Vapor-Phase Photooxidation of Diethyl Ketone[1]

A. S. Kallend and J. N. Pitts, Jr.[2]

Contribution from the Department of Chemistry, University of California, Riverside, California 92502. *Received September 9, 1968*

Abstract: The photooxidation of diethyl ketone has been studied in the temperature range 25–200° and over a range of oxygen partial pressures from 0 to 100 mm. The major initial products of this reaction were found to be acetaldehyde, carbon dioxide, carbon monoxide, and ethanol. Fairly large yields of methanol appeared to be formed through secondary reactions of acetaldehyde. A simple free-radical-chain reaction scheme is proposed to account for the formation of the major products in the initial stages of reaction. The only hydrocarbon product was found to be ethylene which was formed with low quantum yields. The effect of added inert gas suggests that this ethylene arises through decomposition of "hot" ethyl peroxy radicals.

In the gas-phase photolysis of diethyl ketone at 3130 Å the formation of the major products of the reaction, *n*-butane, ethane, ethylene, and *sec*-butyl ethyl ketone, may be adequately explained in terms of combination, disproportionation, and hydrogen-abstraction reactions of the ethyl radical[3] which is produced in the steps

$$h\nu + C_2H_5COC_2H_5 \rightarrow C_2H_5CO + C_2H_5 \quad (0)$$

$$C_2H_5CO \rightarrow C_2H_5 + CO \quad (1)$$

The inhibitory effect on butane formation of traces of oxygen has been noted by several workers, but reports of the effects of oxygen upon the formation of ethylene and ethane vary. Finkelstein and Noyes[4] found quantum yields for C_2 hydrocarbons as high as 0.6 at 100° in the presence of over 1.0 mm pressure of oxygen, whereas the values quoted by Jolley[5] are very much lower ($\phi = 0.05$ at 100° and $P_{O_2} = 0.025$ mm). Jolley suggested that the higher values found by the former group of workers were due to local oxygen depletion. In both cases the C_2 fraction was thought to contain both ethylene and ethane. It is apparent that if indeed ethylene and ethane are products in the photooxidation of diethyl ketone they cannot arise from disproportionation of the ethyl radical since, if this were so, roughly eight times as much *n*-butane would be expected ($k_{\text{comb}}/k_{\text{disp}} \simeq 8.0$). More recently a detailed analytical study by Hoare and Whytock[6] revealed that, although ethylene is formed in small quantum yield, no alkanes are observed among the reaction products in the photooxidation. It therefore seems reasonably clear that a major role of oxygen in this system is to react or combine with and thus remove ethyl radicals.

With one exception,[6] earlier studies were hampered by uncertainty as to the exact nature of the reaction products. Nevertheless, Jolley[5] proposed quite a detailed mechanism, much of which has been substantiated by later workers.[6] In the present work the identities of most of the reaction products have been established, and except in minor detail they agree broadly with the findings of Hoare and Whytock.[6] In addition a distinction is drawn between primary products and those thought to arise through secondary reaction of initially formed molecular products. This leads to a simplified reaction scheme which is thought to apply in the initial stages of the

---

(1) Presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y., 1963.

(2) Author to whom correspondence should be addressed.

(3) K. O. Kutschke, M. H. J. Wijnen, and E. W. R. Steacie, *J. Amer. Chem. Soc.*, **74**, 714 (1952).

(4) A. Finkelstein and W. A. Noyes, Jr., *Discussions Faraday Soc.*, **14**, 76, 81 (1953).

(5) J. E. Jolley, *J. Amer. Chem. Soc.*, **79**, 1537 (1957).

(6) D. E. Hoare and D. A. Whytock, *Can. J. Chem.*, **45**, 2841 (1967).

photooxidation which is the chief region of kinetic interest.

Experimental Section

A conventional mercury-free gas-handling system was used. The reaction cell was about 5 cm in diameter and 358 ml in volume; it was enclosed in an insulated aluminum heating block with quartz end windows and mounted on an optical bench. Thermocouples along its length showed that the cell could be heated quite uniformly up to at least 350°. A short length of narrow-bore tubing provided the inlet to the reaction cell, and the connecting stopcock was heated to avoid absorption of vapors. Samples for analysis could be taken from the cell during a photolysis by means of a greaseless stainless-steel rotary valve[7] and could be injected into either of two selected chromatographic columns by valves controlling the carrier gas flow. Due allowance could be made for the quantity of material removed during each analysis, but since each sample was less than 0.25% of the total, this correction was a minor one. Exhaustive tests showed that the analyses obtained in this way were representative of the average instantaneous concentration of products in the reaction cell. The whole cell unit and the sampling valve were enclosed in a forced air thermostat.

