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High Intensity Photolysis of Acetone

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The photolysis of acetone has been investigated at absorbed intensities of the order of 10^{22} quanta liter^{-1} sec.$^{-1}$ (greater by a factor of about 10^6 than those normally used). Essentially monochromatic light at 2800 Å. was obtained by use of a high intensity spark between magnesium electrodes. Simplifications resulting from the elimination of reactions which are first order in radical concentration have led to new information concerning the primary photochemical acts. The previously accepted mechanism has been modified by the addition of several new steps in the primary process. This modified mechanism is consistent not only with the results of the high intensity photolysis of acetone and the many previous low intensity studies, but also with the results of recent studies of the photolysis of hexafluoroacetone.

Introduction

Extensive investigations have been made of the vapor phase photolysis of acetone using absorbed light intensities of the order of 10^{15} quanta sec.$^{-1}$ liter^{-1}. Complete reviews of the subject have been published.[2-5]

Khan, Norrish and Porter[6] have photolyzed acetone, using a high intensity gas discharge with light intensities of the order of 10^{21} quanta sec.$^{-1}$ liter^{-1}. All first-order radical reactions which are in competition with second-order radical reactions at normal intensities are eliminated at these high intensities. Unfortunately the interpretation of these valuable studies is limited by three complications. First, the gas discharge is a polychromatic source and a range of frequencies was effective in photolysis. Secondly, the large amount of energy absorbed at each flash raised the temperature by an amount which was difficult to determine. To control this temperature rise the photolysis was carried out in the presence of a large excess of carbon dioxide. This is the third complication because the primary process is probably a function of pressure as well as wave length and temperature.

Mains, Roebber and Rollefson[7] have described a condensed spark apparatus which produces monochromatic light at 2800 Å. with an intensity of the order of 10^{22} quanta sec.$^{-1}$ liter^{-1}. Since the total number of quanta is much smaller, there is no significant change in temperature. The present investigation was undertaken in the hope that a study of the high intensity photolysis of acetone with this apparatus would provide further information on the nature of the primary process.

Experimental Procedure

Light Source.—The high intensity condensed spark apparatus has been described.[7] A capacitance of 10 microfarads charged to 20 kilovolts was discharged between 10 pairs of magnesium electrodes in parallel arranged in a circle in a low pressure chamber. A quartz tube into which the reaction vessel could be inserted ran through the middle of the low pressure chamber. In most of the experiments a quartz reaction vessel with an inside diameter of 20 mm. and a length of 30 cm. was used. A quartz vessel of 6 mm. inside diameter and 30 cm. length was used in a few experiments.

No lines were visible in photographs of the spectrum of the spark below the intense group of lines at 2800 Å. to the short wave length limit of the spectrograph somewhat below 2500 Å. The M.I.T. Wavelength Tables[8] list no strong magnesium spark lines from 2500 Å. to the short wave length limit of the tables at 2000 Å. Kayser and Ritsehl[9] list no strong magnesium spark lines from 2500 Å. to below 1800

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(1) Deceased.

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

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

(4) E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Vol. I, Ch. V, Reinhold Publ. Corp., New York, N. Y., 1954.

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(6) M. A. Khan, R. G. W. Norrish and G. Porter, *Proc. Roy. Soc.*, *(London)*, **219A**, 312 (1953).

(7) G. J. Mains, J. L. Roebber and G. K. Rollefson, *J. Phys. Chem.*, **59**, 733 (1955).

(8) "M.I.T. Wavelength Tables," John Wiley and Sons, Inc., New York, N. Y., 1939.

(9) H. Kayser and R. Ritsehl, "Tabelle der Hauptlinien der Linienspectra aller Elemente," Zweite Auflage, Julius Springer, Berlin, 1939.

Å., well beyond the short wave length limit of transmission of fused quartz.

It was found by photolyzing a solution of the potassium ferrioxalate actinometer described by Parker[10,11] alternately in a quartz and a Pyrex reaction vessel that the condensed spark apparatus produced a total light yield of 1.3 × 10^{17} quanta per discharge below the short wave length limit of transmission of Pyrex. This light yield was all attributed to the lines at 2800 Å. and constituted 90% of the light yield measured by the actinometer in the quartz vessel.

The quantum yields of the photolysis products of acetone at 200 mm. pressure were determined immediately after the quantum output had been measured with the potassium ferrioxalate actinometer. Since the deposition of magnesium oxide caused the quantum output to decrease slowly with time, frequent checks were made of the acetone quantum yields at 200 mm. pressure to detect changes in quantum output. The number of quanta absorbed by acetone was calculated from the absorption coefficient of acetone at 2800 Å. given by Porter and Iddings.[12]

The intensity of the photolysis source was varied in two ways. In one method, an inductance of 1.05 millihenries was added to the discharge circuit. The duration of the discharge was lengthened to about 2.4 milliseconds from an initial value of 0.14 millisecond. This reduced the average intensity by a factor of about 20. In the other, an absorbing solution of 10^{-3} M potassium chromate in 0.05 M potassium hydroxide was placed in the annular space (which was non-uniform, varying from about 1 to 2 mm.) between the reaction vessel and the quartz tube of the low pressure chamber. This reduced the light intensity by a factor averaging about eight without changing the duration of the discharge.

