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Photochemical Studies in Flash Photolysis. III. Photolysis of Acetone in Different Wavelength Regions*

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The flash photolysis of acetone was studied at wavelength regions centered around 260, 280, and 300 mμ, using absorbed intensities of the order of 10^{19} quanta/cc/sec for each wavelength region. The light source was an exploding wire, and the maximum temperature increase per flash was calculated to be not more than 5°C. The products, analyzed by gas chromatography using a sensitive electric discharge detector, consisted of C_2H_6, CO, biacetyl, and, in smaller amounts, CH_4. A search was made for other products as well, and detection limits are given.

The C_2H_6/CO ratio decreased with increasing acetone pressure at all wavelength regions and was independent of light intensity in the range investigated. The R_{CO}/p_{acet} ratio, measured over a wide pressure range, was pressure-independent at 260 and 300 mμ but increased appreciably with pressure at 280 mμ. At low pressures, where the C_2H_6/CO ratio approached a limiting value, the ratio decreased with wavelength according to the order $280>260>300$ mμ.

The lifetime of the excited acetone molecules at the respective wavelengths was estimated, from a steady-state treatment, to be 0.6×10^{-9}, 1×10^{-9}, and 4×10^{-9} sec at 260, 280, and 300 mμ, assuming a collision deactivation efficiency of unity. At 300 mμ there was a marked difference in value of C_2H_6/CO at flash and low intensities: certain second-order reactions involving excited states appear to occur completely at the relatively high concentrations prevailing under flash conditions. The transition region of intensity effects is described in subsequent papers of this series.

INTRODUCTION

WHILE acetone photolysis has been the subject of extensive investigation at low intensities[1,2], only a few studies have been made at the extremely high intensities of flash photolysis[3–6] or of spark discharge.[7] Under flash conditions the data are freed from complications of first-order thermal reactions and diffusion

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[†] Alfred P. Sloan Fellow.

[1] Cf. review by E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1954.)

[2] Cf. review by W. A. Noyes, G. B. Porter, and J. E. Jolley, Chem. Rev. **56**, 49 (1956).

[3] M. A. Kahn, R. G. W. Norrish, and G. Porter, Proc. Roy. Soc. (London) **A219**, 312 (1953).

[4] G. K. Oster and R. A. Marcus, J. Chem. Phys. **27**, 472 (1957) (Part I).

[5] N. Slagg and R. A. Marcus, J. Chem. Phys. **34**, 1013 (1961) (Part II).

[6] G. Wettermark, Arkiv. Kemi **18**, 1 (1961).