The chromatograph was an Aerograph A-600-B with a subsidiary oven and detector for a second column. The associated flame ionization detector was normally used, but with compounds not suitable for this method of detection a fairly high sensitivity thermal conductivity detector proved adequate. In some experiments the entire contents of the reaction vessel were removed using a Toepler pump, and after removal of the products condensable at −78° the remaining gases (CO_2, CO, and O_2) could be analyzed by gas chromatography with the advantages of using larger samples. A total of six different columns were used for quantitative analysis and a further two for qualitative analysis only. Details of these and of operating conditions were conventional. Diethyl ketone was obtained from Matheson Coleman and Bell and was purified by preparative gas chromatography on an Aerograph Autoprep.

Filtered light (λ 3130 Å) from a PEK 109 high-pressure mercury lamp entered the cell as a slightly diverging beam which just filled the reaction cell and was focused onto an RCA 935 photocell mounted outside the thermostat. A typical value of absorbed intensity was 7×10^{12} quantum cc^{-1} sec^{-1} for an initial pressure of 20 mm of DEK at 70°. Quantum yields were derived by reference to the quantum yield of carbon monoxide in the photolysis of pure diethyl ketone which was assumed to be unity.

Results

Inhibition of Hydrocarbon Formations. The presence of quite small quantities of oxygen (~0.2 mm) was sufficient to supress entirely the formation of both *n*-butane and ethane in the photolysis of 20 mm of diethyl ketone at 120°. However, a small amount of ethylene was always formed even at oxygen pressures as high as 100 mm and at all temperatures between 25 and 200°. This result agrees with the findings of Hoare and Whytock[6] but differs from those of both Finkelstein and Noyes[4] and of Jolley,[5] who found both ethane and ethylene to be present in their C_2 hydrocarbon fraction. Experiments in the present work in which proper mixing of the reactants was purposely avoided showed that some ethane and *n*-butane were formed under such conditions; also higher yields of ethylene were sometimes obtained. Hence Jolley's view that the high value of Φ_{C_2} observed by Finkelstein and Noyes was due to oxygen depletion is probably correct.

Figure 1 shows the effect upon ethylene formation of the addition of various pressures of an inert gas during the photooxidation of diethyl ketone. Clearly the formation of ethylene is very significantly inhibited by the addition of nitrogen. Moreover, experiments over the whole of the temperature range showed that the rate of production of ethylene was hardly affected by temperature change so that it must have been formed with near-zero activation energy. The implication here is that ethylene is formed in a reaction involving some "hot" radical or molecule.

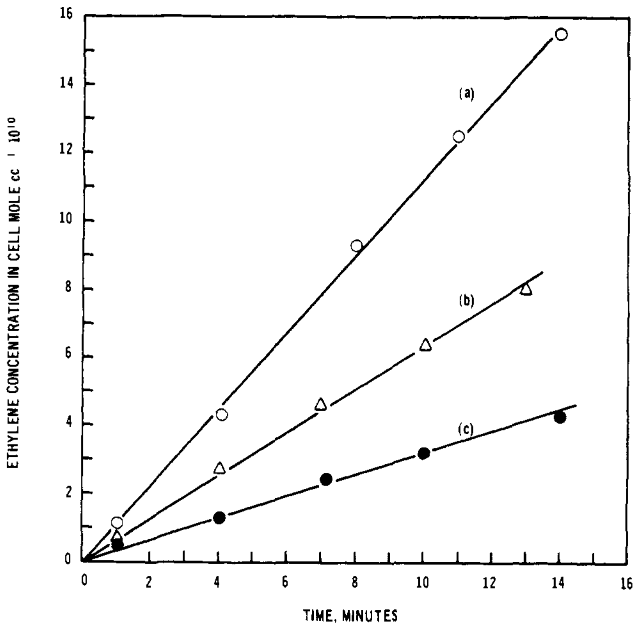


Figure 1. The effect of added inert gas on ethylene formation during photooxidation of 20.0 mm of DEK + 2.0 mm of O_2 at 128°: (a) $P_{N_2} = 0$, (b) $P_{N_2} = 27.6$ mm, (c) $P_{N_2} = 176$ mm.

Products of Photooxidation. The products of the photooxidation and their relative abundance under a typical set of conditions are listed in Table I. The identities of the main products were established by the method of comparison of chromatographic retention times on at least three different columns and were all confirmed by either mass spectrometry or infrared spectrophotometry. The identities of most of the minor products were established using only retention time data. The values of φ quoted in Table I should be taken only as a rough indication of the quantum yields of the various products since, as indicated later, they vary greatly with reaction time.

Table I. Typical Relative Product Yields[a]

Product	Quantum yield (φ)
Acetaldehyde	3.4
Carbon dioxide	2.7
Ethanol	2.4
Carbon monoxide	1.1
Methanol	0.4 at high conversion
Ethylene	0.16
Water	0.15 product of thermal reaction
Ethylene oxide	0.01
Ethyl propionate	0.01
Ethyl vinyl ketone	0.01
Propionic acid	0.02
Perpropionic acid	0.1
Other acidic products	Traces at high conversion

[a] Photolysis of 20 mm of DEK + 1.0 mm of O_2 at 120°.

