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°.

Acknowledgment.—The authors extend their thanks to Dr. David Dutton, who suggested the electronic circuit for fluorescence measurements. Also they wish to thank Dr. P. Ausloos for many helpful discussions.

ROCHESTER, NEW YORK

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

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

BY JULIAN HEICKLEN[2]

RECEIVED SEPTEMBER 27, 1958

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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[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.

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[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).

TABLE I

LIGHT EMISSION FROM BIACETYL VAPOR $T = 40°$

Biacetyl pressure, mm.	Emission yield	Emission / Emission in presence of O_2
	$\lambda = 4358$ Å.	
0.622	0.15	49
1.11	.15	40
5.5	.15	39
7.8	.15	33
14.0	.16	32
19.0	.16	33
28.0	.16	34
35.2	.15	35
43.0	.14	39
45.0	.14	38
60.0	.13	..
64.0	.14	37
	Av.	36.4
	$\lambda = 4047$ Å.	
0.622	0.14	27
1.11	.15	30
5.5	.16	37
7.8	.16	34
14.0	.16	46
19.0	.16	34
28.0	.16	35
35.2	.15	36
43.0	.15	41
45.0	.12	30
60.0	.15	..
64.0	.16	39
	Av.	35.4
	$\lambda = 3655$ Å.	
5.5	0.055	28
7.8	.076	40
14.0	.103	25
19.0	.12	36
28.0	.14	37
35.2	.13	40
45.0	.14	42
64.0	.12	40
	Av.	36.0
	$\lambda = 3340$ Å.	
65.0	0.062	19
	$\lambda = 3130$ Å.	
65.0	0.022	23
	$\lambda = 3020$ Å.	
65.0	0.008	31

The emission yields were obtained by dividing emission less that from the empty cell by radiation absorbed. The absolute values were based on an efficiency of 0.15 at 4358 Å. as determined by Almy and Gillette.[5] Efficiencies at 4358 and 4047 Å. are essentially independent of pressure, but at 3655 Å. they show some increase with pressure as previously observed.[6]

In agreement with earlier work[4] it is seen in the third column that at 4358, 4047 and 3655 Å. the ratio of emission without oxygen to that with oxygen present is independent of incident wave length. It should be remembered that in the present work only radiation at wave lengths greater than 5000 Å. was measured, thus excluding some of the fluorescence from the singlet state.

(b) **Acetone.**—Table II shows data on emission from acetone with several incident wave lengths from 2800 to 3130 Å. Emission too weak to measure precisely was also observed at 2650 and at 3340 Å. but not at 2537 Å. Relative emission efficiencies were obtained as for biacetyl and approximate absolute efficiencies were obtained by comparison with biacetyl excited at 3020 and 3130 Å.

TABLE II

THE EMISSION OF ACETONE VAPOR
EMISSION EFFICIENCIES × 100

Acetone pressure, mm.	2800 Å.	2890 Å.	2970 Å.	3020 Å.	3130 Å.
		$T = 40°$			
24.8	0.194	0.323	0.691	1.25	2.06
48.5	.273	.502	0.938	1.33	2.08
77	.386	.700	1.09	1.44	1.71
100	.543	.893	1.34	1.67	1.96
148	.665	1.07	1.48	1.62	1.94
203	.855	1.22	1.52	1.67	1.78
		$T = 40°$, oxygen present			
24.8	0.194	0.206	0.199	0.189	...
48.5	.159	.153	.180	.178	...
77	.155	.169	.182	...	0.203
100	.169	.194	.208	.210	.208
148	.169	.203	.187	.237	.213
203	.176	.206	.201	.219	.205
Av.	.170	.189	.193	.207	.207
		$T = 63°$			
30					1.55
55					1.48
113					1.31
170					1.16
217					1.26

The following facts emerge from Table II.

(1) Fluorescence yield (*i.e.*, the part remaining when oxygen is present) changes little with pressure and relatively little with wave length.

