unilaterally

$$B^- + A^+B^- \rightleftarrows B^-A^+B^-$$

so that the resultant conductance equation has the form

$$\Lambda[C(K_2 + C)]^{1/2} = \Lambda_{01}(K_1K_2)^{1/2} + \Lambda_{03}\left(\frac{K_1}{K_2}\right)C^{1/2}$$

where K_1 and K_2 are the dissociation constants for ion pairs and the unilateral triple ions, respectively, and $\Lambda_{01}\Lambda_{03}$ have the conventional significance. The graph of $\Lambda[C(K_2 + C)]^{1/2}$–$C^{1/2}$ is predicted to be linear, from which the constants of the above equation are evaluated. For the HBr data, using a series of approximations, it was found that a linear plot was obtained only for values of $K_2 \leqslant 10^{-4}$ in the region up to 10^{-2} *m;* an unequivocal determination of K_2 and the constants in the above equation is not possible. The treatments of interactions in solutions based on coulombic forces only, thus, seem not adequate as an account of the conductances of the hydrogen halides in anhydrous CH_3CN. Additional effects, such as the molecular solute–solvent interactions, would account for deviations from the above theoretical treatments.

Empirical Conductance Equation.—The molar conductances of HCl and HBr have been found to fit an empirical equation of the form

$$\Lambda = A + B/\sqrt{m}$$

In view of the solute–solvent interactions possible in this system based on the ketoid acceptor properties of the ($C{\equiv}N$) group,[2,3] an analysis of the conductance data for HCl in non-aqueous solvents,[18] generally has been undertaken. Preliminary results show that for HCl in acetone and benzaldehyde and for HCl and HBr (as pyridine·HX) in pyridine, an equation of the above form adequately accounts for the conductance–concentration variation, just as in CH_3CN, *i.e.*, for systems where solvent–solute compound formation occurs. Further investigations on this point are in progress in this Laboratory.

On the basis of the interactions possible in the HX–CH_3CN solutions,[2,3] the ionic species CH_3CNH^+, X^-, HX_2^- and $CH_3C(X){=}NH_2^+$ undoubtedly all contribute to the electrical conductance of these solutions. It would appear that the HX_2^- and $CH_3C(X){=}NH_2^+$ species may be predominant in concentrated solutions.

Acknowledgments.—This work was made possible in part by financial support received from the U. S. Air Force, Air Research and Development Command, Office of Scientific Research, and the U. S. Atomic Energy Commission, Division of Research.

[18] G. J. Janz and S. S. Danyluk (unpublished work), R.P.I., 1958.

TROY, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Photolysis and Fluorescence of Acetone and Acetone–Biacetyl Mixtures[1]

BY JULIAN HEICKLEN[2] AND W. ALBERT NOYES, JR.

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The photolysis of acetone vapor has been redone at 3130 Å. to very low conversions and the fluorescence and photolysis of acetone–biacetyl mixtures have been studied. If biacetyl is present during the photolysis of acetone at 3130 Å., an energy transfer occurs between excited acetone molecules and biacetyl; the acetone photodecomposition and phosphorescence are diminished, and biacetyl phosphorescence is observed. Since biacetyl is a reaction product of acetone photolysis, the quantum yield of acetone decomposition decreases as the time of irradiation increases. The ratios of reaction products also change with time of irradiation. A detailed mechanism is presented for the primary process in acetone and for the energy transfer between acetone and biacetyl.

Introduction

Extensive studies have been made of the vapor-phase photodecomposition and fluorescence of acetone. Recently a comprehensive review of the primary process in simple ketones has been published.[3] In the photolysis of acetone at room temperature biacetyl is a product. Okabe[4] and others have shown that biacetyl complicates both the photochemistry and fluorescence of acetone. If acetone is excited by 3130 Å. radiation, the biacetyl fluoresces. Because of this energy transfer the previous interpretation may be incomplete.

Recently Roebber, Rollefson and Pimentel[5] have proposed two primary processes as follows: (1) a direct dissociation of excited molecules into methyl and acetyl radicals; (2) a collision induced dissociation into two methyl radicals and carbon monoxide. These alternative processes will be discussed in a later section of the present article.

The photolysis of acetone has been redone to very low conversions. Also the fluorescence and photolysis of acetone–biacetyl mixtures have been studied. This paper presents the results of these studies.

