of di-*t*-butyl peroxide vapor<sup>7</sup>; therefore, at the nitric oxide pressures used in the present work (9–33 mm.), all unexcited isopropoxy radicals will react according to



The values of  $k_{16}/k_{17}$ , calculated as  $\Phi_{(\text{CH}_3)_2\text{CHONO}}/\Phi_{\text{CH}_3\text{COCH}_3}$ , are given in Table I. At 26°,  $k_{16}/k_{17}$  is about 6.6.

The fate of HNO is uncertain, but it may ultimately form  $\text{N}_2\text{O}$ .<sup>8</sup>



The methyl radicals produced in (2e) may form nitrosomethane:



which would be expected to undergo further reactions, dimerization,<sup>9</sup> for example.

Batt and Gowenlock<sup>10</sup> have shown how the reaction of nitrosomethane with nitric oxide may

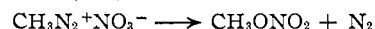
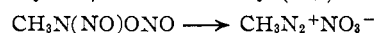
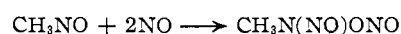
(7) F. W. Birss, C. J. Danby and C. N. Hinshelwood, *Proc. Roy. Soc., (London)*, **A239**, 154 (1957).

(8) P. Harteck, *Ber.*, **66**, 423 (1933); H. A. Taylor and C. Tanford, *J. Chem. Phys.*, **12**, 47 (1944). The paper by R. Srinivasan, *J. Phys. Chem.*, **64**, 679 (1960), gives a lead to more recent references to this reaction.

(9) J. G. Calvert, S. S. Thomas and P. L. Hanst, *J. Am. Chem. Soc.*, **82**, 1 (1960).

(10) L. Batt and B. G. Gowenlock, *Trans. Faraday Soc.*, **56**, 682 (1960).

eventually lead to formation of methyl nitrate and nitrogen.



The first step of the proposed mechanism is the reaction reported by Christie.<sup>11</sup> Christie also observed a competing reaction first order with respect to nitric oxide.

At the pressures used in the work, only the first-order reaction would be important; hence, the Batt-Gowenlock mechanism requires some modification to explain the formation of methyl nitrate and nitrogen in the diisopropyl peroxide-nitric oxide system. The methyl nitrate quantum yield shows no great sensitivity to changes in nitric oxide pressure—in fact all the yields are roughly the same except in the two experiments in which the acetaldehyde yield was also “abnormal.” A quantitative analysis of nitrogen was made in only one experiment. The quantum yield was 0.48, close to the values normally found for the methyl nitrate quantum yield.

The apparent primary quantum yield,  $\varphi$ , computed from

$$\varphi = 1/2(\Phi_{\text{CH}_3\text{CHO}} + \Phi_{(\text{CH}_3)_2\text{CHONO}} + \Phi_{\text{CH}_3\text{COCH}_3})$$

is given in Table I. The yield is close to unity at 26 and at 77°.

The fraction of excited radicals,  $\alpha$ , produced in the primary process, computed from

$$\alpha = \Phi_{\text{CH}_3\text{CHO}}/(\Phi_{\text{CH}_3\text{CHO}} + \Phi_{(\text{CH}_3)_2\text{CHONO}} + \Phi_{\text{CH}_3\text{COCH}_3})$$

takes average values of 0.64 at 26° and 0.69 at 77°.

In other photochemical systems (esters, ketones) involving decomposition of excited radicals, the fraction inevitably decomposing is found to increase markedly with temperature.<sup>2b,d,12</sup> In the dialkyl peroxides, absorption at wave lengths around 2500 Å. is presumably continuous and the absorbed quanta are of energy much greater than required for bond breaking. Thus the temperature dependence of  $\alpha$  may be small. An offsetting effect may arise in the present system, where the absorbed radiation is not strictly monochromatic

(11) M. I. Christie, *Proc. Roy. Soc. (London)*, **A249**, 248 (1959).

