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Carbon Monoxide Yields in the Photolysis of Acetone

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It is shown that inert gases increase the yields of carbon monoxide through a maximum in the photolysis of acetone using light in the 2537 Å. or 3130 Å. region. The variation in the yields of carbon monoxide with both temperature and pressure is compared with similar variations in the absorption coefficient. It is concluded that there is little change in the quantum yield of carbon monoxide with either pressure or temperature variation between 150° and 200°. The effect of inert gases upon the photolysis of acetone can be attributed to reactions of the excited states of acetone.

Introduction

The photolysis of acetone is generally agreed to include the steps

$$CH_3COCH_3 + h\nu \longrightarrow CH_3CO + CH_3 \quad (1)$$

$$CH_3CO \longrightarrow CH_3 + CO \quad (2)$$

$$CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_3COCH_2 \quad (3)$$

$$2CH_3 \longrightarrow C_2H_6 \quad (4)$$

The effect of adding inert gas in the photolysis of acetone was studied at 25° by Howland and Noyes.[1] At this temperature, the reverse of reaction 1 is important and low quantum yields of carbon monoxide were obtained. Inert gases increased the yield of carbon monoxide, a fact which can be attributed to the second-order kinetics of reaction 2.[2,3]

The quantum yield of carbon monoxide has been found to be unity for acetone pressures greater than 100 mm. at 100°[4] but less at lower pressures and temperatures. Therefore it was surprising to find that at 200° carbon dioxide increased the yield of carbon monoxide when 10 mm. of acetone was photolyzed with 3130 Å. light.[3] Further experiments have now been carried out to determine whether this result can be attributed to: (a) an increased absorption coefficient of acetone, (b) an increase in the decomposition of excited acetone molecules or (c) an increase in the rate of reaction 2 when inert gas was added.

Experimental

The apparatus and techniques are similar to those used by Noyes and co-workers. Using a Hanovia U. V. S220 lamp and a Pyrex glass filter 1.5 mm. thick, light was restricted to effective wave lengths in the range 2967 to 3132 Å. Monochromatic 3130 Å. light was obtained by the use of a quartz cell 3 cm. in length containing 5 g./l. of potassium biphthalate solution. Light in the 2537 Å. region was obtained by the use of a quartz cell 5 cm. in length containing chlorine at 1 atmosphere pressure. The quartz reaction cell 14 mm. in radius and 20 cm. in length was filled by a slightly diverging beam of light whose intensity was very steady and decreased very slowly with time.

Analar quality acetone was purified by distillation and was found (by V.P.C.) to contain only small quantities of esters which were unchanged after the photolysis. The carbon dioxide and isopentane used were transparent to light in the 3130 Å. region and completely nonvolatile at liquid air temperatures. The hydrogen, argon and helium were passed from cylinders through a liquid air-cooled trap directly into the apparatus.

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

Results

Previous work[3] has shown that the presence of carbon dioxide raised the yield of carbon monoxide in acetone photolysis at 3130 Å. This work was repeated using carbon dioxide, isopentane, hydrogen and helium added to 10 mm. of acetone at 50°. Figure 1 shows that, with the exception of helium, all gases increased the yield of carbon monoxide by approximately the same amount.

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(1) J. J. Howland and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **63**, 3404 (1941).

(2) W. Davis, *Chem. Revs.*. **40**, 201 (1947).

(3) D. E. Hoare, *Trans. Faraday Soc.*, **53**, 791 (1957).

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

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

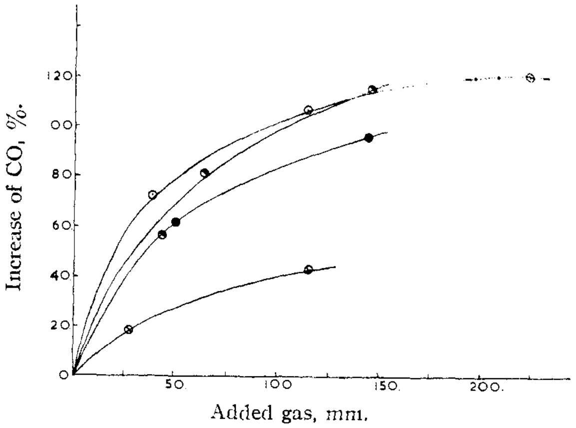

Fig. 1.—Photolysis of 10 mm. of acetone at 50° with 3130 Å. light; added gases: ●, CO_2; ⦶, He; ⊙, isopentane; ◑, H_2.