Experimental

Eastman spectroscopic grade acetone was used. The acetone was placed over Drierite for two days and distilled. The middle third was collected. Its mass spectrum showed no impurities. Eastman white-label biacetyl and diacetone alcohol were used. The purification of the biacetyl was the same as for acetone. The biacetyl used in the fluorescence studies was not dried, but it was fractionated. A

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[1] This research was supported in part by contract AF18(600) 1528 with the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command. Reproduction in whole or in part is permitted for any purpose by the United States Government. Further details may be obtained from the Ph.D. Thesis of J. Heicklen, University of Rochester, 1958.

[2] National Science Foundation Predoctoral Fellow 1954–1955.

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

[4] H. Okabe and W. A. Noyes, Jr., THIS JOURNAL, **79**, 801 (1957).

[5] J. L. Roebber, G. K. Rollefson and G. C. Pimentel, *ibid.*, **80**, 255 (1958).

vapor-phase chromatogram showed minor peaks, but the biacetyl was 98 to 99% pure. Each of the three materials was thoroughly degassed immediately before use.

If mixtures were to be illuminated, the appropriate compounds were transferred to bulbs of known volume. If the pressures in the bulbs were known and if the perfect gas law was obeyed, the amounts of the respective ketones could be computed. At room temperature and for biacetyl pressures below 50 mm. and acetone pressures below 150 mm., only slight deviations from the perfect gas laws were observed. This was verified in two ways: (1) weighed amounts of the material were expanded into a known volume and the pressures observed; (2) known volumes of the liquid were vaporized into a known volume, the amounts of material calculated from the specific gravity, and the pressures observed. The pressures of diacetone alcohol were only approximate. Both the acetone and either the biacetyl or the diacetone alcohol were frozen into a cold finger near the reaction cell. With a stirrer operating, the mixture was allowed to vaporize slowly.

The light source was a British Thompson–Houston 250-watt medium pressure, ME/D box-type lamp. The light was collimated and filtered by a Pyrex plate, a solution of nickel sulfate and cobalt sulfate, and a Corning 9863 filter. The resultant radiation is mainly the group of lines at 3130 Å.[6]

In the photolysis studies, the T-shaped quartz reaction cell was 125 mm. long and 37 mm. in diameter. Fluorescent light was observed through a window 28 mm. in diameter. In the fluorescence studies, the quartz reaction cell was 56 mm. long and 25 mm. in diameter. The fluorescence window was also 25 mm. in diameter.

The intensity of the transmitted light was measured periodically throughout a run by a RCA phototube connected to a Varian G-10 recorder. In several hours the intensity varied only a few per cent. Acetone absorption obeyed Beer's law. The absolute number of quanta absorbed was computed by comparison with acetone vapor at 124° as an actinometer.

Fluorescence was measured by a 1P21 photomultiplier tube connected to a RCA WV-84A Direct-Current Microammeter. Three filter combinations were used to select the wave length of fluorescence. One combination included an interference filter with peak transmission at 4313 Å. and with a transmission half-width of 30 Å. A Corning 3486 filter, 4 mm. thick, was used for wave lengths above 5000 Å. The third combination consisted of a 4-mm. thickness of Corning glass 4308, 2-mm. thickness of Corning glass 3060 and a 5-mm. thickness of Corning glass 5970. Transmission started at 3700 Å., rose to a maximum at about 4050 Å. and dropped to zero at 4200 Å.

In the photolysis runs, fluorescence through the Corning 3486 filter was measured periodically. During the run biacetyl was formed, and its emission increased with time. In this way biacetyl was determined. The method was calibrated by comparison with prepared mixtures of known biacetyl pressure. The analytical method was reproducible, was independent of acetone pressure but was temperature dependent. The accuracy was good to biacetyl pressures of about 20 μ. Above this pressure the readings were too insensitive to pressure change to be useful.

After photolysis the gaseous products were fractionated and measured in a McLeod Gauge-Toepler pump.[7] The fractionation occurred by cooling three traps, the last of which was a coil trap. The first trap was cooled in a Dry Ice–acetone mixture, the second in isopentane at its freezing temperature of −157°, and the coil trap was cooled in solid nitrogen at about −215°. The carbon monoxide and methane were collected and measured in the McLeod Gauge-Toepler pump and then passed into a furnace containing copper oxide. The solid nitrogen was removed from the third trap, and the ethane collected and measured. After the carbon monoxide was oxidized, the methane was separated from the carbon dioxide and measured. It was found that some of the methane was retained in the ethane fraction. For later runs the fractionation procedure was corrected by cooling the coil trap with liquid nitrogen instead of solid nitrogen.