Photolysis Procedure.—In the photolysis of pure acetone degassed acetone was vaporized from a side tube into the reaction vessel to the desired pressure as indicated by a mercury manometer. The reaction vessel was then isolated from the acetone supply. After the desired number of discharges, the acetone and photolysis products were pumped with a Toepler pump from the reaction vessel into a bulb for transfer to the analysis system. The amount of acetone decomposed in a photolysis never exceeded 2% and was usually about 0.3%.

When a photolysis was carried out in the presence of a foreign gas (carbon dioxide or ammonia) the foreign gas was thoroughly mixed with the acetone by means of a Toepler pump attached to the reaction vessel.

Method of Analysis.—The mixture of acetone and photolysis products usually was passed through a trap cooled to −160° by an isopentane-bath at its melting point. The volatile fraction was pumped with a Toepler pump into the micro-gas analysis system. The condensed fraction was allowed to warm to room temperature and the freezing and pumping process repeated to remove any non-condensable gas trapped in the frozen acetone. The non-volatile fraction contained the excess acetone and any higher boiling products of the photolysis such as biacetyl. All of the ammonia, if it had been present as an inert gas, was retained in this fraction. Most of the carbon dioxide, if it had been added, was retained in this fraction. In a few experiments the trap was cooled to −118° by an ethyl bromide-bath at its melting point to check for the presence of acetaldehyde and ketene. The volatile fraction, which should have contained all of the ketene and most of the acetaldehyde, was removed with the Toepler pump and analyzed with a mass spectrometer. In a few instances the fraction volatile at liquid nitrogen temperature was analyzed mass spectrometrically. This fractionation removed the ethane and hence permitted a more accurate analysis for hydrogen.

The fraction volatile at −160° was analyzed for ethane and carbon monoxide in a constant volume micro-gas analysis system similar to the one described by Ransley.[13] After measurement of the total amount of gas volatile at −160°, the amount of ethane was determined from the change in pressure when the ethane was frozen out in a side tube cooled to −210°. The carbon monoxide was oxidized to carbon dioxide on a heated platinum filament in the presence of excess oxygen and the amount determined by condensing the product carbon dioxide at −196°. It was found that methane in small amounts also was oxidized on the platinum filament with the carbon monoxide. The mass spectrometric analysis of the fraction volatile at −118° gave a check on the accuracy of the carbon monoxide analysis. For example, in the photolysis of acetone at 50 mm. pressure the micro-gas analysis for CO was 10% too high, presumably because of the methane present. At 200 mm. pressure of acetone, the micro-gas analyses for carbon monoxide agreed (within the reproducibility of about 5%) with the mass spectrometric analyses and were not systematically too high.

The biacetyl present in the fraction not volatile at −160° was determined in a procedure almost identical to that proposed by Prill and Hammer.[14] This colorimetric method permits the determination of micro-mole quantities of biacetyl (as dimethylglyoxime complexed with ferrous iron) in the presence of a large excess of acetone. The fraction containing the biacetyl was distilled into a flask containing a degassed solution of hydroxylamine acetate. The flask was then removed from the vacuum system and treated in the manner given by Prill and Hammer to develop the colored dimethylglyoxime complex. The concentration of the complex was determined, using a Beckman D.U. spectrophotometer. The optical density was measured at 5280 Å., the center of a broad absorption of the dimethylglyoxime complex. Standard dimethylglyoxime solutions were prepared using J. T. Baker analyzed dimethylglyoxime that had been recrystallized from methanol. It was found that Beer's law is applicable in 1.75 × 10^{-5} M to 1.40 × 10^{-4} M dimethylglyoxime solutions. The extinction coefficient at 5280 Å. based on the concentration of dimethylglyoxime is 4.71 × 10^3.

This extinction coefficient was separately determined starting with Eastman White Label biacetyl which had been dried over magnesium sulfate and distilled through a ten theoretical plate column under an atmosphere of nitrogen. Upon conversion to dimethylglyoxime and then the complex, an extinction coefficient at 5280 Å. of 4.48 × 10^3 was obtained. The discrepancy between this value and that obtained from the dimethylglyoxime solutions was attributed to the difficulty of purifying biacetyl and the instability of biacetyl in water.

In a third procedural check a small sample of vacuum distilled biacetyl was vaporized in the micro-gas analysis system and the number of moles present determined from the McLeod gauge reading. This gas was mixed with the amount of acetone that would normally be present after a photolysis. This mixture was treated in the same way as a photolyzed sample, and the extinction coefficient at 5280 Å. was measured. The two experiments performed give extinction coefficients of 4.31 and 4.75 × 10^3.

In view of the difficulty experienced in preparing these known samples, the extinction coefficient obtained from the dimethylglyoxime solutions (4.71 × 10^3) was used in the analyses for biacetyl among the photolysis products. The experiments with known samples indicated that the analysis was accurate to about 10% and the most probable error would be loss of biacetyl in the conversion to the oxime. The method was conveniently applicable to photolysis samples containing from 2 × 10^{-7} to 4 × 10^{-6} mole of biacetyl. The smallest amount of biacetyl which could be detected was about 5 × 10^{-8} mole.

