Photooxidation of acetone vapor

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The photochemical reaction between acetone and oxygen has been studied at temperatures from 100 to 250 °C at several oxygen pressures with light of 3 130 Å. A study of the quantum yields of all the major products has shown the necessity of introducing the reaction

$$CH_3O + O_2 \rightarrow CH_2O + HO_2$$

to the generally accepted mechanism, with a rate constant about 80 times that of the reaction

$$CH_3O + CH_3COCH_3 \rightarrow CH_3OH + CH_3COCH_2$$

at 100 °C. Both this reaction and the reaction of acetyl radicals with oxygen appear to have low or negative activation energies, consistent with a rate-determining process involving combination of the radical with oxygen. The reaction of acetonyl radicals with oxygen to give carbon monoxide is not important at temperatures below 150 °C, but it becomes the most important reaction at temperatures above 250 °C.

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INTRODUCTION

The photooxidation of acetone has been studied previously at room temperature and at higher temperatures up to 225 °C (15). At all temperatures the major products are carbon monoxide, carbon dioxide, formaldehyde, and methanol. Methyl hydroperoxide, water, and acetic acid have also been found in some experiments in appreciable quantities, and small amounts of other products have been reported (15). Although the main outline for the mechanism has been discovered, details are obscured. A comprehensive analysis of the products over a wide range of conditions should yield information about the importance of several reaction steps which have been previously postulated. In addition, the system provides a suitable vehicle for the estimation of relative rate constants of reactions of simple radicals, about which there are surprisingly few data available in the literature.

EXPERIMENTAL

Experimental procedures were similar to those used previously in this laboratory (1, 2), with a few exceptions. With a Hanovia U.V.S 220 lamp and a Pyrex glass filter 1.5 mm thick, light was restricted to effective wavelengths in the range 2 967 to 3 132 Å (hereafter called the 3 130 Å region). The quartz reaction vessel, 20 cm long and 2.8 cm in diameter, was filled by a slightly diverging beam of light.

Analar grade acetone was purified by preparative gas chromatography and analytical gas chromatography indicated that it contained less than 0.01% of impurity. Oxygen was prepared by heating potassium permanganate under vacuum. Passage through copper at 250 °C showed that it contained less than 0.1% of noncondensable gas (nitrogen).

After the introduction of acetone to the required pressure in the reaction vessel, oxygen was introduced in doses (3). Additional doses of oxygen were added as frequently as necessary during each experiment to keep the oxygen pressure constant (2).

The resultant gases from the reaction vessel were analyzed as follows. The carbon monoxide – methane – oxygen fraction, noncondensable at −196 °C, was analyzed by means of a copper – copper oxide furnace at 250 °C and a gas burette (2). The carbon dioxide fraction was removed from the other condensables at −160 °C with two Le Roy – Ward stills and was measured on the gas burette. Analysis of the carbon dioxide fraction showed that, although a small amount of formaldehyde was sometimes present (4), it was never present in sufficient quantity to seriously affect the carbon dioxide estimations. Of the other condensable products, formaldehyde was estimated colorimetrically (5), whereas methanol was estimated by vapor phase chromatography (v.p.c.) (2). Acetic acid was estimated with a v.p.c. column containing 30% ethyl hexyl sebacate plus 10% sebacic acid on 45–60 mesh celite (6). Neither hydrogen peroxide nor any organic peroxide could be detected by colorimetric (7) or paper chromatographic (8) analysis of the condensable products. No attempt was made to analyze for water, although this was expected to be a product of the reaction under all conditions.

Most experiments were performed in a reaction vessel which had been previously washed with nitric acid. Two series of experiments are reported in

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which a surface coating of (i) potassium bromide and (ii) boric acid were applied to the walls of the vessel.

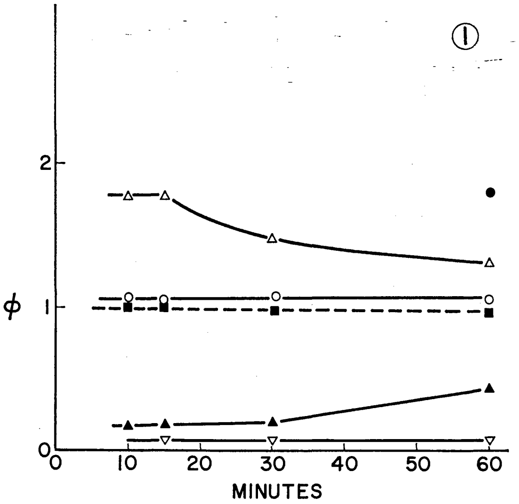
Quantum yields were calculated by reference to the yield of carbon monoxide from acetone under the same experimental conditions, which is assumed to be unity in the absence of oxygen (9). The percentage conversion of acetone was always less than 1%. The absorbed intensity was typically 1.3×10^{12} photons $ml^{-1} s^{-1}$.