Results

The results are shown in tables and figures. In all cases the incident radiation was 3130 Å. One run was done in which diacetone alcohol was photolyzed.

The temperature during a run remained constant to about ± 0.5°. The volume of the beam in the cell was 110 ml. The concentrations of radicals and long-lived excited molecules were probably fairly uniform throughout the cell cross-section.[8] The number of einsteins absorbed per ml. per second (I_a) was calculated from the cell volume. Since absorption amounted to a maximum of 10%, radical and excited molecule concentrations were nearly uniform along the length of the cell.

For early runs the methane values are low and the ethane values high, but the sum of the two is correct. Mass balance leads to

$$\Phi_B + \Phi_{CO} = \Phi_E + (^1/_2 \text{ to } 1)\Phi_{CH_4} \qquad (1)$$

The coefficient for Φ_{CH_4} depends on the method of methane formation and on the fate of the acetonyl radical. Methane values were much smaller than those of ethane, and this coefficient does not greatly affect the sum. For some runs only the sum of the ethane and methane yields are accurately known. Thus the mass balances for all runs are calculated with a coefficient of unity. For the runs in Table III, where the biacetyl cannot be measured directly, the biacetyl was calculated from equation 1 with a methane coefficient of unity.

Primary quantum yields were calculated by considering the acetyl radical. This radical may do five things

$$2CH_3CO = (CH_3CO)_2 \qquad (2)$$

$$CH_3CO + CH_3 = CH_3COCH_3 \qquad (3)$$

$$CH_3CO = CH_3 + CO \qquad (4)$$

$$CH_3 + CH_3CO = CH_4 + CH_2CO \qquad (5)$$

$$CH_3CO + CH_3CO = CH_3CHO + CH_2CO \qquad (6)^9$$

Reaction 6 is neglected in this discussion because it seems to be small compared to (2). Reaction 5 is small compared to (3) and is neglected.[9] The primary quantum yield is approximately

$$\phi = \Phi_{CO} + 2\Phi_B + k_3(CH_3CO)(CH_3)/I_a \qquad (7)$$

where Φ_B is the quantum yield of biacetyl formation. The methyl radical concentration is estimated as $(\Phi_E I_a/k_8)^{1/2}$ from the reaction

$$2CH_3(+A) = C_2H_6(+A) \qquad (8)$$

where Φ_E is the quantum yield of ethane formation. From reaction 2 the acetyl concentration is $(\Phi_B \cdot I_a/k_2)^{1/2}$. The best value for the ratio of rate constants $k_3/k_2^{1/2}k_8^{1/2}$ is 1.65.[10] Thus the primary quantum yield is estimated as

$$\phi = \Phi_{CO} + 2\Phi_B + 1.65\Phi_B^{1/2}\Phi_E^{1/2} \qquad (9)$$

The fluorescence efficiencies are computed by subtracting the reading with the cell empty from the reading with the vapor present and dividing this difference by I_a. Fluorescence yields are in arbitrary units. Comparisons between two different wave lengths of fluorescence may not be valid.

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(6) M. Kasha, *J. Opt. Soc. Am.*, **38**, 929 (1948).

(7) A. N. Strachan and W. A. Noyes, Jr., THIS JOURNAL, **76**, 3258 (1954).

(8) A. J. C. Nicholson, *ibid.*, **73**, 3981 (1951).

(9) P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 47 (1955).

(10) M. H. J. Wijnen, *J. Chem. Phys.*, **27**, 710 (1957); **28**, 271 (1958).

TABLE I

EFFECT OF CONVERSION ON PRIMARY QUANTUM YIELD

T = 40°, acetone pressure = 50.8 ± 0.9 mm., wave length = 3130 Å.