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

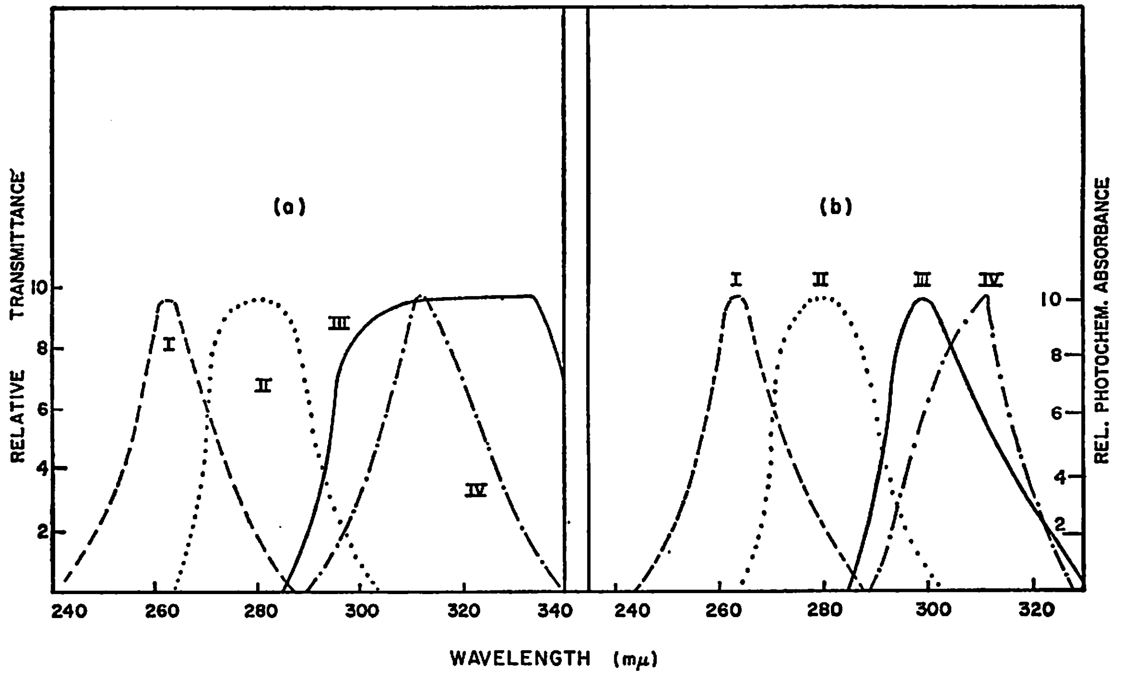

FIG. 1. Spectral characteristics of the filtered light at various wavelengths: (a) radiation transmitted by filters, (b) photochemically effective absorbance. Spectra were obtained by placing immediately in front of the spectrograph two quartz cells, each of 1 cm path length and having parallel optically flat faces. The first contained a $NiSO_4$–$CoSO_4$ solution (40 g of each in 100 cc water) and the second contained one of the following: (I) 1,4-diphenylbutadiene in alcohol (25 mg/liter), (II) CS_2 in CCl_4 (4.65 g/liter), (III) single layer of duPont cellophane 88-CA-48, (IV) K_2CrO_4 0.2*M*, KHPh 0.05*M*, NaOH 0.05*M* in water. Relative peak values in (a) are: (I) 0.75, (II) 0.94, (III) 0.66, (IV) 1.00, and in (b): (I) 0.71, (II) 1.00, (III) 0.57, (IV) 0.22.

to walls, though they are not without other problems. Unfortunately, most flash intensity studies of the acetone and of other systems have been made in a broad region of the spectrum. Moreover, the analysis for the photolysis products was not complete, except in one case,[6] where the radiation contained appreciable contributions from wavelengths below 200 mμ.

In the present studies, pressure and intensity effects were studied in four regions of the spectrum, namely, at wavelengths centered around 260, 280, 300, and 310 mμ. Since the results in the last two regions were somewhat similar to each other, only one of them, 300 mμ, was investigated extensively. The analysis for the photolysis products was performed with a gas chromatography unit specifically designed for that purpose.

EXPERIMENTAL

Apparatus

The apparatus consisted of three main units: (1) the vacuum system where samples were prepared for the photolysis experiments, for analysis and for the calibration of the gas-chromatography apparatus. (The reaction vessel consisted of a Vycor tube 3.0 cm o.d. and 16 cm long rounded at one end, after being reduced at the other end to 1 cm o.d. and attached to a joint through a graded seal. The total cell volume was 94 cc, of which 85 cc were illuminated.) (2) the flash apparatus previously described,[8] (3) the gas chromatography unit employing silica gel, molecular sieve 5A and P.E.G. columns, and a very sensitive electric discharge detector.[9] The molecular sieve required careful preconditioning (heating and passing gases through column) to attain marked improvement of sensitivity for CO.[9b]

Materials

Acetone (99 mole %, Fisher) was purified to remove traces of the possible photolysis products by first treating it with silver nitrate and sodium hydroxide solutions.[10] It was then dried over anhydrous magnesium sulfate and distilled *in vacuo* from −78° to −196°C. The middle fraction was stored at −78°C. The purification procedure for the rest of the materials was the same as in Part I.

Filters

The radiation which was emitted by the exploding nichrome wire consisted of numerous nickel and chromium lines and so was almost continuous throughout the absorption region of acetone. To isolate wavelength regions centered around 260, 280, 300, and 310 mμ, a solution of 1,4-diphenyl butadiene in ethanol,[6,11] one of CS_2 in CCl_4,[6] a single layer of 88-CA-48 du Pont

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[8] G. K. Oster and R. A. Marcus, J. Chem. Phys. **27**, 188 (1957).

[9] (a) R. C. Pitkethly, paper presented before the 132nd meeting of the American Chemical Society, New York, September 1957. The construction used in this paper is rather similar and is described in Ref. 9(b). (b) A. Shilman, Ph.D. thesis, Polytechnic Institute of Brooklyn, June 1961.

[10] A. Vogel, *Practical Organic Chemistry* (Longmans Green and Company, Ltd., London, 1954).

[11] M. Kasha, J. Opt. Soc. Am. **38**, 929 (1948).

TABLE I. Flash photolysis of acetone. Pressure effects at wavelengths near 260 mμ.[a]

Expt.	P_{acet} (mm)	No. of flashes	$CO\times10^{10}/P_{\text{acet}}$ (moles/flash/mm)	C_2H_6/CO	$(CH_3CO)_2/CO$	CH_4/CO
27	26.4	20	0.73	3.2	1.4(?)	0.25
28	74	8	0.62	3.3	2.1	...
...	100[b]	...	...	2.7	...	0.1_9
29	150	4	0.57	2.5	1.4	0.1_8
...	200[b]	...	...	1.9	...	0.10
30	242	4	0.77	1.8	...	0.05
33	200 +747 mm CO_2	4	(0.33)[c]	1.9	...	0.05

[a] *Acetaldehyde* was not present in the product above 2% of biacetyl yield in Expts. 27, 28, and 29. *Methyl ethyl ketone* was not present in the product above 50% and 100% of methane yield in Expts. 27 and 29 respectively, and not above 15% of CO yield at 74 mm. The wire was 3.25 cm from center of reaction vessel.