RESULTS

The main products of the reaction in the temperature range 100 to 250 °C were found to be methanol, formaldehyde, carbon dioxide, and carbon monoxide. Acetic acid was a very minor product when 100 mm of acetone was photolyzed in the presence of 1.2 mm of oxygen at all temperatures studied, but none was detectable at 30 mm and 10 mm of acetone. Methane was a very minor product when 100 mm of acetone was photolyzed in the presence of 1.2 mm of oxygen at 200 and 250 °C, but was not found at 150 and 100 °C. The quantum consumption of acetone was estimated by summing the quantum yields of the carbon-containing products and dividing by 3. If the hydrogen unaccounted for is assumed to lie in water, which was not estimated, an oxygen balance between products and reactants to within an error of 10% was obtained each time.

The photooxidation of acetone proceeds by a non-chain reaction at relatively low temperatures and acetone pressures and relatively high oxygen pressures (2). Thus, in the present case, the photooxidation at 150 °C of 10 mm of acetone, in the presence of 2.4 or 4.8 mm of oxygen, resulted in a non-chain reaction in which quantum consumption of acetone was approximately 1 at all times (Fig. 1). With 1.2 mm of oxygen the quantum consumption of acetone was greater than 1, and an increase in the acetone pressure to 30 mm and then to 100 mm resulted in a progressive increase in the quantum consumption of acetone because of an increase in the importance of radical-abstraction reactions from acetone at higher acetone pressures (Fig. 2). However, the photooxidation of 100 mm of acetone with 1.2 mm of oxygen at 100 °C again produced a reaction in which the quantum consumption of acetone was close to unity.

With increase in temperature to 200 and 250 °C the chain length of the reaction increased (Fig. 3) and even with 10 mm of acetone at 200 °C there was an appreciable amount of chain reaction (Fig. 4).



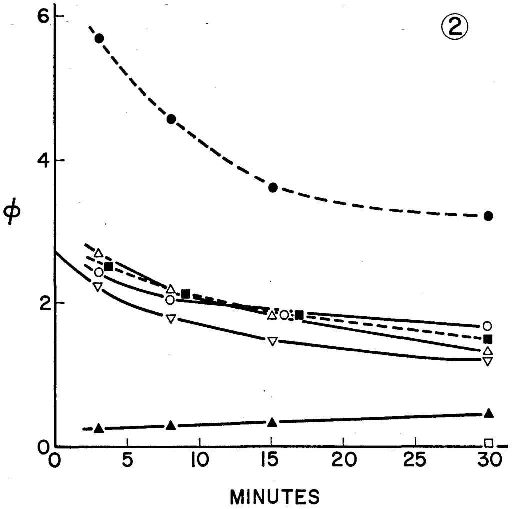
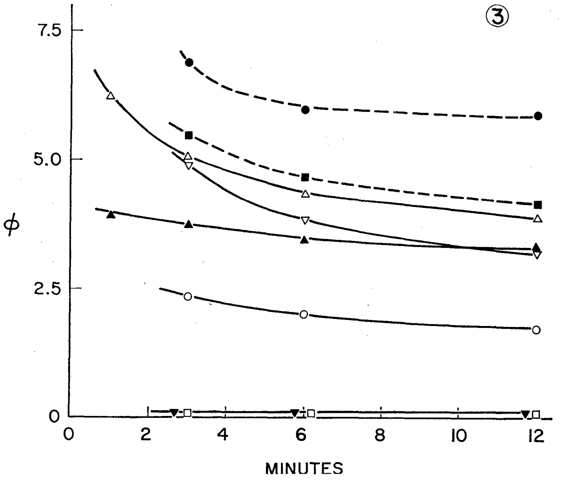


FIG. 1. Variation of quantum yield with time for 10 mm of acetone and 4.8 mm of oxygen at 150 °C. (●) O_2 used, (△) HCHO, (○) CO_2, (■) CH_3COCH_3 used, (▲) CO, (▽) CH_3OH.

