singlet state first formed by excitation may dissociate or lose its vibrational excitation by collision. Transition occurs from a vibrationally excited or non-excited singlet state to a triplet state which, when it has lost its vibrational energy, may decompose or be completely deactivated to the ground state. It seems therefore that A_1 and A_3 may be identified, respectively, as vibrationally excited acetone molecules (possibly in the singlet state) and thermally equilibrated acetone molecules (possibly in the triplet state). Little phosphorescence due to the triplet state occurs under the present experimental conditions,[13] so reactions 8 and 9 must be fast if they involve the triplet state. Volman and Graven[14] postulated a reaction such as 9a when they showed that in the polymerization of butadiene, carbon dioxide and butadiene deactivate excited acetone molecules, whereas acetone does not have a similar effect.

An acknowledgment is due to the Department of Scientific and Industrial Research for a grant to J.C.

[13] D. S. Weir, private communication.

[14] D. H. Volman and W. M. Graven, *J. Am. Chem. Soc.*, **75**, 3111 (1953).

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The Photo-oxidation of Acetone Vapor

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It is shown that in the photo-oxidation at 150 to 200° of 100 mm. of acetone with light in the 2537 Å. and 3130 Å. regions a chain oxidation occurs which is inhibited by the formaldehyde produced. In the photo-oxidation at 150° of 30 mm. of acetone with light in the 3130 Å. region a non-chain reaction occurs at pressures of oxygen exceeding 1 mm. Micro-analysis for all the major products (except water) enables a mechanism to be suggested.

Introduction

When the photo-oxidation of acetone was studied in some detail by Marcotte and Noyes,[1,2] analyses were performed mostly for the gaseous products carbon monoxide, carbon dioxide and methane. In 1953, Hoare[3] showed that formaldehyde was a major product and that it was necessary to proceed to less than 1% reaction if subsequent reactions of formaldehyde were to be avoided. Other condensable products detected were methanol, acetaldehyde, acetic acid and water.[3] The estimation of micro molar quantities of formaldehyde in the presence of large amounts of acetone has since been successfully accomplished,[4] but no systematic estimation of the other liquid products has been reported previously. The present work includes a systematic estimation of both liquid and gaseous products at much smaller conversions than previously achieved.

Experimental

The apparatus and techniques are similar to those used by previous workers. A Hanovia U. V. S220 gave a very steady and reproducible light intensity. A quartz cell 5 cm. in length filled with an atmosphere pressure of chlorine was used to restrict the wave length to the 2537 Å. region and a Pyrex glass filter 1.5 mm. thick allowed the passage of effective light in the range 2967 to 3132 Å. (hereafter called the 3130 Å. region). A neutral filter was used so that the intensity of the light absorbed by the acetone in the 2537 Å. region was approximately the same as that absorbed in the 3130 Å. region.

The acetone used was purified by distillation and was found to contain only small quantities of esters which were unchanged after photolysis. The oxygen was prepared by heating potassium permanganate and contained less than 0.1% uncondensable gas (nitrogen) unaffected by exposure to copper and copper oxide heated to 250°.

The reaction vessel, which was of quartz, 14 mm. in radius and 20 cm. in length, was filled by a slightly diverging beam of light. Acetone was introduced directly to the required pressure, but oxygen was introduced in doses as described by Hoare.[3] A stirrer kept the gases mixed and circulating during the photolysis, the oxygen pressure fluctuating by no more than 30 μ around the mean value.

The resultant gases from the reaction cell were separated and analyzed for carbon monoxide, methane, oxygen and carbon dioxide by a gas analysis train of a trap at −215°, two Le Roy-Ward stills[5] and a combined Töpler pump and McLeod gauge. A mixture of copper and copper oxide heated to 250° was used to remove oxygen and convert the carbon monoxide to carbon dioxide so that it could be condensed and estimated.

The liquid products were analyzed for formaldehyde by a colorimetric method or for, methanol and minor products, by vapor phase chromatography. The method for the estimation of formaldehyde utilized the production with phenylhydrazine and potassium ferricyanide of a color the optical density of which was measured at 5250 Å. (Matsukawa[6]). Acetone in large excess was found to have a small effect on the color intensity, but no other product had any effect in the concentrations in which it was formed.