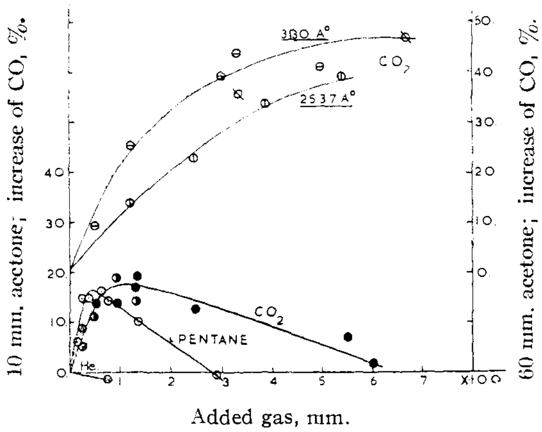

Fig. 2.—Photolysis of acetone at 200°; added gases ● and ⊖, CO_2 at 3130 Å.; ⦶, CO_2 at 2537 Å.; ⊙, isopentane; ◑, H_2; ⊗, He; ⦸, CO_2 at 3130 Å., $^1/_5$ intensity.

At 200° (Fig. 2), the increase in the yield of carbon monoxide was greater with hydrogen than with isopentane or carbon dioxide. Helium had little effect. Using 60 mm. pressure of acetone the increase in carbon monoxide reached over 40%, being a little less if light in the 2537 Å. region was used. Reduction in the light intensity by a factor of 5 had no appreciable effect. The decrease in yield of carbon monoxide at higher pressures was only apparent for 10 mm. pressure of acetone and was most prominent when isopentane was added.

Similar experiments at 120° showed maximum yields of carbon monoxide at 450 and 150 mm. pressure of carbon dioxide when 60 and 10 mm., respectively, of acetone were photolyzed with light in the 3130 Å. region. At higher carbon dioxide pressures the yields of carbon monoxide fell off rapidly in both cases (Fig. 3). Under all conditions the yields of methane and ethane were in accordance with an increase in the number of molecules of acetone decomposed.

To determine quantum yields, monochromatic light is needed. Using a biphthalate filter to obtain 3130 Å. light and photolyzing acetone at 10 and 131 mm. pressure at 200°, the amounts of carbon monoxide produced were 0.37 and 3.40 µmoles per

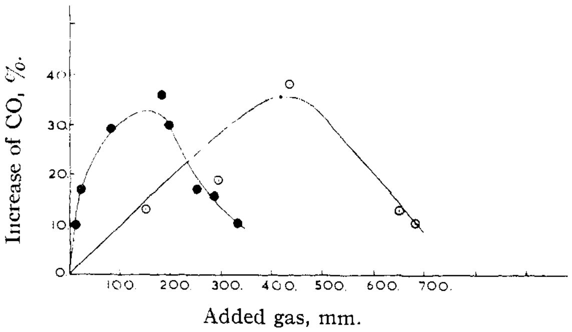

Fig. 3.—Photolysis of acetone at 120° with 3130 Å. light; ●, 10 mm. pressure; ⊙, 60 mm. pressure.