---

(7) G. L. Pratt and J. H. Purnell, *Anal. Chem.*, **32**, 1213 (1960).

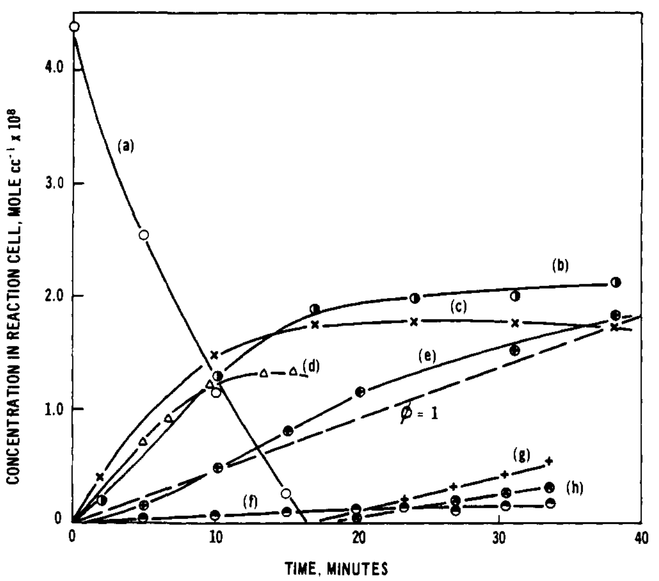


Figure 2. Formation of major products in the photolysis of 20 mm of DEK + 1.00 mm of O_2 at 120°: (a) O_2, (b) C_2H_5OH, (c) CH_3CHO, (d) CO_2, (e) CO, (f) C_2H_4, (g) n-C_4H_{10}, (h) C_2H_6.

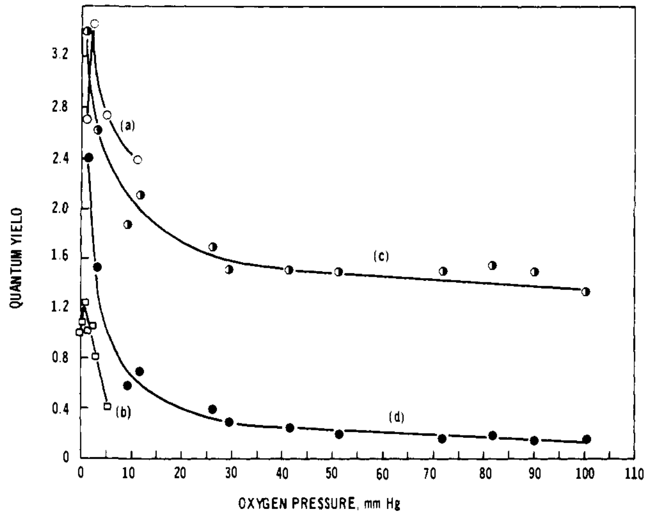


Figure 4. Variation of initial quantum yield of products with oxygen pressure in photooxidation of 20 mm of DEK at 120°: (a) CO_2, (b) CO, (c) CH_3CHO, (d) C_2H_5OH.

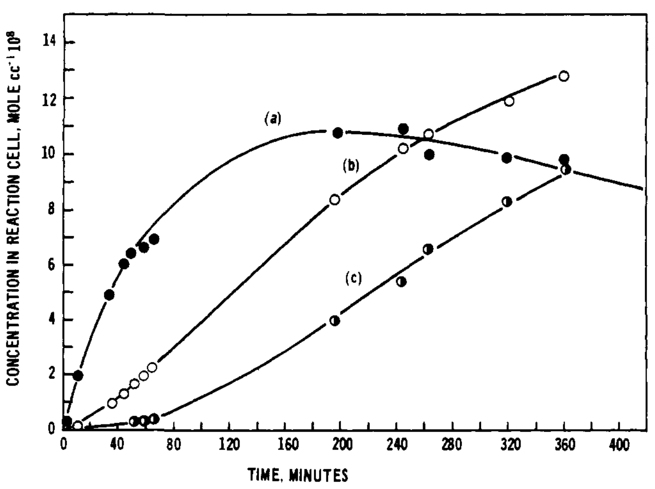


Figure 3. Formation of (a) CH_3CHO, (b) C_2H_5OH, and (c) CH_3OH in the photolysis of 20.3 mm of DEK + 109 mm of O_2 at 121°.