Einsteins absorbed (total at 3130 Å.)	2.6 × 10^{-7}	4.9	6.6	11.4	22	32	73
Primary quantum yield (eq. 9)	0.74	0.63	0.59	0.55	0.34	0.31	0.33
Φ_{CO}	0.16	0.16	0.16	0.15	0.11	0.15	0.10

TABLE II

PRIMARY QUANTUM YIELD WITH ADDED BIACETYL

T = 40°, acetone pressure = 51 ± 2 mm., einsteins absorbed (approx.) = 7.2 × 10^{-7}, wave length = 3130 Å.

Initial biacetyl pressure (mm. × 10^3)	0.0	3.9	10.0	16.0	82	167	530
Φ_{CO}	0.16	0.13	0.12	0.10	0.064	0.059	0.055
ϕ (eq. 9)	0.59	0.47	0.45	0.37	0.21[a]	0.18[a]	0.21[a]
C_2H_6/CO	1.7	1.5	1.5	1.5	1.4	1.4	1.3

[a] Since Φ_B could not be determined when the added amount of biacetyl is large, it is calculated by equation 1.

TABLE III

PHOTOLYSIS OF ACETONE VAPOR TO SMALL CONVERSIONS IN THE PRESENCE OF BIACETYL

Incident wave length, 3130 Å.; cell volume, 145 ml.; cell plus stirrer volume, 325 ml.; illuminated volume, 110 ml.

Acetone press., mm.	30.0	77.0	30.2	77.5	35.3	74.5	30.5	75.5
Initial biacetyl press., μ	126	323	128	328	108	228	119	295
Cell temp., °C.	40	40	50	50	60	60	70	70
Time of run, sec.	2700	1200	2700	1200	1800	900	1800	600
Einsteins absorbed × 10^9/sec.	0.126	0.31	0.136	0.34	0.156	0.34	0.150	0.37
$\Phi_{Biacetyl}$	.444	....	.026	.016	.022	.066	....	...
Φ_{CO}	.066	.062	.103	.079	.163	.137	.245	.194
Φ_{CH_4}	.017	....	.021	.018	.035	.030	.048	.050
$\Phi_{C_2H_6}$	.094	....	.108	.077	.150	.113	.180	.143
ϕ (Primary quantum yield)	.26	....	.24	.18	.30	.19	.24	.19

Some of the principal results may be summarized as follows.

(1) The primary quantum yield calculated by equation 9 decreases with increase in the total number of quanta absorbed. This is ascribed to the accumulation of biacetyl in the system. This point is illustrated by the results (P = 51 mm.) in Table I.

(2) During a given run the concentrations of biacetyl and ethane increase but the rates of formation decrease with time. It has been previously reported[11] that biacetyl tends to disappear from the gas phase during standing in the dark. This effect was very small in the present experiments. Possibly the condition of the walls affects the rate of polymerization of biacetyl.

(3) Addition of biacetyl to acetone lowers the primary quantum yield of the latter, but at relatively low biacetyl pressures a saturation effect is observed and the acetone primary quantum yield approaches a constant value. This point is illustrated in Table II.

Addition of biacetyl not only lowers the primary quantum yield but lowers the ratio C_2H_6/CO. The value of Φ_{CO} with a biacetyl pressure of about 0.5 mm. approaches that with added oxygen at 25°[12] and that at 0° in the absence of oxygen[13] both at 3130 Å., *i.e.*, about 0.04.

(4) The addition of diacetone alcohol at a pressure of about 0.3 mm. produced no effect greater than experimental error on the quantum yields. Since diacetone alcohol is one of the known products of the photolysis of acetone,[14] it was necessary to ascertain whether or not its presence would affect the results. The indications are that it does not.

(5) The data in Table III indicate that added biacetyl in the pressure range 0.1–0.3 mm. maintains the value of the primary quantum yield at a low level. If the mole fraction of the biacetyl is approximately constant, the primary quantum yield decreases with increase in pressure.

(6) Table IV gives a summary of quantum yields at low conversions (not over 0.3% and usually less than 0.1%).

The data for low conversions are necessarily less accurate than for high conversions, partly because the primary yield is very sensitive to the amount of biacetyl formed.

TABLE IV

QUANTUM YIELDS AT LOW CONVERSIONS

Cell volume = 145 ml., illuminated volume = 110 ml., wave length = 3130 Å.

