

technique that the C₃ fraction contained propylene as well as propane. No attempt was made to isolate hexane.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Photoöxidation of Diethyl Ketone¹

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The photochemical reaction between diethyl ketone and oxygen has been studied at temperatures from 35 to 150° at several oxygen pressures and over a wide range of intensities. At all temperatures the carbon monoxide yield becomes small at high oxygen pressures, thus indicating that the propionyl radical reacts with oxygen without producing carbon monoxide. All yields pass through maxima (except possibly carbon monoxide at 35°), and oxygen acts as an inhibitor at high oxygen pressures. At room temperature quantum yields are independent of intensity, but at 150° they are an inverse linear function of the square root of the intensity. Oxygen at very low pressures strongly suppresses the formation of C₂ hydrocarbons so that the reaction between ethyl radicals and oxygen must be very rapid. A fairly complete mechanism for the reaction can be suggested and the relative values of several rate constants estimated. Chains must be propagated mainly by ethoxy and pentanonyl radicals. Since rates of formation of acetaldehyde and carbon dioxide are closely parallel to each other, possibly pentanonyl radicals react with oxygen to give acetaldehyde, carbon dioxide and ethyl radicals.

Introduction

The photolysis of diethyl ketone has been studied, and a mechanism which satisfactorily accounts for the experimental observations has been put forward.³⁻⁶ Information about some of the reactions of radicals with oxygen was obtained⁷ in an investigation of the photolysis of mixtures of diethyl ketone and oxygen. The reaction was shown to be a complex radical chain of short length, and various possible radical reactions were discussed. The primary process is almost certainly reaction 1, and it is known that the propionyl radical dissociates almost completely even at room temperature (reaction 2) in the absence of foreign substances. In the presence of oxygen the low yield of carbon monoxide indicates that reaction 2 is largely suppressed. Reaction 3 has been suggested for the reaction of propionyl radicals with oxygen.^{7,8}

The present paper gives further data on the diethyl ketone-oxygen reaction. In general, oxygen suppresses formation of C₂ hydrocarbons more completely than hitherto indicated. Due to the chain character of the reaction, great care must be exercised to avoid local depletion of oxygen when the oxygen pressure is low. The higher values for C₂ formation previously reported⁷ are thought to be due to such local depletion of oxygen.

Experimental

The reaction was carried out in a high vacuum system consisting essentially of a reaction cell, fractionation spiral,

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(2) Postdoctoral Fellow 1953-1955 under a grant from the Camille and Henry Dreyfus Foundation, Inc.

(3) W. Davis, Jr., *THIS JOURNAL*, **70**, 1808 (1948).

(4) L. M. Dorfman and Z. D. Sheldon, *J. Chem. Phys.*, **17**, 511 (1949).

(5) K. O. Kutschke, M. H. J. Wijnen and E. W. R. Steacie, *THIS JOURNAL*, **74**, 714 (1952).

(6) M. H. J. Wijnen and E. W. R. Steacie, *Can. J. Chem.*, **29**, 1092 (1951).

(7) A. Finkelstein and W. A. Noyes, Jr., *Disc. Faraday Soc.*, No. 14, **76**, 81 (1953).

(8) R. B. Martin, Ph.D. Thesis, University of Rochester, 1953.

McLeod gage and oxidizing furnace. The parallel light beam entirely filled the cell, and homogeneous conditions were maintained by means of a magnetically driven stirrer. The volume of the part of the line which included the McLeod gage was 663.6 ml., the volume of the reaction system (including stirrer) was 198.8 ml., and the volume of the reaction cell was 76.0 ml.

Two light sources were used (1) a Hanovia Alpine Burner and (2) a water-cooled General Electric Co. A-H6 arc. The beam was collimated by a quartz lens, and radiation below 2300 Å. was removed by a Corning 9863 red-purple Corex filter. Since the long wave absorption limit in diethyl ketone is about 3200 Å., the chief absorbed wave lengths were 3130, 2650 and 2537 Å. Some experiments used a chlorine gas filter so that the main transmitted radiation was 2650 Å. Another series was carried out with a 2-mm. Pyrex plate to give mainly 3130 Å. Intensity effects were studied by neutral density filters of two types—silver coated quartz plates and darkened copper screens. Transmissions were determined by a photo cell and also by a Beckman photometer.

The measurement of the radioactivity of the C¹⁴-labeled products was made by freezing them into a proportional counter tube of the type described by Bernstein and Ballantine⁹ and counting on a scaler. It was found that the activities of portions of a given sample were directly proportional to their pressures.