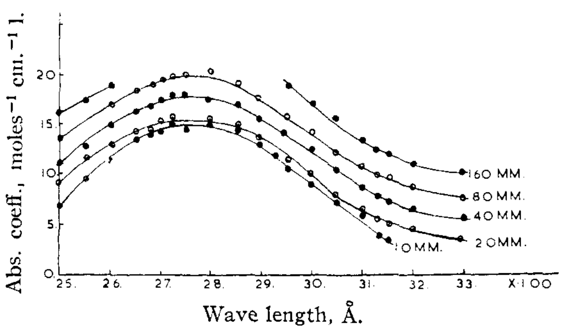

Fig. 4.—Absorption coefficient e of acetone at 20° (successive pressures displaced 2.5 units on absorption scale); $\log I_0/I = ecd$.

hr. If equal quantum yields are assumed for each pressure, this corresponds to an absorption coefficient which is 20% greater for 10 mm. pressure of acetone than for 131 mm. If the absorption coefficients are assumed to be equal, then the quantum yield obtained when using 10 mm. pressure of acetone must be 20% larger than that obtained when using 131 mm.

Using a Unicam spectrophotometer s.p. 500 suitably modified to take a quartz cell 15 cm. in length, absorption coefficients of acetone vapor were found to be constant at 20° between 60 and 160 mm. pressure of acetone, but were apparently 15 to 20% higher at 10 mm. pressure (Fig. 4).

The temperature variation of the carbon monoxide yield is illustrated in Fig. 5. Using light in the 3130 Å. region it was found that with 10 mm. pressure of acetone the yield of carbon monoxide rose over the whole temperature range from 50° to 200°. Using 131 mm. pressure of acetone the yield of carbon monoxide was almost constant between 120° and 200°. Since acetone is less dense at the higher temperatures, this means that either the absorption coefficient rises with temperature or the quantum yield increases between 120° and 200° (as well as at lower temperatures).

The Unicam Spectrophotometer was adapted so that the absorption coefficient could be measured between 50° and 200°. Figure 6 shows the variation in molar extinction coefficient with temperature and wave length using 120 mm. pressure of acetone. For this experiment an evacuated quartz cell 58 mm. in length was placed in the furnace between the source and the detector. The fraction of light absorbed when acetone was admitted to the cell was read directly.

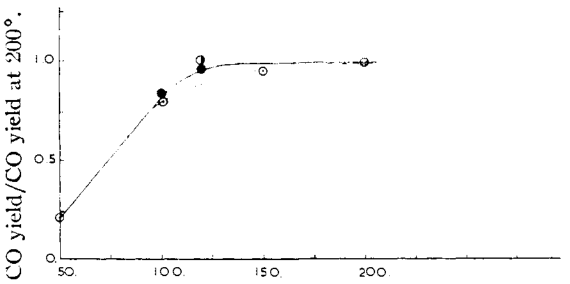

Fig. 5.—Photolysis of acetone using light in 3130 Å. region: ⊙, 10 mm.; ◑, 60 mm.; ●, 131 mm. pressure.

Two effects of temperature were observed. As the temperature was raised the absorption maximum moved to longer wave lengths and the absorption coefficients increased slightly. As a result of these two effects the absorption due to 120 mm. of acetone at 3130 Å. is only a little less at 250° than it is at 25°, despite the change in density of the vapor. Argon, isopentane and carbon dioxide when added to 10 mm. pressure of acetone had no effect on the absorption coefficient.

Discussion

The absorption coefficients obtained at room temperature were similar to those obtained by Porter and Iddings.[6] The shift of the absorption maximum to longer wave lengths and the increase in the absorption coefficients as the temperature was raised are phenomena which can be associated with an increase in the energy of the absorbing molecules.

The results show that the quantum yield of carbon monoxide is almost independent of acetone pressure and temperature between 120° and 200°. Inert gases do not alter the absorption coefficient so they must have an effect either in increasing the decomposition of acetone molecules which have been activated or in causing decomposition of radicals to give more carbon monoxide. In the past it has been postulated that acetone photolysis occurs by a nonchain mechanism below 200° and that the quantum yield of carbon monoxide is unity,[4,7] at temperatures above 110° and pressures above 100 mm.

The photolysis of acetone under conditions where chain decomposition does occur, at 300°, has been studied by Brinton.[8] Under such conditions ketene is formed by the decomposition of acetonyl radicals and there is an increase in the yield of carbon monoxide due to a reaction such as $CH_3 + CH_3COCH_3 \rightarrow C_2H_6 + CO + CH_3$. However, in the present experiments no change was observed in the apparent value of $k_3/k_4^{1/2}$ and it is very unlikely that a chain mechanism was involved at temperatures as low as 120°.