Oximes of compounds with unconjugated carbonyl groups (such as acetone or acetaldehyde) do not form the colored complexes. Prill and Hammer state that certain homologs of biacetyl such as glyoxal, methylglyoxal and acetylpropionyl give intense red complexes. No such homologous products are expected in the photolysis of acetone.

Materials Used.—Baker and Adamson reagent grade acetone was dried over magnesium sulfate and distilled through a thirty-plate bubblecap column. The middle fraction with a boiling point range of less than 0.1° was taken. The acetone was placed in a storage bulb attached to the vacuum system and thoroughly degassed by repeated freezing at −196° under vacuum until the residual gas pressure was less than 10^{-5} mm.

Carbon dioxide (Pure Carbonic Company) was taken from the cylinder, condensed in a storage bulb at −196°,

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(10) C. A. Parker, *Proc. Roy. Soc.* (*London*), **220A**, 104 (1953).

(11) C. G. Halchord and C. A. Parker, *ibid.*, **235A**, 518 (1956).

(12) C. W. Porter and C. Iddings, This Journal, **48**, 40 (1926).

(13) C. E. Ransley, *The Analyst*, **72**, 504 (1947).

(14) E. A. Prill and B. W. Hammer, *Iowa State College J. Sci.*, **12**, 385 (1938).

and degassed by a procedure similar to that used for acetone. Anhydrous ammonia (Dow) was similarly treated. The purity of the carbon dioxide and ammonia was confirmed with the mass spectrometer.

The stopcocks were greased with "Apiezon T" throughout the vacuum system. In the micro-gas analysis system, mercury float valves were used exclusively.

Experimental Results

The products detected after the photolysis of acetone at high intensity were ethane, carbon monoxide, biacetyl and small amounts of hydrogen and methane. In the products of a photolysis of acetone at a pressure of 50 mm. the mass spectrometric analysis suggested the presence of a trace of acetaldehyde (corresponding to a quantum yield of 0.004) but the identification was not positive. Ketene was not found under sensitivity conditions which indicate the quantum yield of ketene is below 0.0004.

The effects of acetone pressure, added inert gas (CO_2 or NH_3), intensity, duration of discharge, and size of reaction vessel, have been studied. The data presented in Tables I–III refer to the experimental conditions $T = 26 \pm 3°$, $\lambda = 2800$ Å., and $\bar{I}_0 = 10^{22}$ quanta/sec./liter. These data show that increase of pressure invariably decreases the quantum yields of ethane and biacetyl, that of biacetyl approaching zero at high pressures. Figure 1 shows the qualitative similarity of the effects of increasing pressure with acetone and with carbon dioxide. As the pressure is raised from 50 mm. of acetone, either by addition of acetone or carbon dioxide, $\Phi(CO)$ increases from a low value and seems to approach a value of about 0.20. Furthermore, the ratio $\Phi(C_2H_6)/\Phi(CO)$ approaches unity as the pressure is raised. While both $\Phi(CH_4)$ and $\Phi(H_2)$ increase at high inert gas pressures, they remain small relative to the other products.

TABLE I

EFFECT OF ACETONE PRESSURE ON THE QUANTUM YIELDS OF ACETONE PHOTOLYSIS PRODUCTS

Acetone pressure (mm.)	$\Phi(C_2H_6)$	$\Phi(CO)$	$\Phi(CH_3CO)_2$	$\Phi(C_2H_6)/\Phi(CO)$
50	0.32	0.074	0.20	4.3
50	.33	.079	.20	4.2
100	.30	.13	..	2.3
100	.29	.13	.14	2.2
150	.24	.15	.074	1.6
200	.24	.18	.040	1.3
200	.23	.17	.042	1.3
274	.21	.19	.028	1.1

TABLE II

EFFECT OF PRESSURE OF ADDED GASES ON THE QUANTUM YIELDS OF ACETONE PHOTOLYSIS PRODUCTS

Acetone press. (mm.)	Pressure added gas (mm.)	$\Phi(C_2H_6)$	$\Phi(CO)$	$\Phi(CH_3CO)_2$	$\Phi(C_2H_6)/\Phi(CO)$
		CO_2			
50	150	0.27	0.12	0.13	2.3
50	304	.26	.16	.099	1.6
50	411	.21	.16	.076	1.3
50	435	.26	.16	.058	1.6
50	454	.25	.20	.076	1.2
50	728	.20	.19	.028	1.05
		CO_2			
200	206	.20	.17	.034	1.15
200	407	.18	.17	.012	1.06
200	711	.17	.17	.007	0.97
200	1580	.15	.14	...	1.1
200	1595	.15	.17	.000	0.86
200	(414)[a]	.24	.17	.046	1.37
200	(1605)[a]	.23	.20	.028	1.14
		NH_3			
200	711	.10	.13	.0063	0.80
200	735	.11	.094	...	1.14
200	(790)[a]	.21	.17	.026	1.23

[a] Gas added *after* photolysis.