[b] Values at 100 and 200 mm taken from Ref. 5.

[c] Low value due to reduced intensity of flash. The degree of reduction in intensity was found to be 0.50 by using acetone vapor in unfiltered Vycor vessel as an actinometer.

Cellophane[5] and a solution of potassium chromate, potassium acid phthalate, and sodium hydroxide in water,[11] respectively, were used. Spectra of the light coming from the flash after passing through these filters were recorded on Kodak 33 plates using a medium quartz Hilger spectrograph. Tracings of these photographic plates were made with a Leeds and Northrup densitometer and are given in Fig. 1. These were multiplied by the absorption coefficients of acetone[12] to give a "photochemically effective absorbance" (Fig. 1).

Actinometry

The relative intensities of radiation were determined with a ferrioxalate actinometer[13] contained in a Vycor vessel identical with the reaction vessel.

Procedure

After the required amount of gas was admitted to the reaction vessel, it was detached, secured on the flash apparatus and surrounded by the filter contained in a 5-cm-i.d. Vycor jacket concentric with the 3-cm-o.d.

TABLE II. Flash photolysis of acetone. Pressure effects at wavelengths near 280 mμ.[a]

Expt.	P_{acet} (mm)	No. of flashes	$CO\times10^{10}/P_{\text{acet}}$ (moles/flash/mm)	C_2H_6/CO	$(CH_3CO)_2/CO$	CH_4/CO
21	4.1	28	1.05	5.3	4.9	0.18
20	9.0	20	1.18	5.9	...	0.18
23	25.4	8	1.37	5.3	4.0	...
22	50	4	1.70	4.6	3.2	0.15
25	75	2	1.87	3.5	...	...
24	75	8	1.86	3.5	2.3	0.15
12	100	4	2.17	2.2	1.2	...
26	201	4	2.20	1.4	0.4	0.15
31	243	4	2.70	1.4	0.4	0.07
32	200 +747 mm CO_2	4	(1.40)[b]	1.1	...	0.07

[a] *Acetaldehyde* was not present in the product above 2% of biacetyl yield in Expts. 12, 21–24, 26, and 31. *Methyl ethyl ketone* was not present in the product above 15%, 25%, 60%, and 100% of methane yield in Expts. 21, 24, 26, and 31 respectively, and not above 10% of CO yield in Expt. 23. The wire was 3.25 cm from center of reaction vessel.

[b] Low value due to reduced intensity of flash. The degree of reduction in intensity was found to be 0.50 by using acetone vapor in unfiltered Vycor vessel as an actinometer.

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

[13] C. A. Parker, Proc. Roy. Soc. (London) **A220**, 104 (1953); cf. **A235**, 518 (1956).

TABLE III. Flash photolysis of acetone. Pressure effects at wavelengths near 300 mμ.[a]

Expt.	P_{acet} (mm)	No. of flashes	$CO\times10^{10}/P_{acet}$ (moles/flash/mm)	C_2H_6/CO	$(CH_3CO)_2/CO$	CH_4/CO
19	3.6	28	2.7	1.9	0.8	···
14	9.7	20	3.0	1.8	0.8	0.1_3
18	16.4	12	2.8	1.5	0.5	0.1_4
15	23.3	8	2.9	1.2	0.2	0.1_3
17	26.7	8	2.9	1.1	···	0.09_6
16	48.8	4	2.8	1.2	···	0.1_5
11	101	4	2.9	1.1	···	0.2_4
P6[b]	52	4	0.56	1.1	···	···
P7[b]	51	4	0.61	1.2	···	···
P8[b]	50	1	4.6	1.1	···	···

[a] *Acetaldehyde* was not present in the product above 10% of biacetyl yield in Expts. 14, 15, 18, and 19, and not above 2% of CO yield in Expts. 11 and 17. *Methyl ethyl ketone* was not present in the product above 10%, 25%, and 30% of methane yield in Expts. 14, 17, and 11. Except in Expts. *P6* to *P8*, the wire was 3.25 cm from center of reaction vessel.

[b] In Expt. *P8*, the wire was 2 cm from the axis of the reaction vessel. In Expts. *P6* and *P7*, the wire was 8 cm distant and the vessel was surrounded both by the filter used on the other experiments of this Table and by a 8.3 cm i.d. Vycor cylinder containing $NiSO_4$–$CoSO_4$ solution (40 g of each in 100 cc water). The effective light path of the latter solution was 1.3 cm.

reaction vessel. A Nichrome wire, 18 cm long, was then placed parallel to the axis of the reaction vessel at the specified distance. The 33-μF bank of condensers of the flash apparatus was then charged to 8000 V and then discharged through the exploding wire to ground. After the required number of flashes the reaction vessel was attached to the vacuum system where 75% of its contents were transferred into a bulb by expansion, diluted with nitrogen to atmospheric pressure, and analyzed by gas chromatography.