Einsteins absorbed/sec. × 10^9	Time, sec.	Acetone pressure mm.	ΦCO	ϕ
		T = 40°		
.014	10800	10	0.12	0.41
.072	5400	30	.11	.52
.044	5400	52	.19	.54
.106	2400	51	.14	.72
.103	1200	75	.18	.66
		T = 50°		
0.044	3600	30	0.26	0.60
.072	2400	50	.32	.68
.111	1200	75	.31	.74
		T = 60°		
0.024	34320	10	0.25	0.52
.152	4050	50	.41	.70
		T = 70°		
0.016	7200	10	0.43	0.43
.104	5400	32	.54	.69
.162	12620	50	.61	.74
.036	36000	51	.52	.52
.117	1800	75	.61	.76

The following statements may be made about the data in Table IV. (a) At a given pressure the

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(11) R. E. Hunt and W. A. Noyes, Jr., THIS JOURNAL, **70**, 467 (1948).

(12) F. B. Marcotte, Ph.D. Thesis, University of Rochester, 1951.

(13) D. S. Herr and W. A. Noyes, Jr., THIS JOURNAL, **62**, 2052 (1940).

(14) G. Damon and F. Daniels, *ibid.*, **56**, 2370 (1933).

primary yield increases slowly with temperature although the scatter in the data tends to obscure the trend. (b) There is an apparent increase with pressure of primary quantum yield at low conversions, but since other factors such as the amount of biacetyl in the illuminated zone and possibly wall effects are not constant the real effect of pressure on the primary yield is difficult to treat quantitatively. All authors with larger conversions find the primary quantum yield at 3130 Å. to decrease with increase in pressure. (c) The carbon monoxide yield increases with temperature, but it changes little with pressure. These statements are in agreement with earlier work. (d) There is no marked effect of intensity on the yields, but scatter in the data would obscure a small trend. (7) Figure 1 shows the effect of added biacetyl on the fluorescence efficiency when observed at two different wave lengths: 4000 and 4313 Å. The exciting wave length was 3130 Å. At both 4000 and 4313 Å. the emission comes almost solely from acetone and virtually none from the biacetyl. The emissions approach a constant value at biacetyl pressures above about 0.5 mm. and the emission is the same as that with added oxygen. Hence at low biacetyl pressures the emission consists of both fluorescence and phosphorescence from the singlet and triplet states, respectively, while fluorescence from the singlet state is all that remains at high biacetyl pressures.

Discussion

The primary process in acetone has been visualized as follows[3]: (1) absorption produces molecules in an upper singlet state, the amount of vibrational energy being dependent on the wave length; (2) some molecules in the upper singlet state dissociate, possibly by passing over to a triplet state, and the remainder lose vibrational energy by collision; (3) molecules fluoresce from low vibration levels of the upper singlet state and phosphoresce from low vibration levels of the triplet state; (4) molecules in the triplet state may dissociate with an activation energy so that as the temperature is raised the primary quantum yield increases and the phosphorescence quantum yield decreases.

In acetone, as distinguished from biacetyl, it appears necessary to postulate two paths from the state initially formed by absorption to the low vibration levels of the triplet state

$$A + h\nu = A_n{}^1 \qquad (10)$$

$$A_n{}^1(+M) = A_m{}^3(+M) \qquad (11)$$

$$A_m{}^3 + M = A_0{}^3 + M \qquad (12)$$

$$A_n{}^1 + M = A_0{}^1 + M \qquad (13)$$

$$A_0{}^1 = A_0{}^3 \qquad (14)$$

where A is a normal acetone molecule, $A_n{}^1$ is a molecule in an upper vibration level of the excited singlet state, $A_m{}^3$ is a molecule in an upper vibration level of the triplet state and $A_0{}^1$ and $A_0{}^3$ are molecules in low vibration levels of the upper singlet and triplet states, respectively.

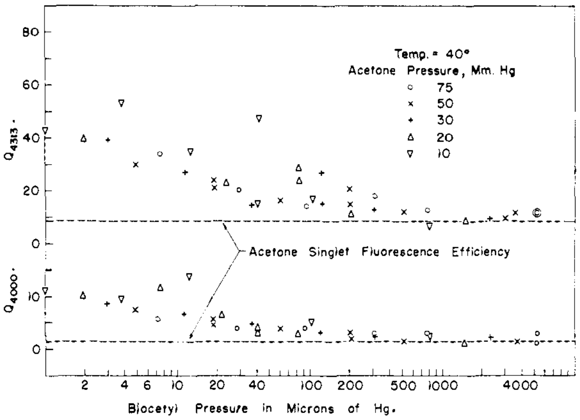

Fig. 1.—Emission efficiency of acetone *vs.* biacetyl pressure.