It was necessary to use a V.P.C. column from which methanol was eluted before acetone in order to determine methanol quantitatively in excess acetone. The experimental success of this research lies in the development of such a column for the estimation of methanol. The column found to be most suitable had 23% of dipropionitrile ether supported on 44–60 mesh Celite in a column 12 ft. long; 0.1% sodium caproate was added to reduce tailing of methanol. The column was heated to 50° in a Pye argon chromatograph using an ionization detector. A flow rate of 35 ml./min. gave elution times for methanol and acetone of 28 and 35 min., respectively.

Results

Marcotte and Noyes[2] found that the quantum consumption of oxygen (computed by reference to the carbon monoxide yield in the absence of oxygen) was independent of the pressures of acetone and oxygen and independent of temperature over the range 120° to 200°. They concluded that the reaction was not a chain reaction. The results shown in Fig. 1 illustrate that this was a simplifica-

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[1] F. Marcotte and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **74**, 783 (1952).

[2] F. Marcotte and W. A. Noyes, Jr., *Disc. Faraday Soc.*, **10**, 236 (1951).

[3] D. E. Hoare, *Trans. Faraday Soc.*, **49**, 1292 (1953).

[4] M. I. Christie, *J. Am. Chem. Soc.*, **76**, 1979 (1954).

[5] D. J. Le Roy, *Can. J. Research*, **B28**, 492 (1950).

[6] D. Matsukawa, *J. Biochem.* (*Tokyo*), **30**, 386 (1939).

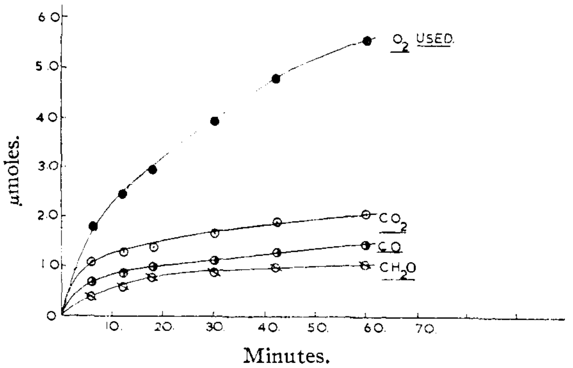

Fig. 1.—Photo-oxidation of 100 mm. of acetone in the presence of 1.2 mm. of oxygen at 200° using light in the 3130 Å. region; 1.12 μmoles/hour equivalent to a quantum yield of unity.

cation. At 200°, using 100 mm. pressure of acetone and light in the 3130 Å. region, chain oxidation occurred as soon as illumination began. At later stages the rate of reaction fell off and in particular the yield of formaldehyde rose only slowly after the initial burst of reaction.

It has been shown[7–9] that methanol and formaldehyde are the chief products in the oxidation of methyl radicals at 200° and that methyl hydroperoxide[10] is also formed. Figure 2 shows the relative yields of methanol and formaldehyde obtained in experiments whose duration varied from 1 to 60 minutes. It can be seen that the yields of methanol and formaldehyde were similar in the early stages of the reaction but after longer reaction times the methanol yields exceeded those of formaldehyde.

When using light in the 3130 Å. region an unstable product was detected with an apparent half-life of 15 minutes. This product, which gave formaldehyde upon decomposition, was eluted at the same time as methyl hydroperoxide.[10]

Experiments were next performed using 30 instead of 100 mm. pressure of acetone. These revealed that at the higher oxygen pressures (1.2 and 2.4 mm.) the quantum yields of products were considerably decreased. Following this line of investigation, it was found that at 150° even less reaction occurred and Fig. 3 shows that under these conditions a steady low yield reaction took place even at the beginning when light in the 3130 Å. region was employed. Since the quantum yields of carbon-containing products added up to three, it seems that a non-chain reaction was taking place.

It is therefore found to be possible to divide the field of study into three. (1) A chain reaction which was prominent at the beginning at 200° when 100 mm. pressure of acetone was photolyzed in the presence of oxygen.

(2) The subsequent quenched chain reaction which has been studied by Marcotte and Noyes.[1,2]

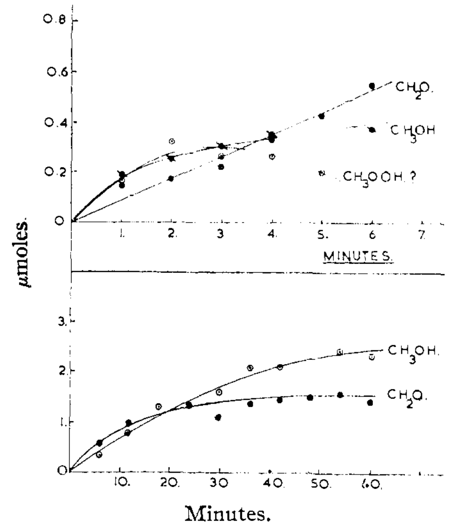

Fig. 2.—Photo-oxidation of 100 mm. of acetone in the presence of 0.35 mm. of oxygen at 200° using light in the 3130 Å. region; 1.12 μmoles/hour equivalent to a quantum yield of unity.