TABLE III

MASS SPECTROMETRIC ANALYSIS OF ACETONE PHOTOLYSIS PRODUCTS

Acetone pressure (mm.)	Pressure added gas (mm.)	Φ-$(C_2H_6)/\Phi(CO)$	Φ-$(CH_4)/\Phi(CO)$	$\Phi(H_2)/\Phi(CO)$	$\Phi(CH_4)$[a] (calcd.)	$\Phi(H_2)$[a] (calcd.)
50	0	4.81	0.098	0.048	0.0066	0.0032
50	0	..	.091	.011	.0061	.00074
200	0	1.29	.060	.015	.011	.0027
200	0	..	.044	.006	.0079	.0011
			CO_2			
200	1640	..	.14	.056	.021	.0083
200	1655	0.97	.16	.046	.024	.0069
			NH_3			
200	704	1.15	.37	.11	.035	.010

[a] $\Phi(CH_4)$ and $\Phi(H_2)$ were calculated from the quantum yields of ethane given in Tables I and II.

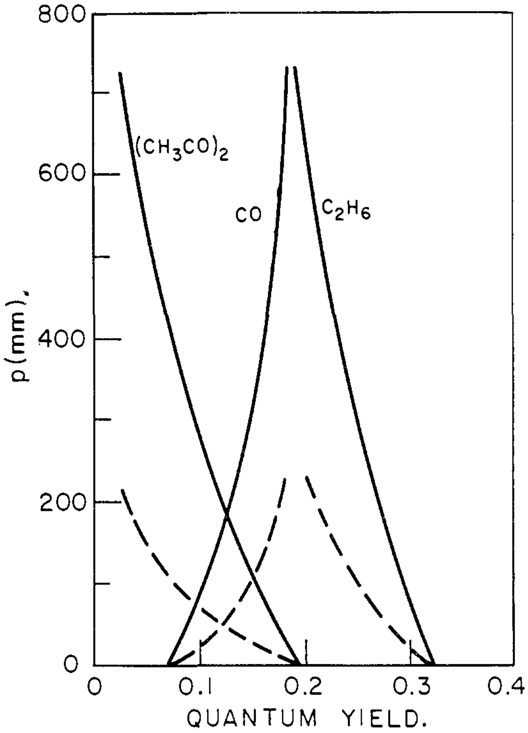

Fig. 1.—Effect of pressure on the quantum yields of the principal photolysis products: ———, acetone pressure = 50 mm., CO_2 added to partial pressure p; - - - - -, acetone only at pressure $p + 50$.

Table IV shows that neither the intensity nor the duration of the discharge affects the quantum yields. The ratio $\Phi(C_2H_6)/\Phi(CO)$ was unaffected by the eightfold decrease in intensity brought about by a potassium chromate filter solution. The duration of the discharge was lengthened by a factor of seventeen by placing 1.05 mh. inductance in the circuit, a change which reduced the intensity by a factor of twenty. Although the discharge became less reproducible, and the uncertainty is higher, there was no significant change of $\Phi(C_2H_6)$, $\Phi(CO)$, or Φ(biacetyl) at acetone pressures of either 50 or 200 mm.

TABLE IV

EFFECT OF INTENSITY AND DURATION OF DISCHARGE ON QUANTUM YIELDS OF ACETONE PHOTOLYSIS PRODUCTS

Acetone pressure (mm.)	Intensity absorbed[a]	Discharge duration (sec. × 10^4)	$\Phi(C_2H_6)$	$\Phi(CO)$	Φ-$(CH_3CO)_2$	$\frac{\Phi(C_2H_6)}{\Phi(CO)}$
50	1.3	1.4	0.32	0.074	0.20	4.3
50	.06	24	.30	.067	..	4.5
50	.06	24	.35	.073	.20	4.8
200	4.0	1.4	.23	.17	.04	1.3
200	.5	1.4	..	..	..	1.3
200	.2	24	.21	.16	..	1.3
200	.2	24	.19	.15	.04	1.3

[a] (Quanta/sec./liter) × 10^{-21}.

To investigate the importance of wall reactions the reaction vessel was changed from 20 to 6 mm. diameter and acetone was photolyzed at 200 mm. pressure. No change in the ratio $\Phi(C_2H_6)/\Phi(CO)$ was observed; quantum yields were not determined.

For the total observed products the mole ratios O/C, H/C and H/O, are listed in Table V. The first ratio, O/C, is consistently below the over-all stoichiometry of acetone, indicating a product with higher ratio of oxygen to carbon is being formed but not detected. Although the analysis for biacetyl is expected to be low, it does not seem likely that error in this analysis could account for all of the discrepancy.