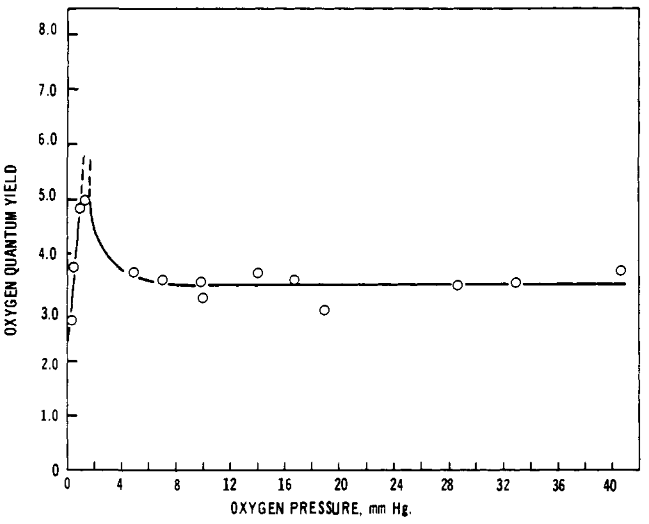


Figure 5. Variation of initial quantum yield of oxygen removal with oxygen partial pressure in photooxidation of 20 mm of DEK at 120°.

Preliminary studies of the rate of product formation during the course of a photolysis indicated that the products could be conveniently divided between those which showed initially a more or less linear increase in concentration with time and those which showed an induction period only reaching their maximum rates of formation late in the reaction. Those which fell into the former category included acetaldehyde, carbon dioxide, carbon monoxide, ethanol, ethylene, and perpropionic acid, while methanol, water, propionic acid, and most of the other minor products fell into the latter group. Formaldehyde, which is known to be a minor product,[6] could not be determined by gas chromatography and so is not included in Table I. The thermal reaction, recently reported by Hoare and Whytock,[6] was noted here to occur at temperatures above about 120°. It accounted for at least 80% of the total production of water at 200°

In Figure 2, the variation with time of the concentrations of the major products from the photolysis of a mixture of 20 mm of diethyl ketone and 1.0 mm of oxygen are plotted. Since no single column could be used for a complete analysis of all of the reaction products, it was necessary to repeat identical runs with different columns. The maxima in the buildup of acetaldehyde and ethanol are seen to coincide closely in time with the point at which all of the oxygen had been used up. The plot also clearly illustrates the fact that no ethane or n-butane is formed at all before the complete removal of oxygen. However, as Figure 3 shows, at higher oxygen pressures and at a point where oxygen remained in the system, acetaldehyde still sometimes reached a maximum concentration. This maximum, when observed, always seemed to follow closely a corresponding induction period in the formation of methanol. It is also clear that

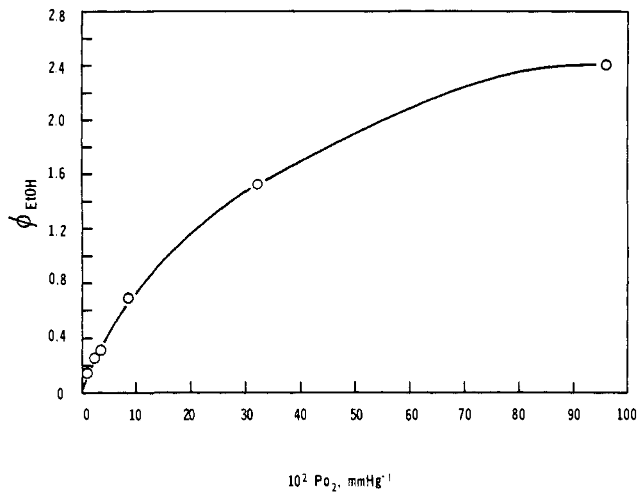


Figure 6. Variation of initial quantum yield of C_2H_5OH with reciprocal oxygen pressure.

methanol was formed in a reaction involving a fairly high activation energy since it was only observed at temperatures above 80°, while at 200° it was the major product of both the photooxidation and of the thermal reaction which took place at this temperature. Hence it appears likely that acetaldehyde is an intermediate in the formation of methanol.

The curvature of plots such as those for the formation of acetaldehyde typified by Figure 3 introduces large inaccuracies where only one analysis has been used to determine quantum yields. Quantum yields quoted here have all been calculated from initial rates of formation of products since the initial stage of the reaction is the chief region of kinetic interest.

Effect of Variation of Oxygen Pressure. The variation of quantum yields of the major products with oxygen pressure at 120° and with an initial pressure of diethyl ketone of about 20 mm are shown in Figures 4 and 5. Most experiments were carried out at oxygen pressures which were higher than those used by previous workers; where a comparison can be drawn the present results are in general agreement. Marked exceptions to this are the quantum yields for oxygen removal at low pressure which are only about half as high as those quoted by Jolley under comparable conditions. However, it is seen from Figures 4 and 5 that the quantum yields for product formation vary very greatly with oxygen pressure at pressures between 0 and 2.0 mm of oxygen, and this is precisely the region of oxygen partial pressures employed by most previous workers. Slight inaccuracies in the measurement of these small partial pressures can therefore lead to quite large variations in measured quantum yields in this region. Indeed the peak quantum yields in Figure 5 might well be higher than any of the experimental points recorded.