FIG. 2. Variation of quantum yield with time for 100 mm of acetone and 1.2 mm of oxygen at 150 °C. (●) O_2 used, (△) HCHO, (○) CO_2, (■) CH_3COCH_3 used, (▲) CO, (▽) CH_3OH, (□) CH_3COOH.



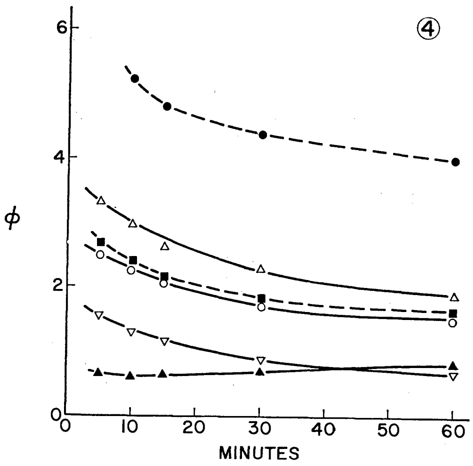


FIG. 3. Variation of quantum yield with time for 100 mm of acetone and 1.2 mm of oxygen at 250 °C. (●) O_2 used, (■) CH_3COCH_3 used, (△) HCHO, (▲) CO, (▽) CH_3OH, (○) CO_2, (▼) CH_4, (□) CH_3COOH.

FIG. 4. Variation of quantum yield with time for 10 mm of acetone and 1.2 mm of oxygen at 200 °C. (●) O_2 used, (△) HCHO, (○) CO_2, (■) CH_3COCH_3 used, (▲) CO, (▽) CH_3OH.

All series of experiments which involved some chain reaction showed a decrease in chain length with increase in time of reaction, indicating inhibition of the reaction by one of the products, presumably formaldehyde (2). Radical attack on formaldehyde, as its concentration builds up in the reaction vessel, should lead to an increase in the yield of carbon monoxide accompanying the decrease in the yield of formaldehyde (10, 11). Thus if the ratio of the quantum yields of the products

$$\frac{CH_3OH + HCHO + CH_4 + CH_3\text{—}\ \text{(in acetic acid)}}{CO + CO_2 + \text{—COOH(in acetic acid)}}$$

is plotted against time (Fig. 5), the value of this ratio extrapolates to a value close to 2 at zero time and decreases progressively with increase in time. This suggests that in the very early stages of reaction the products and group in the numerator of this ratio arise from the carbon atoms of the methyl groups of acetone, while the products and group in the denominator arise from the carbon atom of the carbonyl group. Secondary production of carbon monoxide (and perhaps carbon dioxide (11)) with simultaneous destruction of formaldehyde leads to a progressive decrease in the value of this ratio with time. Figures 6 and 7 show that an increase in the oxygen pressure and a decrease in the acetone pressure tends to increase the importance of formaldehyde relative to methanol as a product of the reaction. Figure 8 shows that an increase in the temperature favors the production of carbon monoxide relative to carbon dioxide.

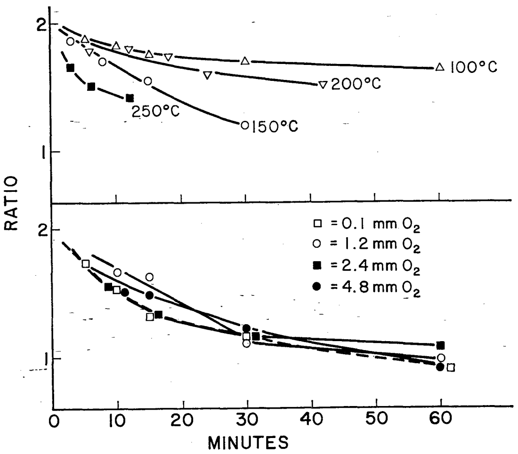


FIG. 5. Variation of the ratio ($\phi(CH_4) + \phi(CH_3OH) + \phi(CH_2O) + \phi(CH_3)$(in acetic acid))/($\phi(CO) + \phi(CO_2) + \phi(COOH)$ (in acetic acid)) with time (*a*) for 100 mm of acetone and 1.2 mm of oxygen and (*b*) for 10 mm of acetone at 150 °C.