TABLE V

MASS BALANCE OF ACETONE PHOTOLYSIS PRODUCTS

Acetone pressure (mm.)	Added gas	Pressure added gas (mm.)	O/C	H/C	H/O
50	..	0	0.31	2.1	6.7
200	..	0	.31	2.1	6.6
200	CO_2	1640	.32	2.1	6.6
200	NH_3	704	.26	2.4	9.4
Acetone mole ratios			.33	2.0	6.0

Discussion

The contrast of the earlier, low intensity photolyses with the present results is based upon the expectation that competition between a first and a second-order reaction can be eliminated by raising the light intensity. This expectation (which has been corroborated by studies with acetaldehyde[6,7]) together with the list of radical reactions proposed by Noyes, Porter and Jolley,[5] permits prediction of the results of high intensity photolysis. If all first order and wall reactions are eliminated, the mechanism of Noyes, *et al.*,[5] predicts that the principal products should be ethane, carbon monoxide and biacetyl with small amounts of methane, ketene and acetaldehyde. Furthermore, the product quantum yields should be independent of pressure and intensity and the quantum yield of carbon monoxide should be equal to a, the fraction of acetyl radicals which decompose due to excess energy carried over from the primary process. These predictions are *not* in agreement with the following results of the high intensity photolysis at 2800 Å.

(a) At low acetone pressure, the yield of carbon monoxide is low, approaching zero while the yields of ethane and biacetyl are high, exceeding, respectively, 0.32 and 0.20.

(b) At high acetone pressure the yield of biacetyl is low, approaching zero, while the yields of carbon monoxide and ethane approach 0.20 and become equal.

(c) Hydrogen and methane are formed in small amounts, the yields being increased by a high pressure of carbon dioxide.

The effect of pressure on the quantum yields of carbon monoxide and biacetyl is a facet of the photolysis of acetone that has not been appreciated.

A suitable mechanism is presented below.

The primary process is assumed to be

$$A + h\nu \longrightarrow A' \tag{1}$$

$$A' \longrightarrow CH_3 + COCH_3 \tag{2}$$

$$A' + A \longrightarrow 2CH_3 + CO + A \tag{3}$$

$$A' + A \longrightarrow 2A \tag{4}$$

The radicals thus produced recombine by

$$2CH_3 \longrightarrow C_2H_6 \tag{6}$$

$$2CH_3CO \longrightarrow (CH_3CO)_2 \tag{7}$$

$$2CH_3CO \longrightarrow CH_2CO + CH_3CHO \tag{8}$$

$$CH_3 + CH_3CO \longrightarrow CH_3COCH_3 \tag{9}$$

Step 1 is the excitation of an acetone molecule from the ground electronic state to an upper electronic state. The large yield of biacetyl at low pressure is strong evidence for step 2. The increase in the carbon monoxide yield as the pressure is increased requires that collisions play a role in its production. Dissociation from the upper electronic state induced by collisions as represented in process 3 seems the simplest explanation for this pressure dependence. Deactivation of excited acetone by collision shown in process 4 accounts for the decrease of the ethane quantum yield with pressure. The increased importance of reactions 3 and 4 at high pressures explains the decrease of the biacetyl yield to zero.

The conventional radical recombination reactions 6 through 9 account for the fate of the radicals produced in the primary process. The absence of ketene in the products is inconsistent with its observation in trace quantities (along with acetaldehyde) by Ausloos and Steacie.[15] On the other hand, the reactivity of ketene, particularly with respect to polymerization, probably explains our failure to detect it. The absence of acetaldehyde may be caused by analytical error since most of any acetaldehyde formed probably would be retained in the acetone fraction. Since the mass balances indicate loss of a product high in oxygen

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(15) P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1062 (1955).

and low in hydrogen relative to acetone, reaction 8 is proposed despite the lack of direct evidence of ketene and acetaldehyde.

The mechanism presented does not account for the observation of methane and hydrogen. Several possible sources of hydrogen must be considered: (a) another primary process; (b) reaction between two A′ molecules; (c) secondary absorption by A′; (d) photolysis by a small amount of short wave length radiation below 2000 Å.; (e) a trace impurity in the acetone; (f) photolysis of acetaldehyde produced by reaction 8. The last alternative, (f), can be eliminated because more hydrogen is formed at high pressures whereas the biacetyl formation, hence acetaldehyde formation, decreases at high pressures. There is no other evidence for the presence of a trace impurity, as suggested in (e). The photolysis by a small amount of high energy radiation, (d), seems unlikely. The absence of lines between 1800 and 2500 Å. in the spectrum of the Mg spark has been mentioned already. Furthermore, the ratio of the percentage transmission of the quartz reaction vessel at 2800 Å. to that at 1950 Å. was measured to be thirteen. The two reactions (b) and (c) are possible if A′ has a lifetime of the order of the duration of the flash, about 100 microseconds. An equally likely possibility is (a), another primary process such as reaction 5.

$$A' (+A) \longrightarrow CH_3COCH_2 + H (+A) \qquad (5)$$

If reaction 5 occurs, several recombination reactions must be considered.

$$CH_3 + CH_3COCH_2 \longrightarrow C_2H_5COCH_3 \qquad (10)$$
$$2CH_3COCH_2 \longrightarrow (CH_3COCH_2)_2 \qquad (11)$$
$$CH_3COCH_2 + H \longrightarrow CH_3COCH_3 \qquad (12)$$
$$CH_3CO + CH_3COCH_2 \longrightarrow CH_3COCH_2COCH_3 \qquad (13)$$
$$CH_3 + H + A \longrightarrow CH_4 + A \qquad (14)$$
$$2H + A \longrightarrow H_2 + A \qquad (15)$$
$$CH_3CO + H \longrightarrow CH_3CHO \qquad (16)$$