(12) J. E. Jolley, *J. Am. Chem. Soc.*, **79**, 1537 (1957).

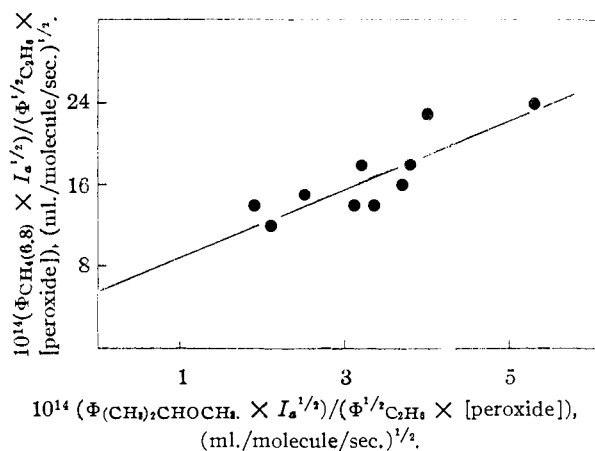
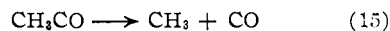
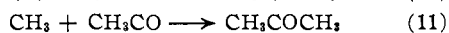
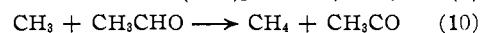
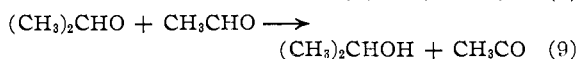
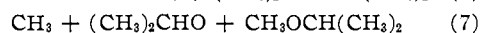
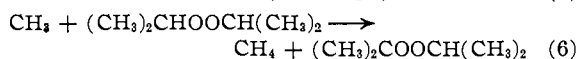
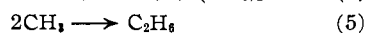
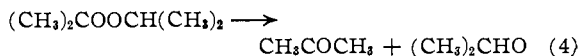
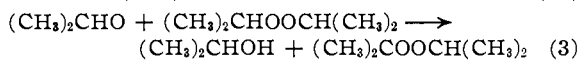
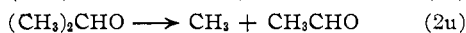
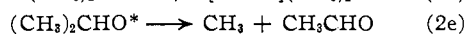
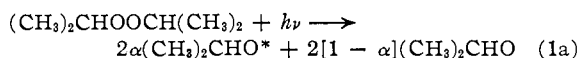


Fig. 1.—Determination of  $k_8/k_7$  at  $26^\circ$ .

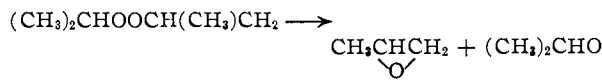
and where absorption is far to the long wave length side of the absorption maximum. Higher temperatures would favor absorption of the longer wave lengths transmitted by the filter, possibly resulting in a decrease in  $\alpha$ .

(b) **Photolysis of Diisopropyl Peroxide Using Filtered Light.** Table II.—



(i) **The System at  $26^\circ$ .**—When diisopropyl peroxide is illuminated at  $26^\circ$  with light in the wave length region 2300–2900 Å., the products include acetaldehyde, acetone, isopropyl alcohol, methane, ethane, biacetyl, methyl isopropyl ether and carbon monoxide. The quantum yield of isopropyl alcohol formation rises above two, giving clear evidence for the participation of chains. Since the yields of isopropyl alcohol and acetone are about the same, the chain sequence is probably (3) followed by (4).