Procedure.—A small sample of diethyl ketone, prepared as previously described⁶ was removed from the black storage bulb and degassed before being admitted to the cell at 35 mm. pressure, at which pressure all runs were carried out. The desired amount of oxygen (prepared by heating potassium permanganate) was added and the well-stirred mixture illuminated. The gases not condensed by liquid nitrogen (oxygen and carbon monoxide) were removed, measured and transferred to a bulb containing copper-copper oxide which could be heated in a furnace. The resultant carbon dioxide enabled oxygen and carbon monoxide to be calculated. At -160° a second sample, carbon dioxide, was removed and measured, and a third fraction was obtained at -115°. The third fraction was acetaldehyde and was readily characterized by freezing it from the system and causing it to react with *p*-hydroxydiphenyl with which it gives a colored compound with a characteristic absorption peak at 5700 Å.¹⁰

In experiments at low oxygen pressure, oxygen was added by a "doser" to keep the oxygen pressure approximately constant.¹¹ Small amounts of ethane and ethylene are produced under these conditions. In these experiments, the non-condensable gases were passed through a fractionation spiral maintained at -215° with supercooled liquid nitrogen. This prevents removal of ethane and ethylene

(9) W. Bernstein and R. Ballantine, *Rev. Sci. Instr.*, **21**, 158 (1950).

(10) E. Stotz, *J. Biol. Chem.*, **148**, 585 (1943).

(11) F. B. Marcotte and W. A. Noyes, Jr., *Disc. Faraday Soc.*, No. 10, 236 (1951).

with the oxygen and carbon monoxide. The C₂ hydrocarbons were then removed through a liquid oxygen trap and measured.

Results

The following quantum yields are reported: oxygen disappearance, C₂ hydrocarbons, carbon monoxide, carbon dioxide, acetaldehyde. They are obtained in each case by dividing the amount of product by the carbon monoxide formed in a photolysis without oxygen, carried out either immediately before or after the oxygen run. This assumes that the quantum yield of carbon monoxide production in the absence of oxygen is unity, and the intensities quoted are also based on this assumption. This is true at temperatures of 100 to 200°, but may be a slight overestimate at 35°. Runs made with pure diethyl ketone in the absence of oxygen failed to show a definite trend in the ratio of carbon monoxide formed to incident intensity at 35°. There may be a slight decrease in quantum yield of carbon monoxide formation at high intensities due to reaction between ethyl and propionyl radicals. Kutschke, Wijnen and Steacie⁵ using higher intensity radiation than used in this work found values of $\Phi_{CO} = 0.6$ at 25° and 0.8 at 50°. Thus while no evidence indicating radical recombination was found in this work, it is possible that the quantum yields quoted at 35° are all 10 to 20% high. This does not affect the conclusions reached. At the higher temperatures, the quantum yields should not be subject to any systematic error caused by low carbon monoxide yields in the absence of oxygen.⁴

Table I shows the quantum yields as functions of oxygen pressure at four temperatures. They are accurate to within about 0.05 except for occasional inexplicable wrong values, and also excepting the quantum yield of oxygen disappearance which may be in error by as much as 0.5 in some runs. In all runs the amount of diethyl ketone reaction was kept well below 1/2% so that secondary reactions of products were negligible. The most interesting feature is that the oxygen consumption passes through a maximum at 35° and that the maximum becomes less pronounced with increasing temperature. The quantum yields of carbon dioxide and acetaldehyde follow a similar course, the former being the larger at low temperatures, while the acetaldehyde predominates at the high temperatures. The carbon monoxide quantum yield falls rapidly from unity at 35°, but at 150° reaches values as high as 1.8. Some experiments were carried out at higher oxygen pressures (about 30 mm.) to determine whether oxygen completely prevents reaction or not. These results are also shown in the tables.

Ethane and ethylene are produced at very low oxygen pressures and then only in very small amounts which increase with increasing temperature. These quantum yields are given in Table II. A few experiments were carried out with 35 mm. of diethyl ketone and high pressures of nitric oxide to act as a "scavenger." The results are shown in Table III. Nitrogen was one of the main products when nitric oxide was present. No attempt is made to explain this fact in view of the small number of runs carried out with nitric oxide present.

The quantum yield of oxygen disappearance is larger than the sum of CO₂ and CH₃CHO, thus indicating that there is at least one major oxygen-

TABLE I
QUANTUM YIELDS IN DIETHYL KETONE-OXYGEN MIXTURES
Ketone pressure = 35 mm.