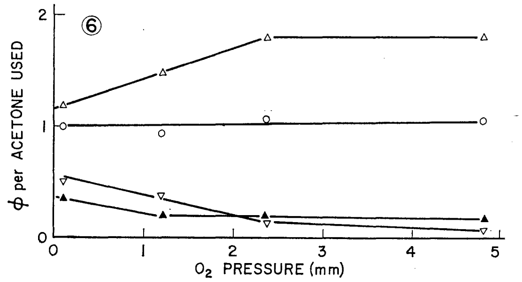
Secondary reactions may be eliminated by extrapolation of the quantum yields to zero time. Such a process is attended by a

TABLE I

Values of ϕ extrapolated to zero time

Temperature (°C)	Acetone pressure (mm)	Oxygen pressure (mm)	$\phi(CH_3OH)$	$\phi(HCHO)$	$\phi(CO)$	$\phi(CO_2)$
250	100	1.2	7.25	7.50	4.10	3.23
200*	100	1.2	7.23	5.40	1.60	5.02
200†	100	1.2	7.08	4.47	3.16	3.55
200	10	1.2	1.92	3.80	0.70	2.72
150	100	1.2	2.72	3.20	0.22	2.80
150	30	1.2	1.25	2.80	0.30	2.20
150	10	1.2	0.64	2.00	0.22	1.28
150	10	0.1	2.55	4.20	0.50	2.80
150	10	2.4	0.16	1.88	0.18	1.10
150	10	4.8	0.07	1.80	0.16	1.06
100	100	1.2	1.00	1.08	0.05	1.03

*Reaction vessel walls coated with boric acid.
†Reaction vessel walls coated with potassium bromide.



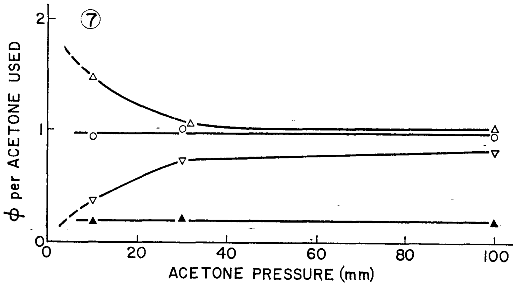


FIG. 6. Variation with oxygen pressure of yield per acetone molecule used for 10 mm of acetone at 150 °C. Reaction time = 10 min. (△) HCHO, (○) CO_2, (▲) CO, (▽) CH_3OH.

FIG. 7. Variation with acetone pressure of yield per acetone molecule used in the presence of 1.2 mm of oxygen at 150 °C. Reaction time = 10 min. (△) HCHO, (○) CO_2, (▽) CH_3OH, (▲) CO.

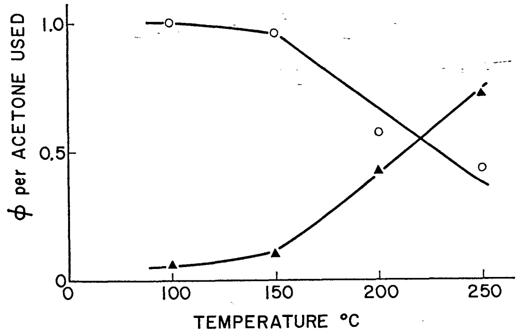


FIG. 8. Variation with temperature of yield per acetone molecule used for 100 mm of acetone and 1.2 mm of oxygen. Reaction time = 5 min. (▲) CO, (○) CO_2.

large uncertainty, but it does allow a more meaningful quantitative analysis of the data. Table I shows the values of the extrapolated quantum yields of the major products at zero time.

DISCUSSION

To facilitate the discussion the main steps in the proposed mechanism are listed, neglecting to a first approximation the formation of the very minor products methane and acetic acid.

[1] $CH_3COCH_3 + h\nu \rightarrow CH_3CO + CH_3$

[2] $CH_3CO \xrightarrow{\beta} CH_3 + CO$

[3] $CH_3CO + O_2 \xrightarrow{(1-\beta)} CH_3O + CO_2$

[4] $CH_3 + O_2 + M \xrightarrow{(1-\alpha)} CH_3O_2 + M$

[5] $CH_3 + O_2 \xrightarrow{\alpha} HCHO + OH$

[6] $2CH_3O_2 \rightarrow 2CH_3O + O_2$

[7] $CH_3O + CH_3COCH_3 \xrightarrow{(1-\delta)} CH_3OH + CH_3COCH_2$

[8] $CH_3O + O_2 \xrightarrow{\delta} HCHO + HO_2$

[9] $CH_3COCH_2 + O_2 \xrightarrow{(1-\gamma)} CH_3O + CO + HCHO$

[10] $CH_3COCH_2 + O_2 \xrightarrow{\gamma} CH_3 + CO_2 + HCHO$

[11] $OH, HO_2 \rightarrow$ chain-ending reactions.