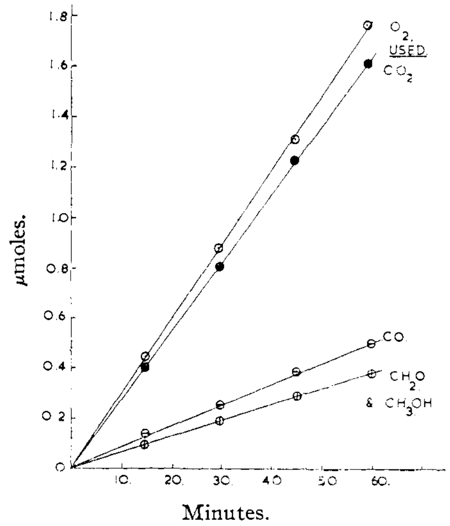

Fig. 3.—Photo-oxidation of 30 mm. of acetone in the presence of 1.2 mm. of oxygen at 150° using light in the 3130 Å. region; 0.97 μmole/hour equivalent to quantum yield of unity.

(3) The non-chain reaction which took place at 150° when 30 mm. pressure of acetone was photolyzed by light in the 3130 Å. region in the presence of 1.2 to 2.4 mm. pressure of oxygen. The variation of the yields of products under these three conditions as the oxygen pressure was varied is illustrated in Figs. 4, 5 and 6. In all cases the CO_2/CO ratio increased as the pressure of oxygen was increased up to 0.7 mm. and it was higher when light in the 3130 Å. region was used than when using light in the 2537 Å. region. In the non-chain reaction the yields of formaldehyde and methanol were equal and in all other experiments the ratio of their yields was almost independent of the oxygen pressure. In no experiment using 30 mm. of acetone was acetaldehyde or acetic acid[11] detected in appreciable amounts. Indeed, the

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

[8] F. Wenger and K. O. Kutschke, *ibid.*, **37**, 1546 (1959).

[9] D. E. Hoare and C. A. Wellington, "8th Symp. on Combustion," 1960, p. 472.

[10] M. Shanin and K. O. Kutschke, *J. Phys. Chem.*, **65**, 189 (1961).

[11] J. Brown, N. T. Mitchell and G. R. Martin, *Proc. Chem. Soc.* 115 (1960).

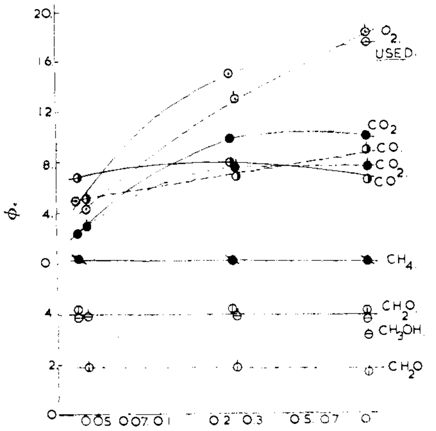

Fig. 4.—Photo-oxidation of 100 mm. of acetone for 6 minutes at 200°: dashed lines through points with single tail, photo-oxidations using light in the 2537 Å. region; full lines through the remaining points, photo-oxidations using light in the 3130 Å. region.

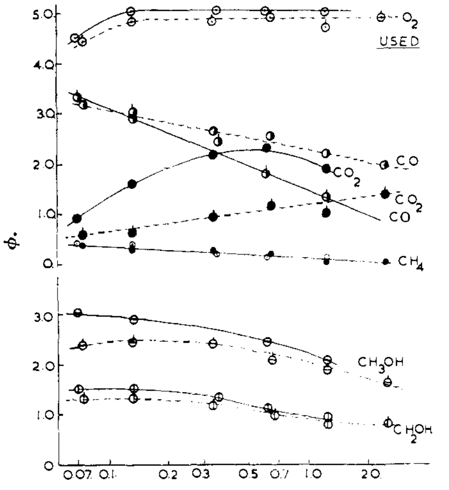

Fig. 5.—Photo-oxidation of 100 mm. of acetone for 1 hour at 200°: dashed lines through points with single tail, photo-oxidations using light in the 2537 Å. region; full lines through the remaining points, photo-oxidations using light in the 3130 Å. region.

amount of oxygen consumed suggests that no products other than water were formed in appreciable quantities. However, acetic acid was a major product when 100 mm. of acetone was photo-oxidized at 200°.