A record of the light output vs time was obtained by placing a 935 RCA phototube some distance (1 m) from the exploding wire to minimize electrical effects and photographing the trace appearing on a calibrated oscilloscope. The trace is given in Fig. 2.[14]

RESULTS

CO, C_2H_6, CH_4, and, in many cases, biacetyl were the products measured. A search was also made for possible formation of CH_3CHO and $CH_3COC_2H_5$. The results obtained on pressure and light intensity effects in the various wavelength regions are described in Tables I–V and Figs. 3–6. The wavelength effects on the C_2H_6/CO ratio vs acetone pressure curve may be compared with the corresponding plot where only radiation below 220 mμ is removed (Fig. 6; results not tabulated).

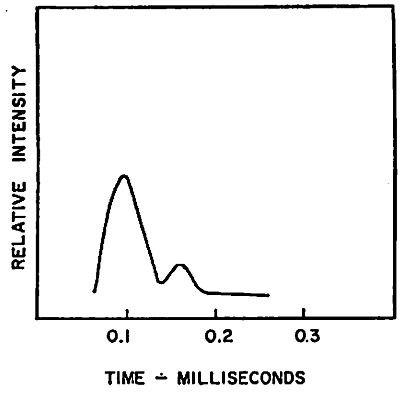

FIG. 2. Trace of flash.

SUMMARY OF RESULTS

A review of the results of acetone photolysis at different wavelengths, given in Tables I–V, Figs. 3–6, yields the following information:

(1) The only reaction products found were carbon monoxide, ethane, biacetyl, and methane. Within experimental error, the amount of biacetyl was equal to

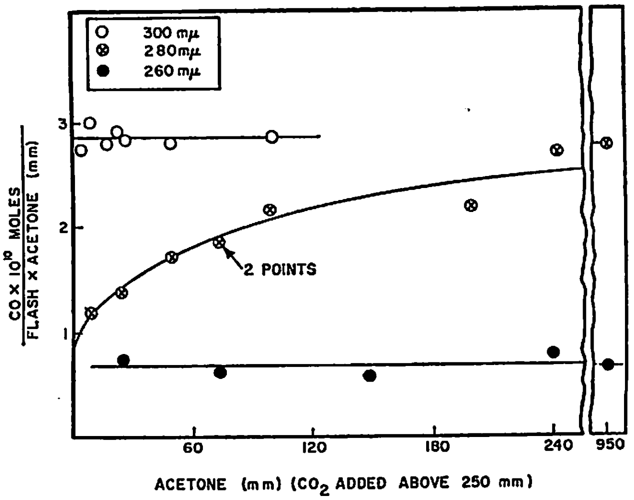

FIG. 3. Variation of CO yield with pressure at different wavelengths.

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[14] We are indebted to J. Knoll of this laboratory for Fig. 2.

TABLE IV. Flash photolysis of acetone. Pressure effects at wavelengths near 310 mμ.[a]

Expt.	P_{acet} (mm)	No. of flashes	CO×10^{10}/P_{acet} (moles/flash/mm)	C_2H_6/CO	$(CH_3CO)_2$/CO	CH_4/CO
38	15.6	24	1.07	1.4	0.4	0.14
37	50	8	1.10	1.1	···	0.15
*P*9[b]	50	10	0.22	1.1	···	···
*P*12[c]	51	7	0.23	1.1	···	···
*P*17[d]	51	40	0.028	1.1	···	···

[a] *Acetaldehyde* was not present in the product above 6% of biacetyl yield in Expt. 38 and not above 3% of CO yield in Expt. 37. *Methyl ethyl ketone* was not present above 20% of methane yield in Expt. 38 and not above 50% in Expt. 37. In Expts. 37 and 38, the wire was 3.25 cm from center of reaction vessel. In Expt. *P*9 it was 8 cm.

[b] The vessel containing the filter solution was surrounded by a 8.3 cm i.d. Vycor cylinder containing $NiSO_4$–$CoSO_4$ solution of same concentration and geometrical arrangement as in Table III for Expts. *P*6 and *P*7.

[c] duPont Cellophane 88-CA-48 was wrapped around a reaction vessel placed in a 5.3-cm-o.d. Pyrex cylinder, which in turn was surrounded by an 8.3-cm i.d. Vycor jacket containing $NiSO_4$–$CoSO_4$ solution of same concentration as in Expts. *P*6, *P*7, and *P*9. The effective light path through the solution was 1.5 cm. The distance of the wire from the reaction vessel was 8 cm. The photochemical absorption of the resulting system consisted of wavelengths near 305 mμ and half-width 20 mμ (width at half intensity).

[d] The reaction vessel was placed immediately behind a 2×15-cm plate, 3-mm Corning Glass 7-60, which was covered on the side exposed to the exploding wire by duPont Cellophane 215 P.D. The distance from the wire to the axis of the reaction vessel was 5 cm. The photochemical absorption of this system involved wavelengths near 323 mμ and halfwidth 10 mμ.

the amount of ethane less that of carbon monoxide (Tables I–IV).