With the exception of reaction [8] these reactions are those commonly postulated to occur in the photooxidation of acetone (13, 15). Figure 6 shows that at high oxygen pressures, under non-chain conditions, the methanol yield decreases towards zero and the formaldehyde yield approaches 2. Under such conditions the photooxidation can be simply represented by reactions [1], [3], [4], [6], and [8], i.e. $\phi(HCHO) = 2$ and $\phi(CO_2) = 1$, with no other carbon-containing products (neglecting the carbon monoxide produced from hot acetyl radicals). The evidence therefore necessitates a reaction such as [8] which results in decreased methanol and increased formaldehyde yields as the pressure of oxygen is increased and the pressure of acetone is decreased (Figs. 6 and 7).

The accuracy of the mechanism given above can be tested by computation of relative rate constants for pairs of reactions, noting the constancy of the values under varying conditions of reactant composition.

Let reactions [5], [2], [8], and [10] occur to the extent α, β, δ, and γ respectively and let x equal the quantum yield of acetonyl radicals. (The value of x is always equal to the chain length minus unity.) The extent to which the other reactions occur follows as shown in the mechanism. The following expressions may then be obtained.

Number of methyl radicals formed per quantum of light absorbed, i.e.

$$\phi(CH_3) = \beta + 1 + x\gamma$$

$$\phi(CH_3O) = (1 + \beta + x\gamma)(1 - \alpha) + x(1 - \gamma) + (1 - \beta).$$

Therefore

$$\phi(CH_3OH) = (1 - \delta)[(1 + \beta + x\gamma)(1 - \alpha) + x(1 - \gamma) + (1 - \beta)].$$

[12] i.e. $$2 + x - \frac{\phi(CH_3OH)}{(1 - \delta)} = \alpha(1 + \beta + x\gamma).$$

Similarly,

[13] $$\phi(CH_2O) - x = \alpha(1 + \beta + x\gamma) + \delta[(1 + \beta + x\gamma)(1 - \alpha) + x(1 - \gamma) + (1 - \beta)]$$

[14] $$\phi(CO) = \beta + x(1 - \gamma)$$

[15] $$\phi(CO_2) = (1 - \beta) + x\gamma.$$

From [12] and [13],

[16] $$\phi(CH_2O) + \phi(CH_3OH) = 2 + 2x.$$

Adding [14] and [15],

[17] $$\phi(CO) + \phi(CO_2) = 1 + x.$$

It is possible to use eqs. [12] to [17], together with certain reasoned assumptions, to calculate, as explained below, values of α, δ, and γ for the different sets of experimental conditions. Essentially there are two more unknowns than equations in the above expressions. However, the very low values of $\phi(CO)$ at 150 and 100 °C necessitate γ having a value close to unity, i.e. little carbon monoxide can be produced by the oxidation of acetonyl radicals under such conditions. β is then readily calculated by eq. [14]. The value of β at 200 and 250 °C is predicted from the values at 100 and 150 °C and γ is then deduced from eq. [14]. The value of x was obtained from eqs. [16] and [17].

The high values of $\phi(CH_3OH)$ make it clear that α and δ are small at 200 °C if eq. [12] is to be satisfied. We would expect α to increase with increase of temperature and δ to decrease. Therefore a value of α can be obtained by assuming δ is zero at 250 °C and δ can be calculated for 150 and 100 °C by assuming α is negligibly small.

Methyl Radical

The quantity α is postulated to arise from a competition between reactions [4] and [5]. Since the energy of activation of reaction [5] is probably larger than that of reaction [4] (14), the latter should be favored by an increase in temperature. A decrease in the total pressure should favor reaction [5], as discussed previously. The