Abstraction of primary hydrogen from diisopropyl peroxide probably is negligible, since no propylene oxide is found in the products. Propylene oxide would be expected to arise according to the reaction



The analogous reaction in the di-*t*-butyl peroxide system is known to occur under comparable conditions.<sup>4</sup>

The remainder of the mechanism accounts for the other products. The disproportionation step 14 is small relative to the combination and will be neglected. Methane may be formed in reactions 6, 8, 10 and 12. Using the low temperature, low intensity value<sup>13</sup> of  $k_{10}/k_5^{1/2}$  of  $8.5 \times 10^{-13}$  (ml./molecule/sec.)<sup>1/2</sup>, it may be shown that (10), abstraction of hydrogen from acetaldehyde by methyl, will contribute 0.002 or less to the methane quantum yield. The reaction is therefore neglected at  $26^\circ$ . Since the quantity  $k_{12}/k_{11}$  is known to be 0.06,<sup>2a,b</sup>  $\Phi_{12}$  may be computed from  $\Phi_{11}$  and subtracted from the over-all methane quantum yield to give  $\Phi_{\text{CH}_4(6,8)}$ . The following equation then may be derived

$$\frac{\Phi_{\text{CH}_4(6,8)} \times I_a^{1/2}}{\Phi_{\text{C}_2\text{H}_6}^{1/2} \times [\text{Peroxide}]} = \frac{k_6}{k_5^{1/2}} + \frac{k_8}{k_7} \frac{\Phi_{(\text{CH}_3)_2\text{CHOOCH}_3} \times I_a^{1/2}}{\Phi_{\text{C}_2\text{H}_6}^{1/2} \times [\text{Peroxide}]}$$

The equation is plotted in Fig. 1 for all  $26^\circ$  experiments where  $\Phi_{(\text{CH}_3)_2\text{CHOOCH}_3} \geq 0.01$ . The ratio  $k_6/k_5^{1/2}$  is found to be  $5.5 \times 10^{-14}$  (ml./molecule/sec.)<sup>1/2</sup>. The ratio of rate constants for disproportionation to combination of methyl and isopropoxy radicals,  $k_8/k_7$ , is found to be 3.4.<sup>14</sup> This value may be compared with the corresponding ratios for the methyl-methoxy-*d*<sub>3</sub> and ethyl-ethoxy pairs of 1.3–1.4.<sup>2b,e</sup>

The quantum yields of some of the other individual reaction steps may be estimated from the equations

$$\Phi_{11} = 2(\Phi_{\text{C}_2\text{H}_6}\Phi_{\text{CH}_3\text{COCOCH}_3})^{1/2} \quad (A)$$

$$\Phi_6 = \Phi_{\text{CH}_4} - 0.06\Phi_{11} - 3.4\Phi_{(\text{CH}_3)_2\text{CHOOCH}_3} \quad (B)$$

$$\Phi_{\text{CH}_3(2)} = \Phi_{2e} + \Phi_{2u} = 2\Phi_{\text{C}_2\text{H}_6} + \Phi_{\text{CH}_4} + \Phi_{11} + \Phi_{(\text{CH}_3)_2\text{CHOOCH}_3} - \Phi_{\text{CO}} \quad (C)$$

$$\Phi_{\text{CH}_3\text{CHO}(2)} = \Phi_{\text{CH}_3\text{CHO}} + 1.06\Phi_{11} + 2\Phi_{\text{CH}_3\text{COCOCH}_3} + \Phi_{\text{CO}} \quad (D)$$

$$\Phi_3 = \Phi_{(\text{CH}_3)_2\text{CHOH}} - 2\Phi_{\text{CH}_3\text{COCOCH}_3} - 1.06\Phi_{11} - \Phi_{\text{CO}} \quad (E)$$

$$\Phi_{\text{CH}_3\text{COCH}_3(3,4)} = \Phi_{(3,4)} = \Phi_{\text{CH}_3\text{COCH}_3} - \Phi_6 - \Phi_{11} - 3.4\Phi_{(\text{CH}_3)_2\text{CHOOCH}_3} \quad (F)$$

The number *two* in equation A is the value<sup>2a,15</sup> of  $k_{11}/k_5^{1/2}k_{13}^{1/2}$ .  $\Phi_{\text{CH}_3(2)}$  and  $\Phi_{\text{CH}_3\text{CHO}(2)}$  are the calculated yields of methyl and acetaldehyde from step 2 (*i.e.*, the sum of 2e and 2u). Equation F, giving the acetone formed in the (3), (4) sequence, assumes (3) is always followed by (4). The calculated yields are given in Table II.