These reactions provide sources of both hydrogen and methane. Two alternate reactions which produce methane are given in the reaction scheme of Noyes, *et al.*[5]

$$CH_3 + CH_3COCH_3 = CH_4 + CH_2COCH_3 \qquad (17)$$
$$CH_3 + CH_3CO = CH_4 + CH_2CO \qquad (18)$$

These reactions are rejected for the following reasons: reaction 17, first order in radical concentration, cannot be important *both* at low intensity (as proposed by Noyes, *et al.*) and at high intensity; the reaction 17 has no apparent pressure dependence that would account for the greatly increased methane yield at high CO_2 pressure; the methane yield from reaction 18 should parallel the biacetyl yield and become very low at a pressure of 200 mm. acetone and even lower at high CO_2 pressure. Reactions 14 and 15 do provide reaction sources of H_2 and CH_4 in reactions for which three body collisions are undoubtedly important. Hence they do provide an explanation of the pressure dependence of $\Phi(H_2)$ and $\Phi(CH_4)$. A steady-state treatment[16] of the proposed primary process gives

$$\Phi(CO) = \frac{(A)}{k_2/k_3 + (k_3 + k_4)(A)/k_3} \qquad (19)$$

(A) = acetone pressure

The small amount of reaction 5 is ignored (although the form of (19) is not affected). By equation 19 the quantum yield of carbon monoxide will approach $k_3/(k_3 + k_4)$ at high acetone pressure. Figure 1 indicates that this quantum yield seems to approach a value of about 0.20. Since (19) can be rearranged to the form

$$\Phi(CO)/(A) = k_3/k_2 - (k_3 + k_4)\Phi(CO)/k_2$$

a straight line should be obtained when $\Phi CO/(A)$ is plotted against $\Phi(CO)$. The dashed line in Fig. 2 shows that a straight line can reasonably be drawn through the points in such a plot. This method gives a separate estimate of the high pressure limiting value of $\Phi(CO) = k_3/(k_3 + k_4)$, in this case the intercept of the dashed line at $\Phi(CO)/(A) = 0$. The dashed line has an intercept of 0.30 rather than 0.20. The solid line is the best straight line that can be drawn through the points with an intercept of 0.22. In Fig. 1 the data do not seem to permit a high pressure limiting value of $\Phi(CO)$ exceeding 0.22.

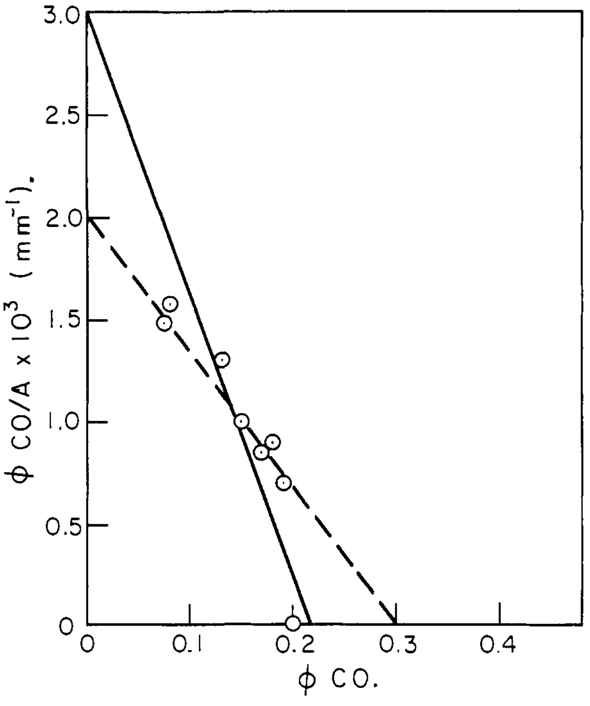

Fig. 2.—The quantum yield of CO as a function of $\Phi(CO)/(A)$; (A) = acetone pressure.

The applicability of equation 19 to the data is best checked by replotting as a function of acetone pressure the value of $\Phi(CO)$ predicted by the easily determined intercepts at $\Phi(CO) = 0$ in Fig. 2. Fig. 3 shows such plots for the intercepts determined by the two curves of Fig. 2 (dashed curve, $k_2/k_3 = 500$ mm.; solid curve, $k_2/k_3 = 333$ mm.). The solid curve in Fig. 3 misses most of the experimental points by more than the experimental uncertainty. While the dashed curve goes through

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[16] Evidence for the validity of a steady-state assumption is offered by the constancy of the quantum yields under a seventeen-fold increase in the duration of the discharge. While this behavior is not conclusive, it seems to offer reasonable justification for proceeding with interpretation on the basis of a steady-state assumption.