O ₂ pressure, mm.	Length of run, min.	I_a , einsteins/ml./sec. $\times 10^{12}$	Φ_{O_2}	Φ_{CO}	Φ_{CO_2}	Φ_{CH_3CHO}	Φ_{CO} calcd.
$T = 35^\circ$							
0.033	10.50	7.75	4.60	0.26	2.26	1.47	0.29
.075	10.20	7.75	4.82	.16	2.49	1.65	.19
.195	10.40	7.75	4.63	.13	2.45	1.18?	.13
.400	10.50	7.75	4.65	.15	2.42	1.66	.11
.745	11.00	7.75	4.16	.13	2.10	1.03	.10
1.56	20.00	7.75	3.36	.11	1.77	1.22	.09
2.89	21.25	7.75	2.90	.09	1.44	1.26	.09
27.5	106.80	7.75	0.93	1.05	.09
$T = 70^\circ$							
0.033	10.50	8.86	4.87	1.11	1.85	1.70	
.06	11.00	8.86	5.25	1.00	1.80	1.65	
.16	12.00	8.86	5.87	0.56	2.85	2.02	
.44	7.00	8.86	6.05	.34	3.37	2.29	
.70	8.00	8.86	6.50	.34	3.25	2.35	
1.14	10.00	8.86	5.50	.24	2.72	1.78	
2.03	10.00	8.86	5.05	.26	2.43	1.44	
34.0	80.00	8.86	1.03	1.10	
$T = 100^\circ$							
0.025	10.45	7.95	3.39	1.73	0.56	1.12	
.05	10.50	7.95	4.31	1.77	.96	1.41	
.10	11.20	7.95	5.28	1.68	1.58	1.86	
.50	9.00	7.70	6.84	0.80	2.88	2.66	
1.10	10.00	9.65	6.70	.63	3.11	2.50	
1.88	10.00	7.70	8.51	.81	2.64	2.42	
4.0	15.00	9.72	..	.41	2.62	2.07	
35.0	85.00	8.00	1.19	1.14	
$T = 150^\circ$							
0.022	15.60	7.62	2.58	1.69	0.40	0.95	
.15	12.00	8.50	4.10	1.86	.71	1.43	
.56	7.00	7.62	5.71	1.66	1.19	1.80	
.91	10.00	7.62	6.88	1.56	1.32	2.24	
1.09	10.00	7.62	6.55	1.59	1.96	2.70	
2.10	11.00	7.62	8.59	1.48	2.35	2.45?	
2.24	11.00	7.62	8.41	1.40	2.24	3.01	
40.0	60.00	7.62	..	0.93	1.83	2.04	

TABLE II
QUANTUM YIELDS OF C₂ HYDROCARBONS IN DIETHYL KETONE-OXYGEN MIXTURES
Ketone pressure = 35 mm.

Temp., °C.	O ₂ pressure, mm.	I_a , einsteins/ml./sec. $\times 10^{12}$	Φ_{C_2}	(C ₂ H ₅), mole ml. ⁻¹ $\times 10^{13}$	k_p , ml. mole ⁻¹ sec. ⁻¹ $\times 10^{11}$
35	0.033	7.75	0.04	1.53	0.8
35	.075	7.75	.02	1.00	.6
35	.165	7.75	.01	0.63	.4
70	.032	7.60	.10	1.91	.9
70	.055	8.86	.035	1.01	1.2
70	.165	8.86	.02	0.65	0.6
100	.025	7.95	.05	.75	3.5
100	.50	7.95	.03	.48	3.0
150	.022	7.62	.15	.83	3.1
150	.155	8.47	.06	.39	1.2

TABLE III
QUANTUM YIELDS IN DIETHYL KETONE-NITRIC OXIDE MIXTURES^a

Ketone pressure = 35 mm., alpine burner			
Temp., °C.	NO pressure, mm.	Φ_{CO}	Φ_{N_2}
35	10	0.07	0.81
35	80	.09	6.6
150	73	.34	2.0

^a The formation of nitrogen in these experiments is interesting but was not pursued further. A similar effect was found in acetone-nitric oxide mixtures by Anderson and Rollefson.²⁰

ated product for which analysis has not been made. Products such as acetic and propionic acids, methyl and ethyl alcohols, water, diketones, etc., all have vapor pressures which would make their fractionation from a large amount of diethyl ketone impossible. An attempt was made to identify some of these products by photographing their ultraviolet spectra after a 36 hour run, but the absorption curve was almost identical with that of the pure ketone. The presence of acid groups was shown, however, by freezing the products of another run into 20 ml. of air-free distilled water and measuring the pH of the resulting solution. A value of 4.5 was obtained, and this when compared to 6.0 for the water corresponds to an acid quantum yield of about 3 if the value of K_A for acetic acid is assumed.