Roebber, Rollefson and Pimentel[5] suggest the primary processes

$$A' = CH_3 + COCH_3 \qquad (15)$$

$$A' + A = 2CH_3 + CO + A \qquad (16)$$

$$= 2A \qquad (17)$$

where A′ is the state formed by absorption of radiation. This mechanism does not quantitatively fit all of their data and these authors point out possible modifications which involve another upper electronic state.

It is not the purpose of the present article to discuss the details of acetone photolysis including possible reactions of radicals. The activation energy for acetyl dissociation to give $CH_3 + CO$ has been discussed recently by Calvert.[15] There is considerable uncertainty both about this activation energy and about the effect of pressure on the rate of dissociation of the acetyl radical. We will not consider, therefore, the detailed effect of pressure on the carbon monoxide yield.[16] It may be remarked in passing that Oster and Marcus[17] with a flash technique found virtually no effect of pressure on the carbon monoxide yield if short wave lengths were removed with a cellophane filter. They did report that the addition of biacetyl lowers the ratio C_2H_6/CO. This is confirmed in the present work. Under conditions of steady illumination most authors[13,18] find only a slight increase of Φ_{CO} with increase in pressure. In view of these facts the mechanism of Roebber, Rollefson and Pimentel[5] which demands a definite increase of Φ_{CO} with pressure may be questioned. The data of these authors show an increase in Φ_{CO} during flash photolysis in going from 50 to 100 mm. pressure, but the effect of higher pressures and of pressure of foreign gases seems to be no greater than experimental error.

Collision induced predissociation is a recognized phenomenon for diatomic molecules and must be presumed to occur, therefore, for polyatomic molecules. Positive proof of such a process may be difficult to obtain. Evidence that (15) and

[15] J. G. Calvert, *J. Phys. Chem.*, **61**, 1206 (1957).

[16] These effects will be discussed later by P. Ausloos on the basis of extensive data obtained at the University of Rochester.

[17] G. K. Oster and R. A. Marcus, *J. Chem. Phys.*, **27**, 472 (1957); *cf.* also R. A. Marcus, *Can. J. Chem.*, **36**, 102 (1958).

[18] D. E. Hoare, *Trans. Faraday Soc.*, **53**, 791 (1957).

(16) lead to different modes of dissociation is, however, not conclusive.

Two other effects must be considered with a flash technique.

(1) Kaskan and Duncan[19] have shown that there is a dependence of lifetime of acetone phosphorescence on intensity. One must conclude that active species are destroyed either by reactions with radicals or by reactions with each other. Too little is known about such reactions to predict either the rates or the nature of the products, but the possibilities of such reactions are so great in flash photolysis that care must be exercised in using results from flash photolysis to interpret results at low intensities.

(2) Radical–radical reactions predominate in flash photolysis as stated by Roebber, Rollefson and Pimentel[5] and hence biacetyl will be rapidly formed during the flash. Much of the reaction must be assumed to occur in the presence of biacetyl, and biacetyl not only lowers the primary quantum yield but lowers the ratio C_2H_6/CO. While it is not possible to offer a complete explanation of the results of Roebber, Rollefson and Pimentel, we believe they are compatible with the mechanism we present except possibly for the increase in Φ_{CO} in going from 50 to 100 mm. pressure of acetone.[20]

The primary process includes reactions 10–14 to which must be added the reactions which lead to dissociation

$$A_n^1 = D \qquad (18)$$

or

$$A_m^3 = D \qquad (19)$$

$$A_0^3(+A) = D(+A) \qquad (20)$$

where D represents dissociation products without specifying their nature. Because Φ_{CO} under otherwise identical conditions increases with increase in frequency of incident radiation, it was suggested[13] that some acetyls retain sufficient energy to dissociate rapidly. The addition of scavengers, particularly iodine[3] at 3 to 4 mm. pressure, nearly completely suppresses carbon monoxide formation so that there must be a delay in carbon monoxide formation after dissociation.