(2) Methyl ethyl ketone was not found in amounts of more than 50% of a minor product, methane, at low pressures of acetone. At still lower pressures the corresponding figure is 10%–20%. (Tables I–IV).

(3) Acetaldehyde was not present in amounts of more than 10% of the amount of biacetyl. At lower pressures the corresponding figure is 5% (Tables I–IV).

(4) The quantum yield of carbon monoxide was not dependent on acetone pressure except at 280 mμ (Table II, Fig. 3), where it increased with increasing acetone pressure (Table II, Fig. 3).

(5) The C_2H_6/CO and biacetyl/CO ratios decreased with increasing acetone pressure at all wavelengths (Tables I–IV, Fig. 4).

(6) The C_2H_6/CO ratio at 260 mμ (Table I, Fig. 4) was not reduced to unity even at 1000 mm pressure of added carbon dioxide and acetone. At all other wavelengths this ratio did reduce to unity at higher pressures.

(7) The C_2H_6/CO ratio approached at low acetone pressures limiting values which decreased with wavelength according to the order 280>260>300 mμ (Fig. 4).

(8) The quantum yields of carbon monoxide, ethane and biacetyl (from mass balance) did not change when the incident light intensity was changed by a factor of 5 at all wavelengths (Table V).

(9) Methane was a minor product (Tables I–IV). The CH_4/CO ratios were essentially constant within the rather large experimental error of the methane analysis. The trend for these ratios, at higher pressures to increase at 300 mμ and to decrease at 260 and 280 mμ is uncertain due to insufficient data at these pressures.

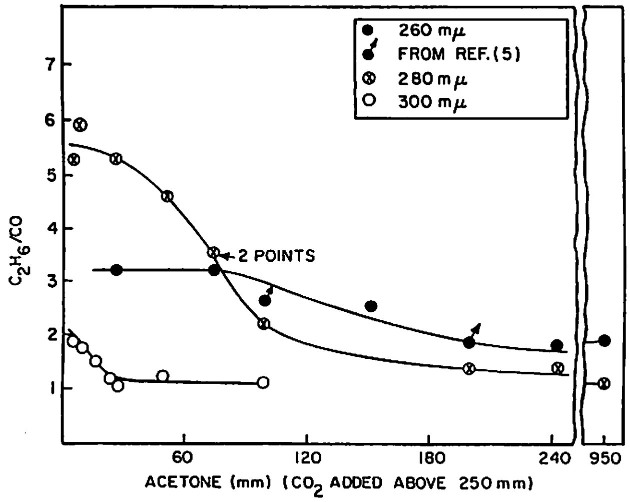

FIG. 4. Variation of C_2H_6/CO ratio with pressure at different wavelengths.

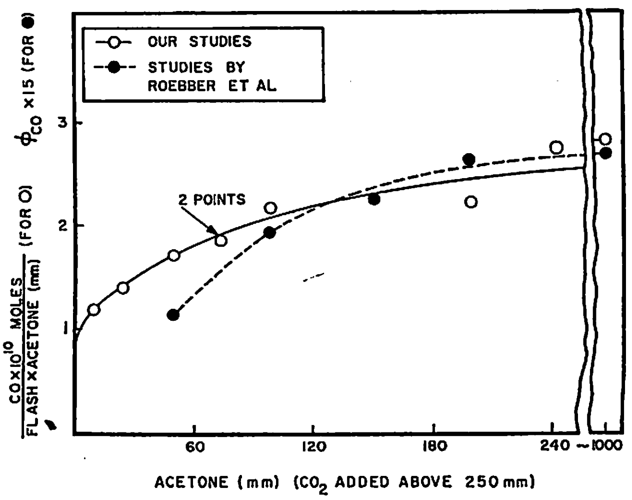

FIG. 5. Comparison of CO yield at 280 mμ with data of Roebber *et al.*[7]

TABLE V. Flash photolysis of acetone. Intensity effects at various wavelengths.

Expt.	Distance of wire (cm)	Relative[a] intensity	Wavelength (mμ)	CO$\times 10^{10}/P_{\text{acet}}$ (moles/flash/mm)	C_2H_6/CO	Relative ϕ_{CO}[b]
39	3.25		300	2.9	1.4	
40	16.3	0.17	300	0.51	1.4	1.05
41	3.25		280	1.86	3.4	
42	16.3	0.18	280	0.36	3.5	1.02
44	3.25		260	0.65	2.5	
45	16.3	0.17	260	0.116	2.4	1.06

[a] Refers to amount of light absorbed at 16.3 cm relative to amount of light absorbed at 3.25 cm, determined actinometrically. At 300, 280, and 260 mμ, the acetone was 16, 75, and 150 mm, respectively, corresponding in each case to the critical pressure regions of Fig. 4.

[b] This column represents the CO quantum yield at 16.3 cm distance relative to CO quantum yield at 3.25 cm.

(10) The C_2H_6/CO and CH_4/CO ratios obtained at wavelengths centered around 310 mμ were similar to the corresponding ratios in the 300 mμ wavelength region (Tables III and IV).