Figure 4 indicates that the quantum yield of ethanol formation decreases much more rapidly with increasing oxygen pressure than does that of acetaldehyde. As the oxygen pressure is decreased, on the other hand, the quantum yields for formation of both products become very nearly equal. This point is brought out rather well if the data from Figure 4 are plotted as the ratio of the initial rates of formation of ethanol and acetaldehyde *vs.* oxygen pressure. Curves are obtained which, within the limits of experimental error, extrapolate to a value of unity at zero oxygen pressure. Similar results were obtained throughout the temperature range.

Discussion

The complete inhibition of *n*-butane formation by traces of oxygen indicates that one of the roles of oxygen in this system is to react rapidly with radicals produced in the primary process and hence to reduce very greatly their steady-state concentrations. From previous photooxidation and hydrocarbon thermal oxidation studies it seems fairly certain that the reaction involved here is

$$C_2H_5 + O_2 \rightarrow C_2H_5OO \qquad (2)$$

Observations which must be accounted for by the reaction mechanism are as follows.

(i) At low oxygen pressures quantum yields for acetaldehyde and ethanol formation are in excess of 2.0, indicating that we are dealing with a chain reaction in this region at least.

(ii) Quantum yields of less than unity for carbon monoxide formation at high oxygen pressures indicate that some propionyl radicals produced in the primary process react with oxygen in a step which does not produce carbon monoxide. Finkelstein and Noyes[4] proposed that this reaction was

$$C_2H_5CO + O_2 \rightarrow CO_2 + C_2H_5O \qquad (3)$$

which is supported by the observations of Dunn and Kutschke,[8] who, using a tracer technique, found that the carbon dioxide originates mainly from the carbonyl group of the ketone and that this group remains intact during the oxidation.

(iii) Since ethanol is a major product, C_2H_5O must take part in the reaction. Moreover, since Φ_{EtOH} is frequently greater than unity, ethoxy radicals must be formed in a reaction other than (3) provided that propionyl arises only from the primary process. There are grounds for thinking that this latter condition is fulfilled since in the photolysis of diethyl ketone alone the quantum yield for carbon monoxide formation is not significantly greater than unity even near 200°. This shows that the radical $CH_3CHCOC_2H_5$ is not subject to decomposition at the temperatures of these experiments.

(iv) The quantum yield for carbon monoxide formation is also frequently greater than unity and so it must be formed in a reaction other than (1).

(v) The equal quantum yields for acetaldehyde and ethanol production at low oxygen pressures suggest that in this region a predominant reaction for the ethoxy radical could be

$$2C_2H_5O \rightarrow C_2H_5OH + CH_3CHO \qquad (4)$$

(vi) Shorter chains at higher oxygen pressures are indicated by the lower quantum yields in this region. This can be explained by a reaction between oxygen and a chain-carrying radical to give products which do not react further.

(vii) Acetaldehyde is the predominant product at high oxygen pressures.

The results cited in (i) indicate the chain nature of the

---

[8] J. R. Dunn and K. O. Kutschke, *Can. J. Chem.*, **36**, 421 (1958).

reaction; hence some radical must abstract hydrogen from the diethyl ketone molecule. Since no ethane is formed, the ethyl radical cannot be directly involved and so this leaves only two other reasonable possibilities

$$C_2H_5O + C_2H_5COC_2H_5 \rightarrow C_2H_5OH + CH_3CHCOC_2H_5 \quad (5)$$

$$C_2H_5OO + C_2H_5COC_2H_5 \rightarrow C_2H_5OOH + CH_3CHCOC_2H_5 \quad (5a)$$

Evidence[9] from the photolysis of pure diethyl ketone suggests that the abstraction of the secondary hydrogen atom is much more rapid than abstraction of the primary hydrogen and so reactions 5 and 5a have been written as producing the *sec*-pentanonyl radical. Measurements[10-14] indicate that the activation energy E_5 is only about 4–5 kcal mole^{-1} while E_{5a} may be as high as 16 kcal mole^{-1} although at least one estimate would put it much lower.[15] Hence we feel that hydrogen abstraction by the ethyl peroxy radical is likely to be less rapid than (5) although both probably occur. At any rate (5) followed by

$$CH_3CHCOC_2H_5 + O_2 \rightarrow CO_2 + CH_3CHO + C_2H_5 \quad (6)$$

would account satisfactorily for the chain nature of the reaction as required by (iv).