Variation in light intensity has very little effect at 35° but, at higher temperatures, the quantum yields all increase with decreasing intensity (Table IV). At the highest intensity, with the A-

TABLE IV
VARIATION OF QUANTUM YIELDS WITH INTENSITY IN DIETHYL KETONE-OXYGEN MIXTURES

Alpine burner; ketone pressure = 35 mm., O₂ pressure = 1 mm.

Temp., °C.	Length of run, min.	I_a , einsteins/ml./sec. $\times 10^{12}$	Φ_{O_2}	Φ_{CO}	Φ_{CO_2}	$\Phi_{\text{CH}_3\text{CHO}}$
35	340	0.27	3.6	0.15	1.5	1.2
35	70	1.20	3.3	.15	2.3	1.4
35	10	7.67	3.7	.14	2.0	1.3
100	480	0.21	8.8	1.03	3.2	2.9
100	40	1.57	7.7	0.73	3.3	3.0
100	10	5.70	7.8	.74	3.2	2.8
100	10	9.65	6.7	.63	3.1	2.5
150	360	0.21	15.4	4.0	3.0	4.8
150	50	1.39	12.7	2.8	2.6	3.0
150	19	5.58	8.9	2.1	2.3	2.8
150	9	9.52	8.5	1.9	1.9	3.0
150	0.21	750 ^a	5.9	1.5	1.5	2.0

^a A-H6 arc.

H6 arc, the quantum yields seem to have approached a lower limit, and the variations can be represented by equations of the form

$$\Phi = k' + k''/I_a^{1/2}$$

where Φ is the quantum yield in question, k' and k'' are constants dependent on oxygen pressure, and I_a is the number of quanta absorbed per second per ml.

Diethyl ketone labeled with C¹⁴ in the carbonyl position, prepared by Finkelstein,⁷ was photolyzed

both in the presence and in the absence of oxygen at 150°. The amount of carbon monoxide produced in the absence of oxygen agreed well with that produced by the unlabeled ketone (8.6×10^{-2} moles ml.⁻¹ sec.⁻¹ compared to 8.4×10^{-2} mole ml.⁻¹ sec.⁻¹), but the amounts of products during photooxidation were somewhat low. The carbon monoxide, carbon dioxide and acetaldehyde were found to be 93, 77 and 4% radioactive, respectively.

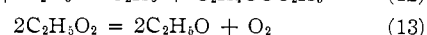
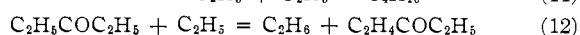
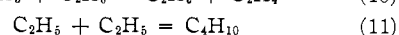
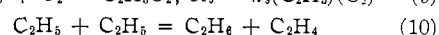
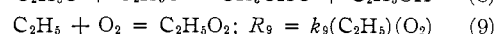
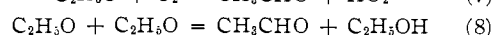
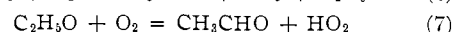
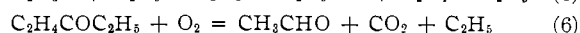
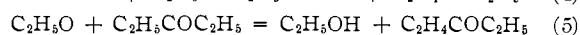
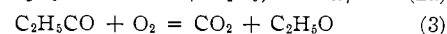
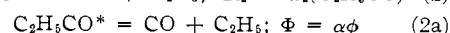
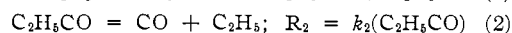
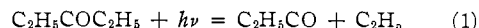
Table V shows the effect of varying the wave length upon the quantum yields of products.

TABLE V
VARIATION OF QUANTUM YIELDS WITH WAVE LENGTH IN DIETHYL KETONE-OXYGEN MIXTURES

Ketone pressure = 35 mm.							
Temp., °C.	Wave length, Å.	O ₂ pressure, mm.	I_a , einsteins/ml./sec. $\times 10^{12}$	Φ_{O_2}	Φ_{CO}	Φ_{CO_2}	$\Phi_{\text{CH}_3\text{CHO}}$
35	2650	0.55	0.82	4.3	0.25	2.1	1.7
35	2650	1.08	0.82	3.8	.23	1.8	1.7
35	{2650 3130}	1.01	1.20	3.3	.15	2.3	1.4
35	3130	1.01	1.22	3.0	.10	2.6	1.3
150	2650	0.52	0.056	9.75	3.0	1.9	3.1
150	2650	0.54	.57	6.8	2.3	1.2	2.5
150	2650	1.10	.57	8.7	2.6	1.7	3.2
150	2650	1.85	.57	10.1	2.6	1.9	3.2

Discussion

To facilitate the discussion it seems advisable to list at one point all of the steps in the mechanism which will be discussed



The photochemical reaction of diethyl ketone with oxygen must have a complex mechanism. The following facts must be borne in mind. (1) Quantum yields are essentially independent of intensity from 35° to about 100°, but at 150° they decrease as the intensity increases. The chain ending step must vary with temperature and is presumably a radical-radical reaction at 150°. (2) All yields pass through maxima (except possibly carbon monoxide at 35°) as oxygen pressure increases. This indicates that whereas oxygen is essential to chain propagation, it must also act as an inhibitor. At high oxygen pressures at all temperatures the yields approach limiting and not very high values.