The following equation may be derived

$$\Phi_{\text{CH}_3(2)}[\text{peroxide}]/\Phi_3 = k_{2u}/k_3 + 2\alpha[\text{peroxide}]/\Phi_3$$

The plot, Fig. 2, yields  $\alpha = 0.66$  at  $26^\circ$  in good agreement with 0.64 determined by nitric oxide

(13) P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 31 (1955).

(14) It is difficult to assess the reliability of the value of  $k_8/k_7$  determined from this equation because of the very small ether quantum yields involved. Furthermore,  $k_8$  may be pressure dependent, since step 6 may take place largely upon the walls at this low temperature. It may be noted that the crude value of the apparent activation energy of 6 which may be obtained in this work,  $\sim 9.5$  kcal., is not unreasonably low for a true gas-phase hydrogen abstraction from the peroxide. The author is grateful to Referee II for help in the development of  $k_8/k_7$ .

(15) J. G. Calvert and J. T. Gruver, *J. Am. Chem. Soc.*, **80**, 1313 (1958); P. Ausloos and E. Murad, *ibid.*, **80**, 5929 (1958).

TABLE II  
PHOTOLYSIS OF DIISOPROPYL PEROXIDE  
 $\lambda$  2300-2900 Å.

$10^{-17}$ [Peroxide] <sub>0</sub> molecules/ ml.	$I_a \times$ $10^{-12}$ , quanta/ ml./sec.	Time, sec.	$\Phi_{(CH_3)_2CHOH}$	$\Phi_{CH_3CHO}$	$\Phi_{CH_3COCH_3}$	$\Phi_{CH_3COCOCCH_3}$	$\Phi_{(CH_3)_2CHOCH_3}$	$\Phi_{C_2H_6}$	$\Phi_{CH_4}$	$\Phi_{CO}$	$\Phi_{H_2}$	$\Phi$	$\Phi_1$	$\Phi_{2,4}$	$\Phi_{CH_3CHO(2)}$	$\Phi_{CH_4(2)}$	$10^{-15}$ [CH <sub>3</sub> CHO] <sub>ave.</sub> molecules/ ml.
Temp. 26°																	
5.18	1.73	1260	3.4	1.0	3.3	0.009	0.009	0.70	0.082	0.021	0.16	0.041	3.2	3.1	1.2	1.63	1.3
5.18	2.01	4320	2.0	0.92	2.0	.031	.009	.56	.065	.046	.27	.018	1.6	1.7	1.3	1.42	4.5
5.25	1.86	3600	2.2	0.97	2.2	.019	.010	.66	.065	.048	.22	.018	1.9	1.9	1.3	1.57	3.7
7.94	2.63	2760	2.9	1.0	3.1	.028	.013	.65	.072	.046	.27	.012	2.5	2.8	1.4	1.61	4.2
7.94	2.63	900	5.0	1.3	4.6	.009	.022	.73	.11	.049	.16	.025	4.8	4.3	1.5	1.70	1.7
7.94	2.70	2280	3.5	0.96	3.4	.033	.012	.64	.070	.031	.28	.012	3.1	3.1	1.4	1.61	3.3