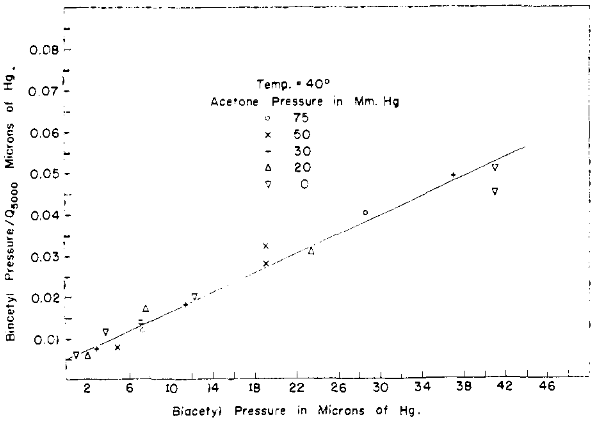

Fig. 2.—Biacetyl pressure/Q_{5000} *vs.* biacetyl pressure.

The complete picture of the primary process must include deactivation and internal conversion to the ground state since primary photochemical yields plus light emission yields do not add up to unity

$$A_0^3 + A = 2A \qquad (21)$$

$$A_0^3 = A \qquad (22)$$

By addition of biacetyl the triplet state is suppressed as indicated by the fact that the phosphorescence of biacetyl appears and the emission due to acetone decreases. Hence one must write[4]

$$A_0^3 + B = B_0^3 + A \qquad (23)$$

Possibly some energy is transferred from the upper singlet state of acetone to the biacetyl but such a transfer must be small. Herr, Matheson and Walters[21] have shown that up to 62° in mixtures of biacetyl-d_6 and acetone no biacetyl decomposition occurs at 3130 Å. The data on emission from acetone at 4000 and 4313 Å. in the presence of biacetyl show that only the singlet emission remains when the biacetyl pressure is a few hundred microns. This emission is the same as that observed when oxygen is added to destroy the triplet emission.

Thus at sufficient biacetyl pressures only the dissociation from the singlet state of acetone should be observed at low temperatures and this should follow the relationship

$$1/\phi_s = 1 + (k_{11} + k_{13})(M)/k_{18} \qquad (24)$$

where (M) is the concentration of acetone in the absence of foreign gases. The data in Table III show this relationship to be reasonably well obeyed and that ϕ_s is nearly independent of temperature as it should be. (ϕ_s is the yield from the singlet state only.)

We must now add the three light emission steps

$$A_0^1 = A + h\nu^1 \qquad (25)$$

$$A_0^3 = A + h\nu^3 \qquad (26)$$

$$B_0^3 = B + h\nu_B{}^3 \qquad (27)$$

At low biacetyl pressures the mechanism indicates that a plot of $(B)/Q_{5000}$ *vs.* (B) should be a straight line. (Q_{5000} is the efficiency of emission from biacetyl in the triplet state.) Figure 2 shows this relationship to be obeyed within the accuracy of the data. From Fig. 2 and the estimated lifetime of the acetone triplet state (2×10^{-4} sec.)[19], it is estimated that reaction 23 occurs about every 10 to 100 collisions.

The observation by Matheson and Zabor[22] that light emission due to biacetyl is observed when acetone is irradiated indicated that biacetyl should reduce the primary quantum yield in acetone. The data presented in this article show this to be the case at 3130 Å. The emission behavior of acetone at shorter wave lengths is discussed in an accompanying article.[23]

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(19) W. E. Kaskan and A. B. F. Duncan, *Trans. Faraday Soc.*, **18**, 427 (1950).

(20) The authors wish to thank Professor G. C. Pimentel for reading this manuscript and for making suggestions concerning it. This discussion of the work of Roebber, Rollefson and Pimentel has been included at his suggestion, although it should not be implied that he agrees with all that has been said.

(21) D. S. Herr, M. S. Matheson and W. D. Walters, THIS JOURNAL, **63**, 1464 (1941).

(22) M. S. Matheson and J. W. Zabor, *J. Chem. Phys.*, **7**, 536 (1939).

(23) J. Heicklen, THIS JOURNAL, **81**, 3863 (1959).

It has been recognized for many years that the photochemical behavior of acetone below 100° is much more complicated than it is at higher temperatures.[3] Part of the difficulty must be ascribed to the formation of biacetyl at low temperatures, a formation which does not occur to an appreciable extent at temperatures over 100°.