TABLE II

Values of α, β, γ, and δ

Temperature (°C)	Acetone pressure (mm)	Oxygen pressure (mm)	α	β	γ	δ
250	100	1.2	0.22	0.90	0.50	0.00
200*	100	1.2	0.04	0.64	0.56	0.00
200†	100	1.2	0.04	0.64	0.82	0.00
200	10	1.2	0.29	0.64	0.88	0.42
150	100	1.2	0	0.22	1.00	0.31
150	30	1.2	0	0.22	1.00	0.54
150	10	0.1	0	0.50	1.00	0.39
150	10	1.2	0	0.22	1.00	0.70
150	10	2.4	0	0.18	—	0.86
150	10	4.8	0	0.16	—	0.94
100	100	1.2	0	0.05	1.00	0.50

*Reaction vessel walls coated with potassium bromide.
†Reaction vessel walls coated with boric acid.

value of α was found to be 0.22 at 250 °C and 0.04 at 200 °C with 100 mm of acetone.

$$\frac{\text{Rate of [5]}}{\text{Rate of [4]}} = \frac{k_5[\mathrm{CH_3}][\mathrm{O_2}]}{k_4[\mathrm{CH_3}][\mathrm{O_2}][\mathrm{M}]} = \frac{\alpha}{1-\alpha}$$

Therefore $$\frac{k_4}{k_5} = \frac{(1-\alpha)}{[\mathrm{M}]\alpha}.$$

At 250 °C, $k_4/k_5 = 1.12 \times 10^3$ l mole^{-1}.

At 200 °C, $k_4/k_5 = 7.08 \times 10^3$ l mole^{-1}.

Notwithstanding the differing efficiencies of various third bodies in reaction [4], these values are in good agreement with previous estimates of k_4/k_5 obtained from other systems (13). They provide an estimate of the activation energy difference $(E_5 - E_4) = 18.0$ kcal mole^{-1}. This value seems very high, but a small error in the value of α at either temperature (the value of α at 200 °C is particularly susceptible to extrapolation inaccuracies) would have a large effect on the value of $(E_5 - E_4)$ obtained here.

By using the value $k_4 = 4.7 \times 10^{10}$ l^2 mole^{-2} s^{-1} (13), k_5 can be calculated to have a value of 0.66×10^7 l mole^{-1} s^{-1} at 200 °C and 4.20×10^7 l mole^{-1} s^{-1} at 250 °C, in good agreement with previous estimates of this quantity (13).

The value of α with 10 mm of acetone at 200 °C was obtained in the following manner.

$$\alpha = \frac{\text{rate of [5]}}{\text{rate of [5]} + \text{rate of [4]}}.$$

Therefore $$\frac{\text{rate of [4]}}{\text{rate of [5]}} = \left(\frac{1}{\alpha^1} - 1\right)$$

$$= \frac{1}{10}\left(\frac{1}{\alpha} - 1\right),$$

where α^1 and α are the values at 10 and 100 mm of acetone respectively at 200 °C. The value of α at 150 and 100 °C was assumed to be negligibly small.

Acetyl Radical

The quantity β is assumed to arise because of a competition between the decomposition (reaction [2]) and oxidation (reaction [3]) of the acetyl radical. In the series of experiments at 150 °C with 10 mm of acetone, no source of carbon monoxide, other than reaction [2], appeared to be of importance. Thus β was given the same value as ϕ(CO) at zero time. The value of β at 100 °C was obtained in a similar manner.

It is more difficult to assign values of β at 200 and 250 °C because the acetonyl radical provides an additional source of carbon monoxide. However, if the assumption is made that the 'hot' radical contribution to reaction [2] is 0.03 in the present case (16) and that this value is effectively constant over the temperature range studied (12), then the 'hot' radical contribution can be subtracted from the β values to provide a value of the fraction β^1 of acetyl radicals decomposing thermally as in reaction [2]. By using the values obtained in this way, the ratio of the rate constants of thermal decomposition to oxidation of the acetyl radical = $k_2/k_3 = [O_2]\beta^1/(1 - \beta)$. The values of k_2/k_3 are included in Table III and are in good agreement with other estimates of the value of k_2/k_3, which have been summarized (13). Although the values of k_2/k_3 show some scatter at 150 °C, if taken together with previous estimates of this quantity they provide a good Arrhenius plot yielding a value of $(E_2 - E_3) = 14.5$ kcal mole^{-1}. The values of β at 200 °C and 250 °C were obtained from this plot and are included in Table II.

If it is assumed that k_2 has the value $1.66 \times 10^{10} \exp(-13500/RT)$ s^{-1} (13), then $k_3 = 1.90 \times 10^8$ l mole^{-1} s^{-1} at 100 °C and 1.60×10^8 l mole^{-1} s^{-1} at 150 °C. These results are in good agreement with other estimates of k_3 (13), and indicate a zero or small negative activation energy for reaction [3] which is in accord with it occurring by a two-stage process where combination of the radical and oxygen is the rate-controlling step.