8.06	3.06	2280	3.2	.93	3.2	.034	.013	.60	.072	.036	.28	.011	2.8	2.9	1.3	1.53	3.7
9.73	3.31	300	5.7	.59	6.5	.005	.019	.77	.12	.027	.13	.047	5.5	6.3	0.8	1.78	0.3
10.7	0.37	7500	6.1	1.1	6.4	.005	.008	.67	.19	.081	.12	.16	5.9	6.1	1.3	1.58	1.9
10.7	0.39	7620	5.5	1.0	5.4	.012	.000	.56	.18	.051	.16	.17	5.3	5.1	1.2	1.42	1.8
10.7	1.50	3300	5.0	0.90	4.9	.020	.014	.57	.093	.040	.21	.032	4.7	4.6	1.2	1.42	2.6
10.7	3.59	480	5.7	.97	5.5	.012	.018	.71	.095	.033	.19	.023	5.4	5.2	1.2	1.69	0.95
10.7	3.61	2220	4.1	.98	4.0	.037	.011	.59	.083	.036	.29	.029	3.7	3.6	1.4	1.53	4.8
10.7	4.14	900	4.9	1.0	4.8	.017	.008	.61	.089	.043	.20	.050	4.6	4.5	1.3	1.47	2.2
14.9	4.49	900	7.4	1.1	7.2	.016	.011	.70	.095	.060	.22	.045	7.0	6.9	1.5	1.67	2.4
Temp. 77°																	
4.42	2.29	3600	0.53	1.5	0.53	•	•	.86	.18	.11	•	.16	0.44	0.37	1.6	1.79	7.1
4.42	1.99	5940	.66	1.6	.70	...	...	1.04	.21	.15	...	.18	.54	.48	1.8	2.14	9.3
4.42 <sup>b</sup>	1.93	5700	.51	n.d. <sup>c</sup>	.57	...	...	0.94	.21	.15	...	.18	.39	.39	n.d.	1.94	n.d.
5.93	2.89	4320	.69	1.5	.76	...	...	.94	.21	.13	...	.19	.58	.57	1.6	1.96	8.9
7.37	3.60	4320	.84	1.9	.84	...	...	.90	.24	.14	...	.21	.73	.63	2.0	1.90	14.0
10.2	4.88	1800	.86	1.5	1.06	...	...	.91	.29	.08	...	.28	.79	.78	1.6	2.03	5.8
10.2	4.85	2700	.95	1.5	1.03	...	...	.89	.26	.14	...	.25	.82	.78	1.6	1.90	9.5
10.2 <sup>d</sup>	4.61	1800	.91	n.d.	n.d.	...	...	n.d.	n.d.	n.d.	...	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
12.7	5.64	1860	1.19	1.6	1.31	...	...	.94	.27	.11	...	.26	1.1	1.1	1.7	2.04	8.2

• Negligible at 77°. <sup>b</sup>  $4.4 \times 10^{17}$  molecules/ml. of CO<sub>2</sub> added. <sup>c</sup> Not determined. <sup>d</sup>  $44 \times 10^{17}$  molecules/ml. of *i*-C<sub>4</sub>H<sub>10</sub> added.

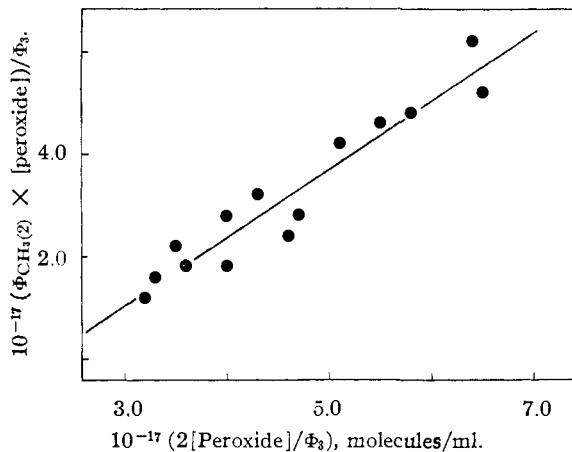


Fig. 2.— $\Phi_{\text{CH}_3(2)} \times [\text{Peroxide}]/\Phi_3$  as a function of  $2[\text{peroxide}]/\Phi_3$  at  $26^\circ$ .

inhibition. The intercept gives  $k_{2u}/k_3$  of  $0.5 \times 10^{17}$  molecules/ml.