The effect of biacetyl in lowering the ratio C_2H_6/CO may be due to several causes: (1) the residual dissociation, presumably from the upper singlet state, when biacetyl is present (reactions 18 or 19) may be mainly into $2CH_3 + CO$ whereas the dissociation from low levels of the triplet state would be into $CH_3 + CH_3CO$; (2) biacetyl itself may undergo some dissociation after acquisition of energy by collision with excited acetone. Evidence against (2) is fairly conclusive[21] but (1) must be considered as a distinct possibility.

While the effect of pressure on the primary quantum yield at low conversions (Table IV) is subject to some uncertainty, an increase in yield with increase in pressure would have to be ascribed to the fact that triplet acetone molecules dissociate by a second-order process. That such a process proceeds probably with a low activation energy is shown both by the phosphorescence and the photochemical data.[3] Failure to observe an increase in primary yield with increase in pressure under ordinary experimental conditions would be due to the effect of biacetyl in deactivating the triplet state. Such an effect would not be observed at high temperatures where biacetyl is not formed and the data show this to be the case.[13] The yield from the singlet state (ϕ_s) certainly decreases with increase in pressure, but at 3130 Å. it is a small fraction of the total primary yield even at 25°.

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The Fluorescence and Phosphorescence of Biacetyl Vapor and Acetone Vapor[1]

BY JULIAN HEICKLEN[2]

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The fluorescence and phosphorescence of biacetyl have been studied at 40° as a function of pressure and incident wave length from 4358 to 3020 Å. A mechanism is proposed which explains both the light emission and the photochemistry. With incident radiation of 3020 or 3130 Å. the absorption is into a second excited electronic state. This state is converted to the first excited singlet and triplet states, and the same emission is observed as with radiation of longer wave lengths. The light emission from acetone has been studied with incident radiation from 2800 to 3130 Å. The fluorescence efficiency is independent of pressure and nearly independent of exciting wave length. The phosphorescence increases markedly with wave length and with pressure at short wave lengths. With incident radiation of 3130 Å. and at 40°, the phosphorescence decreases slightly as the pressure increases. At 63° quenching is more pronounced.

Introduction

The fluorescence and phosphorescence of biacetyl and acetone have been studied extensively. Recently the results have been reviewed.[3] Since then Okabe[4] also has studied the light emission from biacetyl. The study has been extended to incident wave lengths of 3020, 3130 and 3340 Å.

Previous studies of light emission from acetone have been made mainly with incident radiation at 3130 Å. Since phosphorescence and fluorescence differ only slightly in wave length, it has hitherto been impossible to make the data as complete as for biacetyl. In the present article incident wave lengths down to 2800 Å. have been used and effects of pressure have been investigated. Now that more data are available similarities between acetone and biacetyl become more apparent than formerly.

Experimental

Eastman white-label biacetyl was used. Two light sources were used: a British Thompson–Houston 250 watt, medium pressure, mercury arc and a Hanovia type SH mercury arc. The desired wave length was selected by a Bausch and Lomb grating monochrometer with a focal length of 500 mm. The light then passed through a T-shaped quartz cell containing biacetyl vapor. The cell was 56 mm. long and 25 mm. in diameter. It had a fluorescence window 25 mm. in diameter.

The transmitted light was measured by an RCA 935 photocell connected to a Varian G-10 recorder. This reading was corrected for the photocell sensitivity by use of an RCA S-5 spectral sensitivity curve. The absorbed radiation was computed from Beer's law which was verified.

The emitted light passed through a Corning 3486 glass, which only transmits wave lengths above 5000 Å., to a 1P21 photomultiplier tube.

Biacetyl pressures were measured directly except for pressures below 5 mm. Here the biacetyl was passed into a 10 ml. bulb and the pressure measured, the measured pressure being greater than 10 mm. The biacetyl in the bulb was then transferred quantitatively to the quartz cell and the pressure obtained from the perfect gas law.

The procedure for acetone was the same as for biacetyl. The light source was a Hanovia Type SH mercury arc. The emitted radiation passed through a Corning 7380 glass and all radiation above 3500 Å. was measured.

Results

(a) **Biacetyl.**—The emission data for biacetyl are shown in Table I.

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