There are four reactions which have been postulated[16] as possible routes for the formation of ethoxy from ethyl peroxy as required by (iii). These are

$$C_2H_5OO + RH \rightarrow C_2H_5OOH + R \rightarrow C_2H_5O + OH + R \quad (7a)$$

$$C_2H_5OO + R \rightarrow C_2H_5OOR \rightarrow C_2H_5O + RO \quad (7b)$$

$$C_2H_5OO + O_2 \rightarrow O_3 + C_2H_5O \quad (7c)$$

$$2C_2H_5OO \rightarrow 2C_2H_5O + O_2 \quad (7)$$

Reaction 7a may be immediately discounted since, if it were important here, high quantum yields for the formation of water would have been observed through further reactions of the hydroxyl radical. Also, with a molecular intermediate, large induction periods would be anticipated for alcohol formation, at least, and these were never observed. For this latter reason reaction 7b must also be unimportant. Calvert and Hanst[16] proposed a reaction analogous to (7c) to account for the oxidation of methyl radicals but had no direct evidence for it. They discounted (7d) because, they argued, the alkyl peroxy radical concentration must have been low since no abstraction occurred to form the hydroperoxide. Their evidence for ozone formation was that, on addition of tetramethylethylene, acetone was formed. The activation energy for hydrogen abstraction by the peroxyalkyl radical could, however, be high enough to prevent its occurrence to any extent at the temperatures of these experiments even when $[C_2H_5OO]$ is quite high. Hence the rejection of reaction 7 was unjustified. Furthermore, recent mass spectrometric studies[17] indicate that no ozone is formed in the ethyl radical + oxygen system.

Hence reaction 7 seems to be the most likely mode of conversion of C_2H_5OO to ethoxy, and therefore the concentration of the ethyl peroxy radical must be fairly high. The combination of (4) and (7) then becomes analogous to the scheme proposed by Caldwell and Hoare[18] to account for the equal yields of formaldehyde and methanol in the nonchain photooxidation of acetone. The difference between the photooxidation of acetone and of diethyl ketone is thus probably due to the ease of abstraction of the secondary hydrogen atoms by radicals from the latter which thus leads to a chain reaction in that case.

Jolley[5] has proposed that

$$C_2H_5O + O_2 \rightarrow HO_2 + CH_3CHO \quad (8)$$

is the inhibiting reaction which explains (vi). On this evidence alone there are several alternative reactions which would suffice, but the additional requirement of (vii) makes it likely that (8) is indeed the major mode of reaction of the ethoxy radical at high oxygen pressures.

It has already been mentioned that (5a) might not be important here owing to its high activation energy. However, another possible mode of formation of ethyl hydroperoxide which is likely to be more important is

$$C_2H_5OO + HO_2 \rightarrow C_2H_5OOH + O_2 \quad (9)$$

Watson and Darwent[19] first proposed that this reaction was important in the low-temperature mercury-photosensitized oxidation of ethane. Later, Bell and McDowell[20] concluded that the same type of reaction, that is

$$ROO + HO_2 \rightarrow ROOH + O_2$$

took place in the mercury-photosensitized oxidation of isobutane since they were able to show that the observed *t*-butyl peroxide was not formed in a radical-chain reaction. In addition, Heicklen and Johnston[17] have pointed out that hydroperoxides have been observed only in systems which were thought to contain the HO_2 radical. Thus, since it has already been argued that reaction 8 must be important, particularly at high oxygen pressures, the fate of the HO_2 radical must be described by (9). Additional supporting evidence arises from the fact that at all temperatures up to 200° the quantum yield for water formation was low, and it appeared that even then it was only formed in the later stages of the reaction. Hence little of the HO_2 could have taken part in a water-forming reaction. Hydroperoxides are known to be fairly unstable and particularly susceptible to heterogeneous decomposition. It is therefore highly likely that the ethyl hydroperoxide which, following the argument above, must be formed here, eventually decomposes, perhaps at the reaction cell wall. A reaction of this type could well account for the slight increase in the rate of ethanol formation late in the reaction.

Ethylene Formation. Although ethylene is only a minor product, it is quite clearly formed in the initial stages of the reaction rather than as a secondary product and an

---

(9) J. N. Pitts, Jr., and A. S. Kallend, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., 1963.

(10) G. R. McMillan, *J. Amer. Chem. Soc.*, **82**, 2422 (1960).

(11) M. H. J. Wijnen, *ibid.*, **82**, 3034 (1960).

(12) M. H. J. Wijnen, *J. Chem. Phys.*, **27**, 710 (1957).

(13) T. Berces and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 348 (1961).

(14) R. H. Burgess and J. C. Robb, *Trans. Faraday Soc.*, **54**, 1015 (1958).

(15) J. A. Barnard and A. Cohen, *ibid.*, **64**, 395 (1968).

(16) P. L. Hanst and J. G. Calvert, *J. Phys. Chem.*, **63**, 71 (1959).

(17) J. Heicklen and H. S. Johnston, *J. Amer. Chem. Soc.*, **84**, 4394 (1962).

(18) J. Caldwell and D. E. Hoare, *ibid.*, **84**, 3987 (1962).

(19) J. S. Watson and B. deB. Darwent, *J. Phys. Chem.*, **61**, 577 (1957).