A complete material balance has not been achieved. Products other than those quantitatively determined are formed. This statement may be easily verified by attempting to base a material balance on the determined products: CO, CO₂, CH₃CHO, C₂ hydrocarbons. Semi-quantitative analyses indicate that the missing products are mainly acids⁷ and ethanol.

Certain conclusions may be drawn about the mechanism, and fairly good estimates made of the rates of a few of the steps.

(a) **The Decomposition of the Propionyl Radical.**—No reliable estimate seems to have been made of the rate of this reaction although it is generally considered to be higher than that of the decomposition of acetyl radicals.¹²

The primary process may be assumed to be¹³ reaction 1 where ϕ , the primary quantum yield, is probably about one in the absence of oxygen, although a weak fluorescence has been observed.¹⁴ The same is almost certainly true at low oxygen pressures at all temperatures, but the effect of oxygen at pressures of several millimeters, particularly at low temperatures, needs further investigation.¹⁵ The error introduced by assuming $\phi = 1$ is probably negligible.

At 35° neither oxygen nor nitric oxide at pressures of several millimeters suppresses carbon monoxide formation completely (Tables I and III). If reaction 1 is the sole primary process, a small fraction of propionyl radicals must retain enough energy to dissociate immediately. This conclusion resembles one which also appears to be necessary in the case of acetone.^{13,16-20} Let us designate the fraction of propionyl radicals which inevitably dissociate as α (all Φ 's designate quantum yields). Thus propionyl radicals will decompose by reactions 2 and 2a where C₂H₅CO* indicates propionyl radicals which have retained energy from the primary process, and reaction 2 indicates that some of the propionyl radicals have reached thermal "equilibrium" and react either by (2) or with molecules in the system such as oxygen.

The quantity α will not be discussed in detail. At 35° with the radiation used in most of the experiments $\alpha = 0.09$ since this is the approximate limiting value for Φ_{CO} at both high oxygen and at high nitric oxide pressures. The data in Table V show that α increases with decrease in wave length. The dependence of α on temperature is uncertain since even at 70° any source of CO other than (2a) may not be suppressed completely even when 2 mm. of oxygen is present. Estimates from Tables I and III

place $\alpha \sim 0.15$ at 70° and ~ 0.3 at 150°. Hence $\alpha \sim 0.2$ at 100° by interpolation.

Equilibrated propionyl radicals react with oxygen without giving carbon monoxide. Since $\Phi_{\text{CO}} + \Phi_{\text{CO}_2} = 1$ at high oxygen pressures at 35° and is but little greater than unity at 70° and at 100°, one may with considerable assurance write reaction 3 with a rate $R_3 = k_3(\text{C}_2\text{H}_5\text{CO})(\text{O}_2)$. C₂H₅O is introduced to balance the equation, and the only evidence for this is the presence of ethanol in the products. Reaction 3 might be broken down into a series of steps, but there is no real basis for so doing.

From eq. 1-3 one may write, if C₂H₅CO radicals are produced only in the primary process

$$\Phi_{\text{CO}} = \frac{1 + \alpha k_3(\text{O}_2)/k_2}{1 + k_3(\text{O}_2)/k_2} \quad (14)$$

$$\Phi_{\text{CO}_2} = \frac{(1 - \alpha)k_3(\text{O}_2)/k_2}{1 + k_3(\text{O}_2)/k_2} \quad (15)$$

and

$$\Phi_{\text{CO}} + \Phi_{\text{CO}_2} = 1 \quad (16)$$

Equation 14 reproduces the data at 35°, from which the value of k_3/k_2 at this temperature may be estimated as 20×10^5 l./mole. Values of Φ_{CO} calculated by use of this ratio and $\alpha = 0.09$ are shown in Table I. Above 35° the CO yield does not obey eq. 14, and eq. 15 is not valid at any temperature. Equation 16 is valid at high oxygen pressure at 35°, approximately valid at 70° and may even be valid at 100 and 150° at higher pressures than were used in this work.