The present work showed that although the amount of light absorbed was independent of the temperature at 3130 Å. and the yield of carbon monoxide was similarly independent of temperature at pressures above 60 mm. of acetone, addition

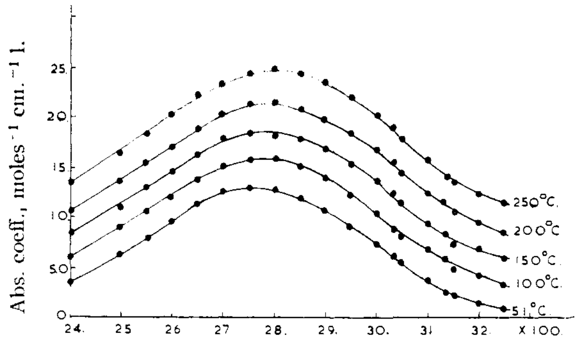

Fig. 6.—Absorption coefficient e of 120 mm. of acetone; $\log I_0/I = ecd$ (successive temperatures displaced 2.5 units on absorption scale).

of inert gas raised the yield of carbon monoxide by up to 40%. This rise was independent of the absorbed intensity. Since reaction 2 should be temperature dependent, any competing reaction would also have to be temperature dependent and the competition independent of intensity. A reaction of acetyl radicals with acetone would be suitably temperature dependent and would explain why the rise in carbon monoxide yield was greater when inert gas was added to 60 mm. pressure than when added to 10 mm. pressure of acetone (Fig. 2).

However, no acetaldehyde was found in the products and the number of methyl radicals found in the products methane, ethane and methyl ethyl ketone was exactly double the yields of carbon monoxide. One must assume that between 150 and 200° acetyl radicals decompose according to reaction 2 under the conditions of the present experiments.

The experiments performed at 50° revealed quite a different phenomenon. The carbon monoxide yield increased both with rise in temperature and decrease in absorbed intensity. This indicates that the alternative reaction of acetyl radicals at 50° is a reaction with another radical. In conformity with this, the formation of biacetyl and the reverse of reaction 1 to give acetone[9] have both been shown to occur below 100°.

The results obtained at temperatures between 120° and 200° are consistent with the mechanism

$$A + h\nu \rightsquigarrow A_1 \quad (5)$$

$$A_1 \longrightarrow \text{decomposition} \quad (6)$$

$$A_1 + \text{inert gas} \longrightarrow \text{decomposition} \quad (6a)$$

$$A_1 + A \rightsquigarrow A_3 \quad (7)$$

$$A_3 + A \longrightarrow \text{decomposition} \quad (8)$$

$$A_3 + \text{inert gas} \longrightarrow \text{deactivation} \quad (9a)$$

$$A_3 \longrightarrow \text{deactivation} \quad (9)$$

where A, A_1 and A_3 represent acetone molecules in the normal and two activated states, respectively.

A considerable number of publications has been devoted to the fluorescence of acetone and to the primary process.[10-12] It is postulated that the

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[6] C. W. P. Porter and C. Iddings, *J. Am. Chem. Soc.*, **48**, 40 (1926).

[7] J. A. Leermakers, *ibid.*, **56**, 1899 (1934); H. W. Anderson and G. K. Rollefson, *ibid.*, **63**, 816 (1941).

[8] R. K. Brinton, *ibid.*, **83**, 1541 (1961).

[9] S. N. Naldrett, *Can. J. Chem.*, **33**, 750 (1955).

[10] J. Heicklen and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **81**, 3858 (1959).

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

[12] J. L. Roebber, G. K. Rollefson and G. C. Pimentel, *J. Am. Chem. Soc.*, **80**, 255 (1958).

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.

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

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

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, QUEEN'S COLLEGE, DUNDEE, SCOTLAND, U.K.]

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).