(20) K. M. Bell and C. A. McDowell, *Can. J. Chem.*, **39**, 1424 (1961).

examination of its likely mode of formation leads to some interesting conclusions concerning the nature of the radicals present in the system. There are three immedately obvious reactions to consider. The first is a disproportionation of the type

$$C_2H_5 + C_2H_5O \rightarrow C_2H_4 + C_2H_5OH$$

or

$$C_2H_5 + C_2H_5OO \rightarrow C_2H_5OOH + C_2H_4$$

This is unlikely for several reasons. First, the ethyl radical concentration is known to be low because no *n*-butane is formed. Secondly, the other mode of disproportionation involving the same radicals

$$C_2H_5 + C_2H_5O \rightarrow C_2H_6 + C_2H_4O$$

$$C_2H_5 + C_2H_5OO \rightarrow C_2H_6 + C_2H_4OO$$

might then also be expected, yet no ethane was ever observed. Finally, this mode of ethylene formation cannot account for the inert gas effect.

The second possibility is that ethylene is formed by heterogeneous decomposition of some molecular or radical intermediate. The heterogeneous decomposition of a stable intermediate can be ruled out since no induction period was observed in the formation of ethylene. The heterogeneous decomposition of a radical is unlikely since a few runs carried out with a reaction cell surface treated with HF produced no change in quantum yield of ethylene under otherwise identical conditions.

The third and most likely possibility is that it is formed in a reaction involving some "hot" radical. The over-all reaction

$$C_2H_5OO \rightarrow C_2H_4 + HO_2$$

is probably thermoneutral or slightly endothermic, but has a high activation energy since it necessarily involves the isomerization

$$CH_3CH_2OO \rightarrow CH_2CH_2OOH$$

It is therefore unlikely to be important here. However, it is highly likely that some ethyl peroxy radicals retain enough of the energy released in their formation so that the sequence

$$C_2H_5 + O_2 \rightarrow CH_3CH_2OO^{**} \tag{10}$$

$$CH_3CH_2OO^{**} \rightarrow CH_2CH_2OOH \tag{11}$$

$$CH_2CH_2OOH \rightarrow C_2H_4 + HO_2$$

where $CH_3CH_2OO^{**}$ denotes a vibrationally excited radical, would account satisfactorily for the inert gas effect and for the apparent near-zero activation energy for ethylene formation. A similar effect has been observed in *n*-hexane oxidation[21] where the addition of inert gas reduced the rate of decomposition of peroxy radicals presumably due to collisional deactivation of "hot" radicals.

Methanol Formation. Methanol was formed with a considerable induction period under all conditions (see Figure 4 for example) and therefore cannot be regarded as an initial product. Finkelstein and Noyes[4] proposed that an important reaction of the ethyl peroxy radical was

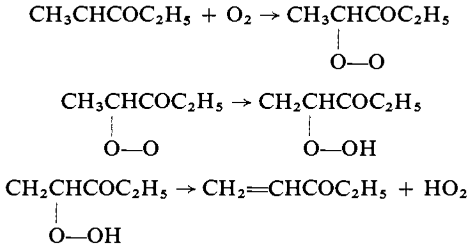
$$C_2H_5OO \rightarrow CH_3CO + H_2O$$

If this were so, further reaction of acetyl and methyl radicals could well lead to the formation of methanol. However, the present results quite conclusively show that this reaction could not have been important because of the low quantum yields of water. The observation that the maximum rate of methanol formation could always be associated with a maximum in the concentration of acetaldehyde in the reaction cell suggests that

$$CH_3CHO + R \rightarrow CH_3CO + RH$$

is, perhaps, a more likely route. The aldehydic hydrogen atom is known[22] to be extremely labile, and the reaction would have sufficient activation energy to account for the fact that methanol was only formed at higher temperatures.

Formation of Minor Products. The formation of traces of a number of minor products, particularly at the upper end of the temperature range, lends support to the theory first proposed in detail by Semenov[23] that alkoxy and alkyl peroxy radicals are readily subject to isomerization reactions similar to (11). For example, a plausible scheme for the formation of ethyl vinyl ketone would be



$$CH_3CHCOC_2H_5 + O_2 \rightarrow \underset{\displaystyle O\!-\!O}{CH_3\underset{|}{C}HCOC_2H_5}$$

$$\underset{\displaystyle O\!-\!O}{CH_3\underset{|}{C}HCOC_2H_5} \rightarrow \underset{\displaystyle O\!-\!OH}{CH_2\underset{|}{C}HCOC_2H_5}$$

$$\underset{\displaystyle O\!-\!OH}{\underset{|}{CH_2}CHCOC_2H_5} \rightarrow CH_2{=}CHCOC_2H_5 + HO_2$$

Other products, including propionic and other unidentified acids, are only formed late in the reaction and are most likely, therefore, to result from further reaction of initially formed products.