(11) The C_2H_6/CO ratio at 300 mμ was much lower than that obtained at low (nonflash) light intensities, being 1.1 to 1.2 at 50 mm acetone instead of 1.7 [15] to 1.9,[16] and much lower than that obtained with very low flash intensities.[17] Detailed experiments were described in Part IV[17] where the flash intensity was lowered by as much as a factor of 10^4 and the transition region for change of value of C_2H_6/CO was located. Similar differences were not found at 260 mμ however, at the flash intensities equal to or less than those used in this paper.[18]

(12) The drop in C_2H_6/CO ratio at 300 mμ mentioned in No. 11 is due largely or entirely to a change in quantum yield of CO formation.[17,18]

(13) The independence of the carbon monoxide and ethane quantum yields of light intensity suggests that any temperature changes occurring during the flash were relatively small or, if appreciable, were without effect on the yield. Indeed, because of the low flash intensities used, as a result of using filters, the expected rise in temperature can be calculated to be less than 5°C.[19]

DISCUSSION OF CH_3CO AND CO FORMATION

Throughout the discussion we note that only second-order reactions of the radicals need be considered, except where the radicals are "hot," since the competitive processes which are first order in radical concentration are too slow (e.g., Part II). These competitive processes are primarily hydrogen-atom abstraction from acetone by methyls, unimolecular decay of acetyls, and diffusion to the walls of either.

Considering first the behavior at 300 mμ, where the C_2H_6/CO ratio is much less when high flash intensities are used, one interpretation of the above data is the following: (A denotes acetone, A_1 and A_2 being two different excited states).

$$A + h\nu \longrightarrow A_1^*, \qquad (1)$$

$$2\,A_1^* \longrightarrow 2\,CH_3 + CO + A, \qquad (2)$$

$$A_1^* \xrightarrow{\text{decay}} A, \qquad (3)$$

$$A + h\nu \longrightarrow A_2^*, \qquad (4)$$

$$A_2^* \longrightarrow CH_3CO + CH_3, \qquad (5)$$

$$M + A_2^* \longrightarrow M + A, \qquad (6)$$

$$A + h\nu \longrightarrow \qquad \longrightarrow 2\,CH_3 + CO, \qquad (7)$$

where "decay" in (3) means phosphorescence and

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[15] J. Heicklen and W. A. Noyes, Jr., J. Am. Chem. Soc. **81**, 3858 (1959). These authors used a BTH medium-pressure lamp with a Pyrex-$NiSO_4$-$CoSO_4$-Corning 9863 filter. The intensity was such that the CO production rate per unit illuminated volume was about 10^{-13} mole cc^{-1} sec^{-1}. The percent conversion of acetone to biacetyl was of the order of 0.01%, the importance of small conversions having been shown by these authors.

[16] In unpublished results we have used an AH 6 lamp with the same filter as that used in Ref. 15 and, in other experiments, with the filter used in the present paper (to make the absorbed light wavelength distribution approximate that of the flash photolysis system at 300 mμ). The intensity corresponded to a CO production rate per unit reaction volume of 10^{-12} mole cc^{-1} sec^{-1} and the percent conversion to biacetyl was of the order of 0.01%. The corresponding figures for the flash system in the experiments labeled *P* in Tables III and IV are: CO production = 10^{-6} mole/cc/sec and percent conversion of acetone actually illuminated = 0.01%.

[17] A. Shilman and R. A. Marcus, Bull. Soc. Chim. Belges **71**, 653 (1962).

[18] A. Shilman and R. A. Marcus (unpublished results, presented at the Photochemistry Symposium, Rochester, New York, 27–29 March 1963). Results are currently being obtained at 280 mμ.

[19] At 260 and 280 mμ at 50 mm pressure, ϕ_{CO} is 0.2[20] and 0.05,[7] respectively, and R_{CO} is 3×10^{-9} and 8.5×10^{-9} mole/flash, respectively. Using a C_v value of 16 cal/mole for acetone,[21] the temperature rise is computed to be less than 1°C at both wavelengths. At 300 mμ and 16 mm pressure, the incident radiation was determined by actinometry to be 5.1×10^{-5} einsteins. The molar extinction coefficient of acetone at 300 mμ is 7.03 liter/mole/cm.[12] Employing the above C_v the temperature rise is calculated to be 5°C. This value is a maximum due to the photochemical geometry, for refraction effects would cause the amount of light entering the liquid actinometer to exceed that entering acetone vapor in a similar vessel.

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

[21] R. E. Pennington and K. A. Kobe, J. Am. Chem. Soc. **79**, 305 (1957).