Discussion

It is generally accepted that decomposition of excited acetone molecules occurs according to the reaction

$$CH_3COCH_3^* \longrightarrow CH_3CO + CH_3 \qquad (1)$$

Since oxygen may readily deactivate an excited triplet state of acetone, it is important to determine if the amounts of oxygen used would affect the extent to which reaction 1 occurred. More triplet state phosphorescence is observed when acetone absorbs light in the 3130 Å. region than when 2537 Å. light is used.[12] Therefore light in the 3130 Å. region was used to photolyze acetone at a temperature of 150° in the presence of 1.2 and 2.4 mm. pressure of oxygen. Under these conditions a steady photo-oxidation reaction occurred and the quantum yields of carbon containing products added up to three (Fig. 6). This means that as many molecules of acetone were decomposed in the presence of oxygen as in its absence. Since, in addition, there is no evidence for a reaction between activated acetone molecules and oxygen such as occurs for biacetyl,[13] it seems likely that the rate of reaction 1 is unaffected by small additions of oxygen to the system.

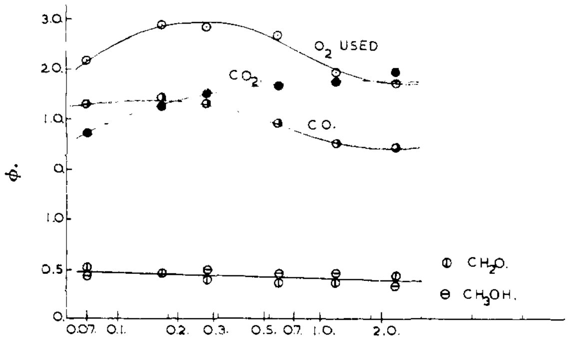

Fig. 6.—Photo-oxidation of 30 mm. of acetone for 1 hour at 150° using light in the 3130 Å. region.

Methyl radicals produced by reaction 1 formed chiefly methane and ethane in the absence of oxygen. When oxygen was added, most methyl radicals reacted with it and the yields of ethane were reduced to negligible proportions while the amounts of methane were considerably reduced. It has been shown[14] that the reaction of oxygen with methyl radicals is third order at temperatures up to 200° and that the chief products are formaldehyde and methanol[7-9] with methyl hydroperoxide as a minor product.[10]

In the non-chain photo-oxidation of acetone at 150° the yields of methanol and formaldehyde were so remarkably equal under a variety of conditions of oxygen pressure and time of reaction that some mechanism similar to that proposed by Raley, Porter, Rust and Vaughan[15] can be postulated to account for the facts; *i.e.*

$$CH_3 + O_2 + M \longrightarrow CH_3O_2 + M \qquad (2)$$

$$2CH_3O_2 \longrightarrow 2CH_3O + O_2 \qquad (3)$$

$$2CH_3O \longrightarrow CH_2O + CH_3OH \qquad (4)$$

No methyl hydroperoxide was detected and none would be expected since hydrogen atom abstraction by methyl peroxy radicals from acetone would lead in the first case to a chain reaction and in the second to a variation with time (and formaldehyde concentration) in the methanol and formaldehyde quantum yields.

In the chain oxidation at 200° methyl hydroperoxide was formed in important amounts in the initial burst of chain reaction, but decreased in

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

(13) G. B. Porter, *J. Chem. Phys.*, **32**, 1587 (1960).

(14) D. E. Hoare and A. D. Walsh, *Trans. Faraday Soc.*, **53**, 1102 (1957).