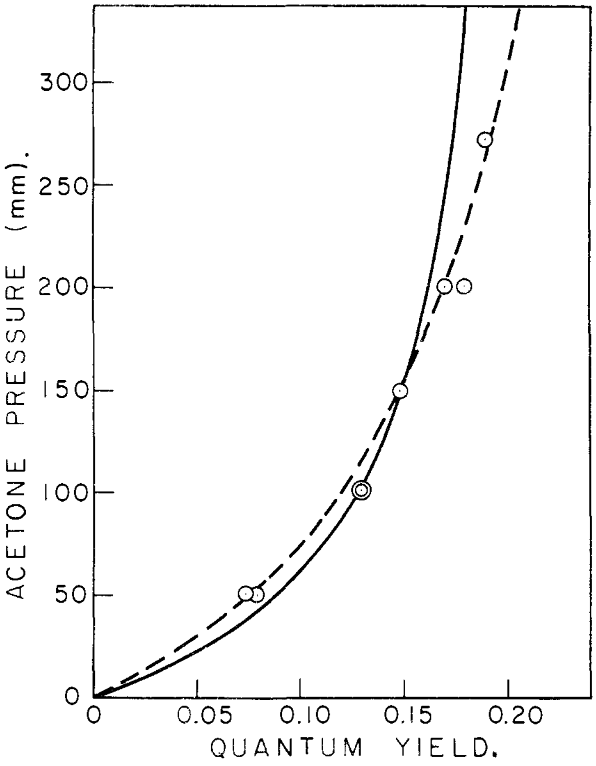

Fig. 3.—The quantum yield of CO as a function of acetone pressure: ———, equation 19 with $k_2/k_3 = 333$ mm., $(k_3 + k_4)/k_3 = 4.55$; - - - - - -, equation 19 with $k_2/k_3 = 500$ mm., $(k_3 + k_4)/k_3 = 3.33$.

all the points well within the experimental error, the asymptotic value of Φ(CO) at infinite acetone pressure is 0.30, much higher than the expected value, 0.20.

A possible explanation for these difficulties is found in a more complicated primary process than shown by reaction 3. It is possible that a second electronically excited state of acetone, A*, is produced from A′ by a collision and carbon monoxide is formed by the dissociation of A*. Equation 3 would then be replaced by a series of steps

$$A' + A \longrightarrow A^* + A \qquad (3a)$$

$$A^* \longrightarrow 2CH_3 + CO \qquad (3b)$$

$$A^* + A \longrightarrow 2A \qquad (3c)$$

The steady-state solution of the primary process would then give

$$\Phi(CO) = \frac{(A)}{a + b(A) + c(A)^2} \qquad (20)$$

where

$$a = k_2/k_{3a}$$
$$b = (k_{3a} + k_4)/k_{3a} + (k_2k_{3c})/(k_{3a}/k_{3b})$$
$$c = k_{3c}(k_{3a} + k_4)/(k_{3a}k_{3b})$$

Equation 20 predicts that the quantum yield of carbon monoxide will increase to a maximum as the acetone pressure increases and then decrease to zero at very high acetone pressure. If process 3b is fast compared to process 3c, equation 20 will approach equation 19 at low pressure. A plot of Φ(CO)/(A) *vs.* Φ(CO) should give a straight line at low acetone pressures but curve off at higher pressures.

In the presence of a foreign gas, M, the following reactions are added to the primary process

$$A' + M \longrightarrow 2CH_3 + CO + M \qquad (3')$$

$$A' + M \longrightarrow A + M \qquad (4')$$

Equation 19 then becomes

$$\Phi(CO) = \frac{(A) + k_{3'}(M)/k_3}{k_2/k_3 + (k_3 + k_4)(A)/k_3 + (k_{3'} + k_{4'})(M)/k_3}$$

At infinitely high foreign gas pressure

$$\lim_{(M) \longrightarrow \infty} \Phi(CO) = 1/(1 + k_4'/k_3')$$

The slight decrease in the carbon monoxide quantum yield observed in the photolysis of acetone at 200 mm. pressure in the presence of a large excess of carbon dioxide merely suggests that k_4'/k_3' is larger than k_4/k_3 or that deactivation of A* by the foreign gas occurs in a reaction analogous to (3c). The proposal of reactions 3a, 3b and 3c could be checked by determining Φ(CO) in the presence of a very large excess of an efficient quenching agent. Decrease of Φ(CO) to zero at very high pressure would require the inclusion of these reactions.

The results obtained by Khan, Norrish and Porter[6] in the flash photolysis of acetone are qualitatively in agreement with our conclusions. High carbon dioxide pressure should produce a small biacetyl to carbon monoxide ratio. Even though their ratio of less than 0.0005 is surprisingly small for the pressure of carbon dioxide that was present in their experiments, the polychromatic nature of the light used and the presence of an undeterminable temperature rise make their system extremely complicated.

Investigations of the photolysis of acetone using light of normal intensities have been made at other wave lengths, 3130 and 2500–2700 Å. In these investigations also, an increase of acetone or carbon dioxide pressure decreased the biacetyl quantum yield and increased the carbon monoxide yield.[17–20] This pressure effect was explained by assuming that biacetyl was formed on the walls. An increase of pressure should then decrease the quantum yield of biacetyl and increase the quantum yield of carbon monoxide by increasing the number of acetyl radicals that decompose thermally. Steacie and Darwent[21] have shown that wall coatings (Pb or KCl) do not influence the ratio of ethane to carbon monoxide in the acetone pressure range 50–100 mm. This result suggests that the walls are not important in biacetyl formation. The mechanism proposed in this paper does explain the effect of pressure on the quantum yields found in the low intensity work without invoking wall reactions. Despite the applicability of the present mechanism to both the high and low intensity results, further work using high intensity light at wave lengths other than 2800 Å. would be desirable. Furthermore, preliminary experiments

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suggest that an investigation of the effect of temperature on the primary process using high intensity light should provide additional information.