(ii). **The System at  $77^\circ$ .**—At  $77^\circ$ , biacetyl is not found among the products, hence the acetyl radical is presumed to be completely decomposed to methyl and carbon monoxide. Thus the combination and disproportionation reactions 11 through 14 are unimportant. Likewise 7 and 8 are ruled out by the absence of methyl isopropyl ether in the products.

Methane will now be formed by (6) and (10). Since a detailed study of the conversion dependence of methane was not made, the amount of methane formed from acetaldehyde must be estimated using data from the study of reaction 10 at high acetaldehyde pressures. Using a value of  $k_{10}/k_3^{1/2}$  of  $35 \times 10^{-13}$  (ml./molecule/sec.)<sup>1/2</sup> interpolated from the work of Ausloos and Steacie,<sup>13</sup> it is possible to compute  $\Phi_{10}$  and hence the quantum yields of the other steps in the mechanism. The equations are

$$\Phi_{\text{CH}_3(2)} = 2\Phi_{\text{C}_2\text{H}_5} + \Phi_{\text{CH}_4} - \Phi_{\text{CO}} \quad (C')$$

$$\Phi_{\text{CH}_3\text{CHO}(2)} = \Phi_{\text{CH}_3\text{CHO}} + \Phi_{\text{CO}} \quad (D')$$

$$\Phi_3 = \Phi_{(\text{CH}_3)_2\text{CHOH}} - \Phi_9 \quad (E')$$

$$\Phi_{\text{CH}_3\text{COCH}_3(3,4)} = \Phi_{\text{CH}_3\text{COCH}_3} - \Phi_6 \quad (F')$$

The computation of  $\Phi_{(3,4)}$  depends, as before, on the assumption that the large peroxy radical is completely dissociated.

(iii). **Material Balance.**—At  $26^\circ$ , the material balance for isopropoxy radicals predicts that

$$2 + \Phi_8 = \Phi_{\text{CH}_3(2)} + 4.4\Phi_{(\text{CH}_3)_2\text{CHOCH}_3} + \Phi_{\text{CO}} + 1.06\Phi_{11} + 2\Phi_{\text{CH}_3\text{COCOCCH}_3}$$

if the primary quantum yield is unity. An average of 6% of the total radicals is unaccounted for. Likewise at  $77^\circ$ , the mechanism requires equality between  $\Phi_{\text{CH}_3(2)}$  and  $2 + \Phi_{\text{CH}_4} - \Phi_{\text{CO}}$ . An average of 93% accountability is achieved. In the nitric oxide inhibited decomposition, the average "apparent primary quantum yield" was 0.93 at  $26^\circ$  and 0.98 at  $77^\circ$ .

At both temperatures,  $\Phi_{\text{CH}_3(2)}$  is greater than  $\Phi_{\text{CH}_3\text{CHO}(2)}$  by about 20%. The ratio of the two calculated yields shows no trend with peroxide concentration, intensity nor extent of conversion. The true yield of (2) is taken as  $\Phi_{\text{CH}_3(2)}$  because this

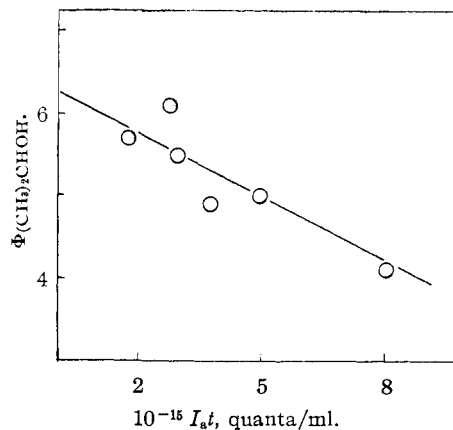


Fig. 3.—Dependence of isopropyl alcohol quantum yield on extent of photodecomposition at  $26^\circ$ . Peroxide concentration is  $10.7 \times 10^{17}$  molecules/ml.