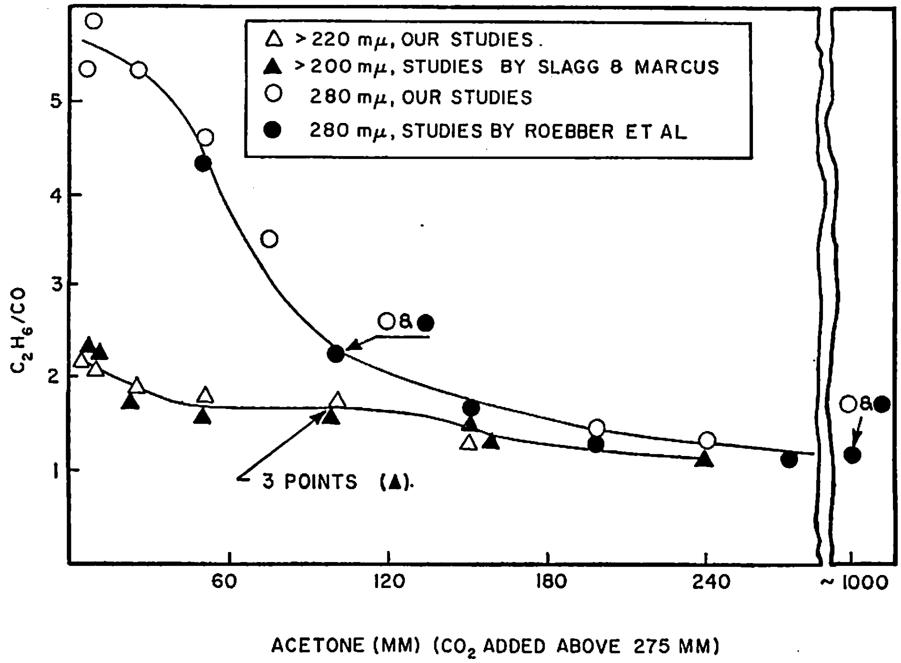

FIG. 6. Comparison of C_2H_6/CO ratios of different investigations.

internal conversion, and where the intermediate in (7) could be A_1^*, A_2^*, etc. (Projected experiments at low flash intensities should establish its nature). At high flash intensities at 300 mμ, however, (2) must swamp (7), according to the data.[22]

A major feature of the interpretation is that at *high* flash intensities (and conceivably at low), two *unconnected* mechanisms for CO and CH_3CO production at 300 mμ are introduced. The mechanisms were taken to be unconnected to explain two facts:

(i) $\phi_{(CH_3CO)_2}$ and the estimated[17] ϕ_{CH_3CO} appear to be essentially constant over an intensity variation of at least a factor of 10^2, but ϕ_{CO} is appreciably increased (by a factor of 4) from one limiting value at low flash intensities to another one at high flash intensities.[17,18]

(ii) At high flash intensities ϕ_{CO} is pressure independent but $\phi_{(CH_3CO)_2}$ is not.

The mechanism (1) to (7) is consistent with the fact that the quantum yields at high flash intensities are independent of intensity, that ϕ_{CO} is independent of acetone pressure, and that $\phi_{C_2H_6}$ decreases with pressure. Moreover, long-lived excited acetone molecules, with a lifetime of 2×10^{-4} sec, have been detected at 300 mμ,[23] and one may calculate that under the flash conditions used here Reaction (2) is at least a possibility.[24] Phosphorescence experiments by J. Knoll in this laboratory are now in progress at these flash intensities to see if, in fact, any correlation does exist between the quantum yields of CO production and phosphorescence. Evidence for a reaction similar to (2) has been obtained for excited biacetyl molecules under nonflash conditions.[25]

To explain the small residual ϕ_{CO} at 300 mμ, found at very low flash intensities,[18,26] Reaction (7) is postulated.

At 260 mμ, Fact No. 11 indicates that Reaction (2) does not occur at flash intensities equal to or less than those employed in this paper. Since the quantum yield of CO production at 260 mμ was pressure-independent but that of biacetyl was not (Facts 4 and 5), the formation of CO and CH_3CO appear to be unconnected, so we assume in Reaction (7) that the intermediate is not A_2^*. Perhaps it is A_1^*. At 260 mμ, part of biacetyl formation was not suppressed by increased pressure, although part was, suggesting that at this wavelength a portion of (5) occurs via a very short-lived molecule.

It has been suggested that a collision-induced dissociation occurs[7] at 280 mμ to form CO and we have no evidence against this postulate. Such a postulate offers one explanation for the increase of ϕ_{CO} with increasing acetone pressure.

In the mechanism (1) to (7) at 300 mμ we did not consider two alternative possibilities to Reaction (2): (i) $A_1^*+CH_3CO\rightarrow A+CH_3+CO$ and (ii) $A_1^*+h\nu\rightarrow 2CH_3+CO$. The first possibility is excluded by the

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[22] Although $\phi_{(CH_3CO)_2}$ was essentially constant in Refs. 17 and 18 over the wide intensity variation, ϕ_{CO} increased by a factor of 4.

[23] W. E. Kaskan and A. B. F. Duncan, J. Chem. Phys. 18, 427 (1950).