The following conclusions seem valid: (a) there is a CO or C₂H₅CO producing step other than reactions 1, 2 and 2a, which is temperature dependent and becomes appreciable above 35°; (b) there is a source of CO₂ other than reaction 3 at all temperatures; and (c) at high pressures of oxygen these additional sources of CO and CO₂ are suppressed.

Estimates lead to a value of about 2.2×10^5 l./mole for k_3/k_2 at 70°. This gives an activation energy difference for $E_2 - E_3$ of about 13 kcal., but this is uncertain to at least 3 or 4 kcal. The ratio of pre-exponential factors a_2/a_3 is about 10^5 and hence to give a reasonable collision diameter to reaction 3, the pre-exponential factor for reaction 2 must not be greater than about 10^{13} sec.⁻¹.

(b) **The Chain Propagating Steps.**—Quantum yields of oxygen disappearance are such that under most conditions more than one molecule of ketone must disappear per quantum absorbed. There must be a radical attack on ketone molecules, and this is probably an abstraction of the form shown in reaction 4. At very low pressures of oxygen (see Table II) the formation of C₂H₆ is good evidence that C₂H₅ partakes in reaction 4, but it seems almost certain that C₂H₅O is the main hydrogen abstractor as shown in reaction 5.

Quantum yields for carbon monoxide formation in pure diethyl ketone are but little more than unity even at 150°. Hence the radical C₂H₅COC₂H₅ does not dissociate appreciably under conditions employed in this work. It may be expected to react with oxygen prior to dissociation in these experiments. Reactions of pentanonyl radicals with oxygen are proposed as chain propagating steps. The

(21) A. N. Strachan, Ph.D. Thesis, University of Rochester, 1954.

(12) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York N. Y., 1954, p. 630.

(13) W. A. Noyes, Jr., G. B. Porter and J. E. Jolley, *Chem. Revs.*, **56**, 49 (1956).

(14) M. S. Matheson and J. W. Zabor, *J. Chem. Phys.*, **7**, 536 (1939).

(15) See W. A. Noyes, Jr., *Helv. Chim. Acta*, in press.

(16) D. S. Herr and W. A. Noyes, Jr., *THIS JOURNAL*, **62**, 2052 (1940).

(17) W. A. Noyes, Jr., and L. M. Dorfman, *J. Chem. Phys.*, **16**, 788 (1948).

(18) J. S. A. Forsyth, *Trans. Faraday Soc.*, **37**, 312 (1942).

(19) R. W. Durham and E. W. R. Steacie, *J. Chem. Phys.*, **20**, 582 (1952).

(20) H. W. Anderson and G. K. Rollefson, *THIS JOURNAL*, **63**, 816 (1941).

mechanism seems less complicated at 35° than at higher temperatures.

(c) **The Reaction at 35°.**—A source of carbon dioxide other than reaction 3, which depends on the chain length and which is important at all oxygen pressures except the very highest is required by the considerations of section (a). Reaction 6 fulfills these conditions. Evidence for reaction 6 is provided by the data at 35° since

$$R_{CO} + R_{CO_2} = \alpha I_a + k_2(C_2H_5CO) + k_3(O_2)(C_2H_5CO) + k_6(P)(O_2) \quad (17)$$

where (P) represents the concentration of pentanonyl radicals.

From the steady state for C₂H₅CO

$$I_a = \alpha I_a + k_2(C_2H_5CO) + k_3(O_2)(C_2H_5CO) \quad (18)$$

Hence

$$\Phi_6 = \Phi_{CO} + \Phi_{CO_2} - 1 \quad (19)$$

where Φ_6 is the number of pentanonyl radicals which react per quantum by reaction 6. Comparison of the right-hand side of eq. 19 with Φ_{CH_3CHO} (Table I) shows good agreement up to pressures of about 0.4 mm. oxygen. At higher pressures Φ_{CH_3CHO} exceeds $\Phi_{CO} + \Phi_{CO_2} - 1$, the excess increasing with oxygen pressure until at 27.5 mm. it equals unity. The appearance of another acetaldehyde producing step, increasing with oxygen pressure, coincides with the decrease of quantum yields from their maxima and suggests a chain stopping step of the form of reaction 7.