quantity approaches the limiting value. Since  $\Phi_{\text{CH}_3(2)}/\Phi_{\text{CH}_3\text{CHO}(2)}$  is the same at  $26$  and  $77^\circ$ , the discrepancy may not be attributed to difficulties in correcting the acetaldehyde yield for degradation, nor has it been possible to ascribe the discrepancy to analytical errors. No satisfactory explanation can be offered at this time.

(iv). **The Chain Reaction.**—The system at  $26^\circ$  is complicated by auto-inhibition. Figure 3 shows the rapid decrease of the isopropyl alcohol quantum yield with increase in total photodecomposition at constant initial peroxide concentration. The highest conversion in the figure is about 0.7%. The effect is qualitatively the same at lower peroxide concentrations. A plot of  $1/\Phi_{(\text{CH}_3)_2\text{CHOH}}$  vs.  $I_a t/[\text{peroxide}]$  for all the  $26^\circ$  experiments is a reasonably straight line. The probable time dependent chain breaking reaction is (9), the abstraction of hydrogen from acetaldehyde by isopropoxy. The acetyl radical produced does not normally start a new chain. The ratio of rate constants of abstraction from acetaldehyde and diisopropyl peroxide may be estimated from

$$\frac{k_9}{k_3} = \frac{1.06\Phi_{11} + 2\Phi_{\text{CH}_3\text{COCOCCH}_3} + \Phi_{\text{CO}} [\text{peroxide}]}{\Phi_9 [\text{CH}_3\text{CHO}]}$$

if the average acetaldehyde concentration is substituted. A ratio  $k_9/k_3 = 27 \pm 4$  embraces most of the values calculated for the  $26^\circ$  experiments. Serious deviation is observed only in the two experiments at the very lowest conversions. A  $k_9/k_3$  of this magnitude is sufficient to explain the inhibition shown in Fig. 3.

Since  $\Phi_{\text{CH}_3(2)}$  at  $26^\circ$  exceeds  $2\alpha$ , some chains must be stopped by decomposition of the isopropoxy radicals of thermal energies, step 2u. At  $77^\circ$ , this is the only chain ending step of importance, and  $\Phi_{\text{CH}_3(2)}$  approaches the maximum value.

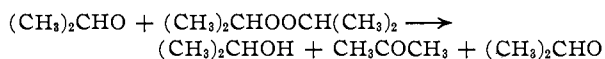
The chain lengths, given by  $\Phi_3/[\Phi_6 + 2(1 - \alpha)]$ , always exceed two at  $26^\circ$ . The value at the highest pressure studied was ten. At  $77^\circ$ , the chain length is greater than unity only at the highest pressure studied.

The calculated values of  $\Phi_3$  and  $\Phi_{3,4}$  are in fair agreement; therefore, (4) nearly always follows (3). A concerted process

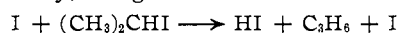
TABLE III  
PHOTOLYSIS OF DIISOPROPYL PEROXIDE—EFFECT OF WAVE LENGTH  
 $T = 77^\circ$ ; rates in molecule/ml./sec.  $\times 10^{-12}$