It should be emphasized that over 90% of the decomposed diethyl ketone may be accounted for in the major initial products so that it is justifiable at this stage to write a mechanism consisting of reactions already discussed which accounts satisfactorily for the formation of these products.

$$C_2H_5COC_2H_5 + h\nu \rightarrow C_2H_5CO + C_2H_5 \tag{0}$$

$$C_2H_5CO \rightarrow C_2H_5 + CO \tag{1}$$

$$C_2H_5 + O_2 \rightarrow C_2H_5OO \tag{2}$$

$$C_2H_5CO + O_2 \rightarrow C_2H_5O + CO_2 \tag{3}$$

$$2C_2H_5O \rightarrow CH_3CHO + C_2H_5OH \tag{4}$$

$$C_2H_5O + C_2H_5COC_2H_5 \rightarrow C_2H_5OH + CH_3CHCOC_2H_5 \tag{5}$$

$$CH_3CHCOC_2H_5 + O_2 \rightarrow CO_2 + CH_3CHO + C_2H_5 \tag{6}$$

$$2C_2H_5OO \rightarrow 2C_2H_5O + O_2 \tag{7}$$

$$C_2H_5O + O_2 \rightarrow HO_2 + CH_3CHO \tag{8}$$

$$HO_2 + C_2H_5OO \rightarrow C_2H_5OOH + O_2 \tag{9}$$

In this scheme, which is essentially a simplification of that proposed by Jolley[5] with the addition of reaction 9, no account is taken of the fact that some of the propionyl radicals probably retain energy from the primary process and so inevitably decompose giving carbon monoxide.

---

(21) G. J. Minkoff and C. F. H. Tipper, "Chemistry of Combustion Reactions," Butterworth & Co., Ltd., London, 1962.

(22) R. E. Dodd, *Can. J. Chem.*, **33**, 699 (1955).

(23) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Vol. 1, Princeton University Press, Princeton, N. J., 1958.

This follows since even at quite high oxygen pressure, *i.e.*, in the region where reaction 3 must be faster than reaction 1, a small quantity of carbon monoxide is still formed. However, since this yield of CO is small the reactions of "hot" propionyl radicals have been neglected.

Steady-State Treatments. The complexity of the reaction scheme as well as the occurrence of rapid secondary decomposition reactions precludes all but a very cursory mathematical treatment of the kinetics. At high oxygen pressures, reaction 8 will be responsible for the inhibition of the radical chain reaction by reducing the concentration of the chain-carrying ethoxy radical and thus account for the predominance of acetaldehyde in the reaction products. Under these conditions C_2H_5O will be low so that eventually (4) will become relatively unimportant due to the bimolecular dependence of its rate upon the ethoxy radical concentration. In this situation the small quantity of ethanol observed must arise mainly through (5) since the rate of this reaction depends only upon the first power of the ethoxy concentration and so will not be reduced by such a large extent as (4). Further support for the fact that (5) still occurs at high oxygen pressures arises from the measured quantum yields for oxygen removal. For example, the value obtained at high oxygen pressures at 120° was about 3.5 (see Figure 5), and it is easy to verify that it can only be as high as this if a chain reaction still occurs.

Solution of the steady-state equations for the radicals involved in reactions 0–9 yields

$$I_{abs} - k_8[C_2H_5O][O_2] - k_4[C_2H_5O]^2 = 0$$

which gives

$$[C_2H_5O] = I_{abs}/k_8[O_2]$$

when $[O_2]$ is large. Use of this approximation leads to

$$\phi_{C_2H_5OH} = \frac{k_4 I_{abs}}{k_8^2[O_2]^2} + \frac{k_5[DEK]}{k_8[O_2]} \qquad (12)$$

and

$$\phi_{CH_3CHO} = 1 + \phi_{C_2H_5OH} \qquad (13)$$

Reference to Figure 4 shows that at high oxygen pressures the experimental results obey eq 13 to a good approximation.

Equation 12 predicts that if $\phi_{C_2H_5OH}$ is plotted against $1/[O_2]$ it should tend toward a line through the origin for regions corresponding to high oxygen pressures with a slope at the origin from which the ratio k_5/k_8 may be derived. Figure 6 shows such a plot for a series of experiments at 120° which gives $k_5/k_8 = 0.25$. Similar experiments at 27 and 71° yielded almost identical values for this ratio. This result suggests that reactions 5 and 8 have about equal activation energies and that their rates should be about equal when the oxygen partial pressure is about half the partial pressure of ketone. It follows, in agreement with the conclusion arrived at above, that (8) is the predominant mode of reaction of the ethoxy radical at oxygen pressures in the region of 20 mm with the partial pressure of ketone used here.

Acknowledgment. The authors wish to acknowledge the support of this research by Grant AP00109, Research Grants Branch, National Center for Air Pollution Control, Bureau of Disease Prevention and Environmental Control, U. S. Public Health Service. We appreciate helpful discussions with Dr. Eric Whittle and Dr. John Coomber.