If all pentanonyl radicals react with oxygen by 6 and pentanonyl radicals are formed solely by 5, one obtains

$$\frac{(\Phi_{CH_3CHO} - \Phi_{CO} - \Phi_{CO_2} + 1)(K)}{(\Phi_{CO} + \Phi_{CO_2} - 1)(O_2)} = \frac{k_7}{k_5} \quad (20)$$

where (K) and (O₂) are concentrations of ketone and of oxygen, respectively. Since $(\Phi_{CH_3CHO} - \Phi_{CO} - \Phi_{CO_2} + 1)$ is very close to zero, small errors in the individual quantum yields cause relatively large errors in k_7/k_5 , real values of from 5 to 16 being obtained. Substituting a value of $k_7/k_5 = 10$ in eq. 20 and calculating Φ_{CH_3CHO} gives values which are in reasonable agreement with the experimental data. If the mechanism is correct, then $k_7/k_5 \cong 10 \pm 5$. The greater efficiency of reaction 7 over 5 is qualitatively evident from the fact that 2 mm. of oxygen in 35 mm. of ketone causes a considerable reduction in the quantum yields. At higher temperatures the decreasing effectiveness of oxygen as a chain stopper indicates that k_7/k_5 decreases with increasing temperature.

(d) **The Reaction 70–150°.**—The oxygen pressure at which the maxima in the quantum yields of O₂, CO₂ and CH₃CHO occur increases with temperature. At 35° the maxima occur at very low oxygen pressures. At 150° the quantum yields are small at low oxygen pressures and rise slowly so that they have not begun to decrease even at 2 mm. pressure. At each temperature the CO quantum yield decreases nearly to its lowest value in the same oxygen pressure range as the other quantum

yields attain their maximum values. These facts are in accord with the mechanism put forward so far, as can be seen by comparing the total effect of step 2 with that of the sequence 3, 5 and 6. In each case one ethyl radical is formed, but the second sequence gives four product molecules and uses up two oxygen molecules compared to the single carbon monoxide molecule produced by step 2. Thus high quantum yields will be obtained when propionyl radicals react with oxygen before they dissociate and when the oxygen pressure is low enough to make reaction 7 of minor importance. These conditions are found at relatively low oxygen pressures at 35° and at relatively high oxygen pressures at 150° (where radical-radical reactions largely replace (7) as chain ending steps).

The carbon monoxide quantum yields increase with temperature at any given oxygen pressure. Values over unity are observed at 70, 100 and 150°, indicating another CO or C₂H₅CO producing step with a suitable activation energy. Since Φ_{CO} always decreases with increasing oxygen pressure (except for an initial rise at 70, 100 and 150°), the direct formation of carbon monoxide is not possible, and almost certainly propionyl radicals are produced which may dissociate to give carbon monoxide. It is possible to suggest a second mode of reaction of pentanonyl radicals with oxygen (in addition to (6)) which would yield acetic acid and propionyl radicals. Such a step has the formal qualifications to satisfy the facts, but the kinetic expressions may not be used because the data are not accurate enough.

The reaction undoubtedly increases in complexity as the temperature increases. Previous work⁷ indicates that carbon monoxide and carbon dioxide are formed almost entirely from the carbonyl group at 30° and that acetaldehyde comes from the ethyl groups. This is in agreement with the mechanism so far proposed. At 100° part of the carbon dioxide comes from the α -carbon atoms and in the present work at 150° possibly one quarter of the carbon dioxide does not come from the carbonyl group.

These facts indicate strongly that compounds containing one carbon atom should be formed from the end carbon atoms. No formaldehyde was found in the present work, and formic acid could not have been detected.

The chain terminating step at 35° and at 70° apparently involves oxygen and reaction 7 is at least formally satisfactory. The HO₂ radicals (formed from 7) are often considered to be inert and not to propagate chains at low temperatures, but satisfactory data about these radicals are almost completely lacking.²²

At high temperatures (150°) the effect of intensity indicates strongly a radical-radical chain stopping step. This raises the question as to what happens to the C₂H₅O₂ radicals. If these radicals are relatively inert, they may last long enough to yield ethoxy radicals by reacting with each other.²³ Probably most C₂H₅O₂ radicals yield ethoxy radi-

(22) See ref. 12, p. 607 et ff.

(23) J. H. Raley, L. M. Porter, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **73**, 15 (1951).

cals by some process. A quantitative method of determining ethyl alcohol was not available when these experiments were performed. In any case the most logical chain stopping step is reaction 8. For (8) to be important at 150° and not at 35 and 70°, the concentration of ethoxy radicals must be far greater even at the lowest intensity used. This is so because (5) and (7) must have appreciable activation energies whereas (8) would probably have a low activation energy. This may mean that the intermediate steps preceding ethoxy formation (such as (6) and (3)) proceed far more rapidly at 150° than at lower temperatures.

(e) **The Reaction of Ethyl Radicals with Oxygen.**—The rapid reduction of the quantum yield of C₂ hydrocarbons with increase in oxygen pressure is an indication of the speed with which ethyl radicals react with oxygen and provides a means whereby the method of competing reactions may be used to measure the rate of reaction 9.