$10^{-17}$ [Peroxide] molecules/ ml.	Time, sec.	Wave length region	$R_{C_2H_6}$	$R_{CH_4}$	$R_{CO}$	$R_{i-C_4H_{10}}$	$R_{O_2}$	% (1b.)
0.55	12600	Full <sup>a</sup>	1.65	0.41	0.79	0.15	0.22	5.5
2.48	4500	Full <sup>a</sup>	7.67	1.37	1.90	.58	.48	4.4
3.45	2700	Full <sup>a</sup>	10.07	1.43	1.77	.25	.21	1.5
3.59	2700	Full <sup>a</sup>	9.99	1.43	1.81	.25	.34	1.5
8.56	720	Full <sup>a</sup>	20.08	2.85	2.06	.63	.16	1.8
10.2	660	Full <sup>a</sup>	24.84	3.97	2.76	.52	.17	1.2
4.14	4500	2300-2900	3.54	0.66	0.58	.02	.00	...
7.87	2400	2300-2900	6.31	1.42	0.90	.00	.00	...
10.2	1740	2300-2900	8.96	2.29	1.44	.00	.00	...
10.2	4500	>2600	2.07	0.86	0.51	.01	.00	...

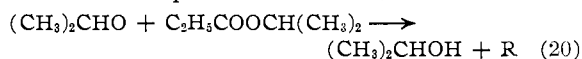
<sup>a</sup> Full light of quartz mercury arc.



is a possibility, being similar to the reaction<sup>16</sup>



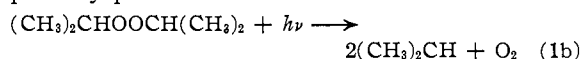
but the distinction is more difficult to make in the peroxide case. The alcohol forming step does not seem abnormal. The value of  $k_{21}/k_3$  at  $26^\circ$  estimated above,  $0.5 \times 10^{17}$  molecules/ml., is close to the value reported<sup>2d</sup> for  $k_{21}/k_{20}$ ,  $1 \times 10^{17}$  at  $28^\circ$ .



Furthermore, the value of  $k_6/k_5^{1/2}$  at  $77^\circ$  which may be estimated from the present work,  $6 \times 10^{-13}$  (ml./molecule/sec.)<sup>1/2</sup> is in line with normal hydrogen abstraction reactions of methyl radicals.

(c) **Photolysis of Diisopropyl Peroxide Using Unfiltered Light.** Table III.—The system using unfiltered light will not be discussed in detail. In addition to the products observed when filtered radiation was used, isobutane and oxygen were produced, and there was indication of propylene and propane and possibly methyl alcohol. Table III shows the rates of formation of some of the products. Neither isobutane nor oxygen is formed when a filter opaque below 2300 Å. is interposed in the light beam.

The formation of these products requires a primary process such as



analogous to the step found by Frey<sup>17</sup> in the di-

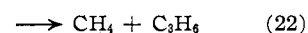
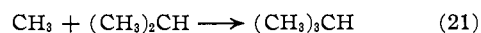
(16) G. R. McMillan and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **80**, 2108 (1958).

(17) H. M. Frey, *Proc. Chem. Soc. (London)*, **385** (1959).

butyl peroxide photolysis. Frey reported no oxygen in the products, and there seems to be no direct evidence from Frey's results nor from the present results that oxygen is formed in the primary photochemical process. For example, the oxygen may be formed by some reaction of alkylperoxy radicals actually formed in the primary process.

The new products are accounted for by the usual reactions of isopropyl radicals and of oxygen.

Isopropyl radicals will disappear mainly by reaction with methyl



a value of 0.22 has been reported<sup>18</sup> for  $k_{22}/k_{21}$ . If the other reactions of isopropyl are ignored, the fractional contribution of (1b) to the primary process will be given roughly by  $1.22R_{i-C_4H_{10}}/2R_{C_2H_6} + 2.22R_{i-C_4H_{10}} + R_{CH_4} - R_{CO}$ . The importance of (1b) is indicated in Table III as a percentage. The low wave length process contributes about 1% to the total at high pressures and 5.5% at the lowest pressure studied, 2 mm.

In any case, the importance of the low wave length process will depend strongly upon the wave length distribution of the radiation and upon the transmission of the cell window in any given system.

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(18) J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1609 (1960).