(15) J. H. Raley, L. M. Porter, F. F. Rust and W. E. Vaughan, *J. Am. Chem. Soc.*, **73**, 15 (1951).

concentration when the over-all reaction became slower. It seems then that initially a chain propagation reaction occurred between radicals and acetone molecules at 200° but that some product stopped the chains by preventing this reaction. The evidence that formaldehyde was this intermediate is: (1) It is the only stable product given in sufficient quantities with a hydrogen atom sufficiently easy to remove by abstraction. (2) It is known to cause chain ending in the presence of oxygen even at temperatures as high as 500° in the hydrogen–oxygen system.[16] (3) Figures 1 and 2 show that in the later stages of a chain reaction formaldehyde tended to approach an equilibrium concentration and the amounts of formaldehyde found decreased relative to the other products. (4) Formaldehyde added to the system reduced the consumption of oxygen.[3]

It seems likely then that the chain-propagating reaction was

$$CH_3O_2 + CH_3COCH_3 \longrightarrow CH_3OOH + CH_3COCH_2 \qquad (5)$$

and the chain-ending reaction was

$$\dot{R} + CH_2O \longrightarrow RH + HCO \qquad (6)$$

where $\dot{R}$ is a chain center.

Methyl hydroperoxide decomposes heterogeneously to give formaldehyde[10] while the formyl radical does not yield a hydrogen atom but reacts with oxygen to give carbon monoxide[15]; *e.g.*

$$HCO + O_2 \longrightarrow HO_2 + CO \qquad (7)$$

Since reaction 5 may have a higher activation energy than reaction 3, it follows that it may not occur at lower temperatures and acetone pressures, *i.e.*, under just those conditions where a non-chain reaction was found to take place.

In the non-chain oxidation at 150° the combined yield of carbon monoxide and carbon dioxide was twice as large as the combined yield of methanol and formaldehyde (Fig. 6). If one assumes that formaldehyde and methanol were formed from methyl radicals, then carbon monoxide and carbon dioxide must have been formed from both carbon atoms of acetyl radicals. Therefore, in order to give the observed dependence of the CO_2/CO ratio upon the oxygen pressure (Fig. 6), acetyl radicals must have been oxidized according to a mechanism similar to

$$CH_3CO + O_2 \longrightarrow X \qquad (8)$$

$$X \longrightarrow CO + Y \qquad (9)$$

$$X + O_2 \longrightarrow CO_2 + Z \qquad (10)$$

Y and Z may in turn have decomposed to give carbon monoxide or reacted with oxygen to give carbon dioxide.

In the partially suppressed chain oxidation of 100 mm. pressure of acetone at 200° the combined yield of formaldehyde plus methanol was higher and was nearly equal to that of carbon monoxide plus carbon dioxide (Fig. 5). This means that (particularly at the lower oxygen pressures) more methyl radicals were produced. Reaction 11

$$CH_3CO + M \longrightarrow CH_3 + CO + M \qquad (11)$$

which occurs in the absence of oxygen was naturally chosen to account for this increase in the production of methyl radicals at higher temperatures. Since it is a second-order reaction,[14] one can understand why, when using 30 mm. pressure of acetone, less methanol and formaldehyde were formed (*i.e.*, less methyl radicals were produced).

The CO_2/CO ratio was significantly lower when light in the 2537 Å. region was used except at lower oxygen pressures and during the initial chain reaction. This suggests that in reaction 1 acetyl radicals were produced with excess energy[17] and their subsequent decomposition to give carbon monoxide followed more readily.

Chain oxidation of acetone probably involves hydrogen abstraction from an acetone molecule. This could be according to reaction 5 and otherwise; *e.g.*

$$\dot{R} + CH_3COCH_3 \longrightarrow RH + CH_3COCH_2 \qquad (12)$$

Although the quantum yields in the chain photo-oxidation of 100 mm. pressure of acetone at 200° were much larger than in the subsequent slower reaction, there was no marked difference in the relative amounts which were found of carbon monoxide, carbon dioxide, methanol and formaldehyde. This suggests that each acetonyl radical must have been oxidized to give a methyl radical, a radical which could propagate the chain oxidation and a radical which, like X, could be oxidized to give two molecules of carbon monoxide or carbon dioxide; *e.g.*

$$CH_3COCH_2 + O_2 \rightsquigarrow CO{\cdot}CHO + CH_3 + OH \qquad (13)$$

In so far as some methyl radicals would have reacted to give methyl hydroperoxide according to reaction 5, this is a branched chain mechanism inhibited by reaction 6 (where $\dot{R} = OH$).

An acknowledgment is due to the Department of Scientific and Industrial Research for a grant to J.C.

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[16] R. R. Baldwin, N. S. Corney and R. W. Walker, *Trans. Faraday Soc.*, **56**, 803 (1960).

[17] D. S. Herr and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **62**, 2052 (1940).