[24] At the highest flash intensity and at 50 mm acetone, the CO production which should be roughly one-half that of A_1^*, according to Reaction 2, was about 10^{-10} moles/cc/flash.[17] The transition region in C_2H_6/CO ratio occurred at an intensity about 50-fold less.[17] Thus, if the collision frequency of excited molecules was about 10^{15} cc/mole/sec, an A_1^* in that region would make about 4×10^3 collisions/sec with another A_1^*. If the A_1^* had a natural decay rate constant given by the observed lifetime of the phosphorescent species, 2×10^{-4} sec, namely 3.5×10^3 sec,$^{-1}$ these two competitive fates for A_1^* would be of the same order magnitude in the transition region, assuming the above collision frequency.

[25] W. A. Noyes, Jr., W. A. Mulac and M. S. Matheson, J. Chem. Phys. 36, 880 (1962) and references cited.

[26] It may be noted that E. O'Neal and S. W. Benson found negligible CO when acetone was photolyzed in the presence of HI, with steady illumination at 313 mμ and 126°C. [J. Chem. Phys. 36, 2196 (1962)]. In Ref. 18 the data at low flash intensities (no HI added) showed small but not negligible CO. It is not yet known whether the difference of these two results arises from the different conditions or from possible deactivation of the pertinent A* by HI.

need for making the CO and CH_3CO productions independent. The second possibility is very unlikely since the maximum pressure of A_1^* in the C_2H_6/CO transition region can be estimated to be about 5×10^{-4} mm at 50-mm acetone (cf. Ref. 24). Thus, the extinction coefficient of A_1^* would have to be unusually large for a comparable decomposition to occur.

Other Aspects

If a steady-state treatment were assumed (not a strictly accurate assumption under these flash conditions but presumably sufficient for our purposes), the pressure effects in Fig. 4 indicate values for the lifetimes of the excited state A_2^* of 0.6×10^{-9}, 1×10^{-9}, and 4×10^{-9} sec at 260, 280 and 300 mμ, respectively, assuming a frequency of successful deactivating collisions of 10^{14} cc mole^{-1} sec^{-1} in Stern–Volmer plots [Figs. 14 and 15 of Ref. 9(b)].

The absence of acetaldehyde relative to biacetyl shows that the disproportionation reaction, postulated in earlier flash work[7] at 280 mμ, $CH_3CO+CH_3CO\rightarrow CH_3CHO+CH_2CO$, is unimportant relative to the recombination to form biacetyl.

The CH_4 data are not sufficiently accurate to distinguish among mechanisms for CH_4 formation.

COMPARISON WITH PREVIOUS STUDIES

Our studies are in agreement with the flash photolysis studies in Part II made at high acetone pressures and in the same wavelength regions.

Roebber *et al.*[7] have flash photolyzed acetone using a monochromatic light source (Mg spark) at 280 mμ at intensities similar to ours. They found no significant changes in the quantum yield of CO, C_2H_6, and biacetyl when the light intensity was changed by a factor of 8, nor when the duration of the discharge was increased by a factor of 17 (from 0.14 to 2.4 msec). In our work, where the flash duration was 0.1 msec the quantum yields of CO and C_2H_6 were not changed when the incident light intensity was changed fivefold.

A comparison of the effects of acetone pressure observed by Roebber *et al.* (50 to 274 mm) on the CO quantum yield and on the C_2H_6/CO ratio at 280 mμ with those observed by us (4 to 243 mm) in the same wavelength region is given in Figs. 5 and 6. In their common range, the results of the two studies are very similar, with one exception, even though the light was monochromatic in Ref. 7 and contained a range of wavelengths in our case. The exception involves the low value of Ref. 7 for ϕ_{CO} at their lowest pressure (50 mm). Roebber *et al.* extrapolated the ϕ_{CO} plot to zero pressure, found the value zero and assumed that CO arose only from collision induced dissociation. Their extrapolation leaned heavily on the 50-mm point and it would be desirable to extend their study to lower pressures.

Acetaldehyde, which was assumed, from mass balance considerations, to be present in the work of Ref. 7 to the extent of 10%–25% of biacetyl, was not found here in amounts greater than 2% (at 280 mμ) of the biacetyl yield.

In a recent study with the full spectrum of the flash which, as in Part I, showed major photochemical contributions from wavelengths below 200 mμ, Wettermark[6] made a very detailed analysis of the reaction products. He found hydrogen, methyl ethyl ketone and acetaldehyde in small amounts, in addition to the products found in this paper. Except at 280 mμ, where we took special pains in the analysis because of the work of Ref. 7, Wettermark's percent yields of acetaldehyde and methyl ethyl ketone were normally lower than our limits of detection.

Wettermark also made measurements[6] of the ethane quantum yield as a function of acetone pressure, in a system where the radiation below 270 mμ and above 380 mμ was eliminated by a filter. He found it to decrease with increasing acetone pressure in a way similar to our C_2H_6/(acetone) vs acetone pressure behavior at 280 mμ.

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