The C₂ hydrocarbons are formed along with butane by the well characterized reactions 10, 11 and 12,⁴⁻⁶ at a rate given by

$$R_{C_2} = 2k_{10}(C_2H_5)^2 + k_{12}(K)(C_2H_5) \quad (21)$$

The total number of ethyl radicals introduced into the system may be assumed to be the sum of those introduced by reactions 1, 2, 2a and 6. Thus from the yields of CO and CO₂ and the number of quanta absorbed, one can estimate the number of ethyl radicals formed. They may now be assumed to disappear only by reactions 9, 10, 11 and 12. Since those which disappear by reactions 10, 11 and 12 can be calculated from Φ_{C_2} , the number which disappear by reaction 9 can be calculated. If one uses k_{10} , k_{11} and $k_{12}/k_{11}^{1/2}$ from previous work,^{5,24} the instantaneous value of (C₂H₅) can be calculated from eq. 21. Hence all of the information necessary for calculation of k_9 is available. The results are shown in Table II. Considerable scatter is to be expected due to uncertainties in Φ_{C_2} , but the activation energy of (9) must be very low, and the steric factor is of the same order as that of (12), *i.e.*, about 10⁻³. The steric factor for the correspond-

(24) K. J. Ivin and E. W. R. Steacie, *Proc. Roy. Soc. (London)*, **A208**, 25 (1951).

ing methyl radical reaction has a similar order of magnitude.^{15,25,26}

The initial product of (9) must be C₂H₅O₂ radicals but no definite conclusions about their subsequent reactions can be drawn from the present work although some suggestions can be made. At 35°, for example, since the formations of CO, CO₂ and CH₃CHO have been accounted for by the mechanism, these products may not result in appreciable quantities from reactions of C₂H₅O₂ radicals. Decomposition, either directly or following hydrogen abstraction to form a hydroperoxide, would almost certainly produce acetaldehyde in much larger amounts than observed at all temperatures. It seems probable that reaction 13 takes place²³ although reaction with oxygen to form C₂H₅O and ozone cannot be eliminated. From the mechanism the expression $2(\Phi_{CO} + \Phi_{CO_2}) - \Phi_{O_3}$ should be zero if none of the oxygen consumed by the radicals is returned to the system. The values for this expression show considerable scatter but are about 0.4 (35°), 0.7 (70°), 1.0 (100°), and at 150° there are about as many negative as positive values. Support is obtained therefore for a reaction which returns some oxygen to the system.

Further speculation about reaction mechanism does not seem to be warranted.

Thus the photochemical diethyl ketone-oxygen reaction may be described in much the same terms as the acetone-oxygen reaction.^{11,25,27,28} Many important questions remain to be answered, particularly as regards the detailed behavior of the RO₂ intermediates. It seems fairly evident that their main fates are not the formation of hydroperoxides.

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(25) F. B. Marcotte and W. A. Noyes, Jr., *THIS JOURNAL*, **74**, 783 (1952).

(26) G. R. Hoey and K. O. Kutschke, *Can. J. Chem.*, **33**, 496 (1955).

(27) D. E. Hoare, *Trans. Faraday Soc.*, **49**, 1292 (1953).

(28) Margaret I. Christie, *THIS JOURNAL*, **76**, 1979 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Thermal Decomposition of Ethylcyclobutane¹

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The thermal decomposition of ethylcyclobutane has been studied over the pressure range 7–400 mm. at 450° and at 420–460° for pressures of 10 to 200 mm. The products were found to be almost exclusively ethylene and 1-butene. The decomposition is a homogeneous, first-order reaction which is not inhibited by nitric oxide, propylene or toluene. The temperature dependence of the experiments with initial pressures of 10–200 mm. gave an activation energy of 62 ± 1 kcal./mole. The first-order rate constant can be expressed as $k = 3.6 \times 10^{15} e^{-62000/RT}$ sec.⁻¹.

Earlier investigations² have indicated that the

(1) This work was supported by a grant from the Celanese Corporation of America.

(2) (a) C. T. Genaux and W. D. Walters, *THIS JOURNAL*, **73**, 4497 (1951); (b) C. T. Genaux, F. Kern and W. D. Walters, *ibid.*, **75**, 6 (96 (1953)); (c) F. Kern and W. D. Walters, *Proc. Natl. Acad. Sci. U. S. A.*, **38**, 937 (1952).

homogeneous thermal decomposition of the cyclobutane molecule produces two molecules of ethylene by a first-order reaction which is not inhibited by the presence of nitric oxide, propylene or toluene. The first-order rate constants fall off as the initial pressure is lowered (10 mm. and below) and the