Acetonyl Radical

The chain reaction must involve oxidation of the acetonyl radical. The quantity γ is postulated to arise because of a competition between the overall reactions [9] and [10]. The value of γ was found to increase with decrease in temperature (Table II) so that at 150 °C the importance of reaction [9] was negligible. This finding agrees with the results of Hoare and Ogilvie (17). The higher values of γ which were obtained when using a potassium bromide coated surface or lower pressure reflect the larger yields of oxides of carbon found under such conditions. It seems likely therefore that heterogeneous combustion, which is normally more marked in a potassium bromide coated surface (20) and at lower pressures, is causing γ to be abnormally high. This would be accomplished by oxidation of methyl groups to an oxide of carbon so that extrapolated values of $(\phi(CH_4) + \phi(CH_3OH) + \phi(CH_2O) + \phi(CH_3COOH))$ are no longer equal to twice $(\phi(CO) + \phi(CO_2) + \phi(CH_3COOH))$. Table I shows that little heterogeneous reaction was found for mixtures using 100 mm of acetone except when a potassium bromide surface was used.

However, the yield of carbon monoxide at 150 °C and 100 mm of acetone shows that little carbon monoxide can be coming from reaction [9] under these conditions and γ must be close to unity. This evidence strongly supports a value of γ in the region of 0.8 at 200 °C. Barnard and Honeyman (21) found that in the oxidation of acetone at 284 °C the chief oxide was carbon monoxide, while at 498 °C relatively little carbon dioxide was formed. This is further evidence for the strong dependence of γ on temperature (Fig. 8). k_{10}/k_9 can be calculated to have a value of 1.0 at 250 °C and $E_9 - E_{10}$ may be of the order of 14 kcal mole^{-1}.

Methoxy Radical

The high value of $\phi(CH_3OH)$ at 200 °C and 100 mm of acetone suggested that essentially all methoxy radicals took part in reaction [7] to form methanol, i.e. δ is close to zero at 200 and 250 °C.

Since $$\frac{k_8[CH_3O][O_2]}{k_7[CH_3O][CH_3COCH_3]} = \frac{\delta}{1 - \delta},$$

TABLE III

Values of relative rate constants

Temperature (°C)	Acetone pressure (mm)	Oxygen pressure (mm)	k_8/k_7	k_2/k_3 (mole l^{-1} × 10^{-5})
200	10	1.2	6.0	—
150	100	1.2	37	1.1
150	30	1.2	29	1.7
150	10	0.1	63	0.35
150	10	1.2	20	1.1
150	10	2.4	26	1.7
150	10	4.8	33	2.8
100	100	1.2	83	0.11

one can calculate k_8/k_7. The fact that this quantity is approximately independent of oxygen and acetone pressure (Table III) is strong evidence for the mechanism postulated. $E_7 - E_8$ may be calculated to be approximately 7 kcal mole^{-1} from the more accurate values of δ (at 150 and 100 °C).

There is evidence that the activation energy difference between the corresponding hydrogen-abstraction reactions of methyl and methoxy radicals is about 3 kcal mole^{-1} in most cases (18). Since the activation energy of the reaction

$$[18] \quad CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_3COCH_2$$

is approximately 9.7 kcal mole^{-1} (19), it would appear that E_7 should be approximately 7 kcal mole^{-1}. If $E_7 - E_8 = 7$ kcal mole^{-1}, then $E_8 = 0$ kcal mole^{-1}, which suggests that this reaction (which is exothermic by only 22 kcal mole^{-1}) may be controlled by a combination process in the same way as reaction [3]. The values of k_8/k_7 given in Table III suggest that δ may not be completely negligible at 200 °C and 100 mm of acetone as was originally suggested, but further refinement of the calculations is not justified in view of the inaccuracy of the extrapolations used to obtain ϕ values at zero time.

There seems no evidence for great importance of the reaction

$$[19] \quad 2CH_3O \rightarrow CH_3OH + CH_2O,$$

which is often postulated to account for the nearly equal yields of methanol and formaldehyde. It was clearly unimportant when the higher pressures of oxygen were used, and the low activation energy of reaction [8] suggests that it may not become important until higher concentrations of methoxy radicals are produced.

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