Hexafluoroacetone.—Ayscough and Steacie[22] recently have investigated the photolysis of hexafluoroacetone at 3130 Å. The only volatile products were hexafluoroethane and carbon monoxide in a ratio that varied from 1.00 at 27° to 0.90 at 300°. High ratios of fluoroform to hexafluoroethane were found when hexafluoroacetone was photolyzed in the presence of a hydrocarbon, proving CF_3 radicals were formed in the photolysis. The absence of tetrafluoromethane shows that trifluoromethyl radicals do not abstract a fluorine atom from the hexafluoroacetone even at 350°. Since the ratio of hexafluoroethane to carbon monoxide does not rise above one at any of the temperatures and pressures studied, and since perfluorobiacetyl is not a product, perfluoroacetyl radicals, if present, must decompose before they can take part in any other reaction. A straight line was obtained when $\Phi(CO)/(1 - \Phi(CO))$ was plotted against the reciprocal of the hexafluoroacetone pressure.

Because of the similarity between hexafluoroacetone and acetone, it is possible that the mechanism postulated here to explain the high intensity photolysis of acetone might also explain these results of Ayscough and Steacie. This mechanism, when applied to hexafluoroacetone, becomes

$$A + h\nu \longrightarrow A' \qquad (21)$$

$$A' \longrightarrow CF_3CO + CF_3 \qquad (22)$$

$$A' + A \longrightarrow 2CF_3 + CO + A \qquad (23)$$

$$A' + A \longrightarrow 2A \qquad (24)$$

$$2CF_3 \longrightarrow C_2F_6 \qquad (25)$$

$$CF_3CO \longrightarrow CF_3 + CO \qquad (26)$$

Here it is assumed that the perfluoroacetyl radical decomposes by reaction 26 before it can enter any other radical reactions. This is true of the acetyl radical above 100° in photolyses conducted at normal intensities and is expected to be true of the perfluoroacetyl radical at even lower temperatures.

A steady-state solution of the steps contained in this mechanism predicts the linear relationship observed by Ayscough and Steacie.

$$\Phi(CO)/(1 - \Phi(CO)) = k_{23}/k_{24} + k_{22}/k_{24}(A)$$

Hence the data are consistent with this mechanism.

Ayscough and Steacie give a mechanism that fits the data equally well. Their mechanism, however, is inapplicable to the photolysis of acetone at high intensity. This seems to be the only basis for preference of the mechanism 21–26.

Summary

The photolysis of acetone has been investigated with monochromatic light (2800 Å.) at absorbed intensities greater by about 10^6 than those normally used. The resulting predominance of reactions which are second order in radical concentrations has led to distinctly new information concerning the primary process of this much-studied reaction. Consideration of this information together with all of the earlier data leads to a mechanism which differs in several details from the previously accepted mechanism. This new set of reactions is also applicable to recent studies on the low intensity photolysis of hexafluoroacetone.

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[CONTRIBUTION FROM THE U. S. NAVAL ORDNANCE TEST STATION]

Photolysis and Pyrolysis of 2-Pentanone-1,1,1-3,3-d_5

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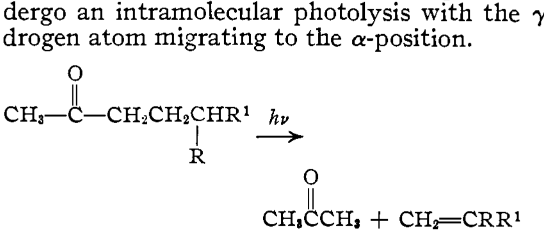
The photolysis of $CD_3COCD_2CH_2CH_3$ was studied over a range of temperatures from 35 to 300°. In addition, some pyrolysis was done at about 500°. In the low temperature photolysis range, the ethylene/acetone ratio was found to be sensitive to the flux density of the radiation. If a γ-hydrogen shift mechanism is postulated, all the acetone formed should be -d_5. However, there was more d_6-acetone than d_5-acetone in the products. The results have been interpreted in terms of an excited molecule mechanism. In the pyrolysis region, the reaction appears to follow a free radical mechanism.

Introduction

A considerable amount of research has been reported on the mechanism of the photolysis of methyl ketones.[1–4] Acetone and methyl ethyl ketone appear to proceed *via* free radical mechanisms. However, there is a considerable amount of evidence[1–4] that methyl *n*-propyl ketone and other methyl ketones which have a γ-hydrogen atom undergo an intramolecular photolysis with the γ-hydrogen atom migrating to the α-position.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_2\underset{\underset{\displaystyle R}{|}}{C}HR^1 \xrightarrow{h\nu} CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3 + CH_2{=}CRR^1 \qquad (1)$$

The reported quantum yields of olefin and acetone are clearly independent of temperature[3,4] which

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