(2) Phosphorescence (*i.e.*, the total emission less the part remaining when oxygen is present) diminishes with decrease in wave length and except at 3130 Å. increases with pressure. Thus the behavior of acetone at wave lengths 2800 to 3020 Å. is analogous to that of biacetyl at 3650 Å. while behavior at 3130 Å. (and presumably at 3340 Å.) is similar to that of biacetyl at 4047 and 4358 Å. Details of the mechanism must, however, be different since the ratio of phosphorescence to fluorescence is not independent of pressure and wave length.

(3) Absolute emission yields are always low so that a very small fraction of the energy input reappears as radiation. The results in general agree with previous work except that the absolute emission yield is higher than previously given[7] and is probably more reliable.

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(5) G. M. Almy and P. R. Gillette, *J. Chem. Phys.*, **11**, 188 (1943).

(6) See W. A. Noyes, Jr., G. B. Porter and J. E. Jolley, *Chem. Revs.*, **56**, 49 (1956), for a review.

(7) G. W. Luckey and W. A. Noyes, Jr., *J. Chem. Phys.*, **19**, 227 (1951).

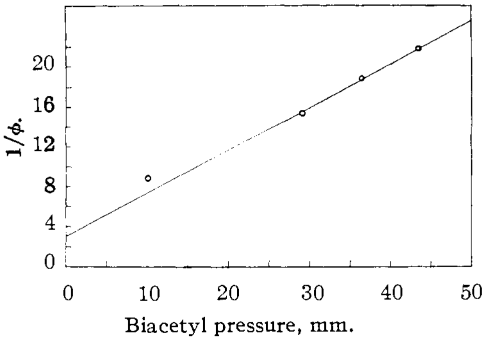

Fig. 1.—Plot of reciprocal primary quantum yield *versus* biacetyl pressure in mm. Temperature is 28°. Incident wave length is 3655 Å. Data taken from Sheats and Noyes.[6]

Discussion

To facilitate discussions of mechanism the various steps for biacetyl and for acetone will be given side by side and then justified later. (B = normal biacetyl molecule, B_n^1 = biacetyl molecule in upper vibration level of excited singlet state, B_0^1 = biacetyl molecule in low vibration level of upper singlet state, B_0^3 = biacetyl molecule in low vibration level of triplet state. A = normal acetone molecule, A_n^1 = acetone molecule in upper vibration level of excited singlet state, A_0^1 = acetone molecule in low vibration level of upper singlet state, A_m^3 = acetone molecule in upper vibration level of triplet state, A_0^3 = acetone molecule in low vibration level of triplet state.)

Biacetyl		Acetone	
$B + h\nu = B^{1n}$	(1B)	$A + h\nu = A^1_n$	(1A)
$B^1_n = D$	(2B)	$A_n^1 = A^3_m$	(2A)
$B^1_n = B$	(3B)	$A^3_m = D$	(3A)
		$A^3_m + A = A_0^3 + A$	(4A)
$B^1_n + B = B_0^1 + B$	(5B)	$A^1_n + A = A_0^1 + A$	(5A)
$B_0^1 = B + h\nu_B{}^1$	(6B)	$A_0^1 = A + h\nu_A{}^1$	(6A)
$B_0^1 = B_0^3$	(7B)		
$B_0^3 = B + h\nu_B{}^3$	(8B)	$A_0^3 = A + h\nu_A{}^3$	(8A)
$B_0^3 = B$	(9B)	$A_0^3 = A$	(9A)
$B_0^3(+B) = D(+B)$	(10B)	$A_0^3(+A) = D(+A)$	(10A)
$B_0^1 = B$	(11B)		

The following points of contrast between the mechanisms for acetone and biacetyl should be noted.

(1) Reaction 2B which leads to dissociation could be replaced by reactions similar to (2A) followed by (3A) with the exception that B_m^3 if formed must always dissociate and not ultimately give B_0^3. This is true because the ratio of phosphorescence to fluorescence in biacetyl is independent of exciting wave length[4] and this is not true (Table II) in acetone.

(2) Reaction 10B[8] has a much higher activation energy than (10A)[9] and its rate is negligible at temperatures below 70 to 80°.

(3) Internal conversion steps are (3B), (9B) and (11B) for biacetyl and (9A) for acetone. Of these the arguments in favor of (3B) and (11B) are not conclusive but their introduction seems to give a better fit to the data.

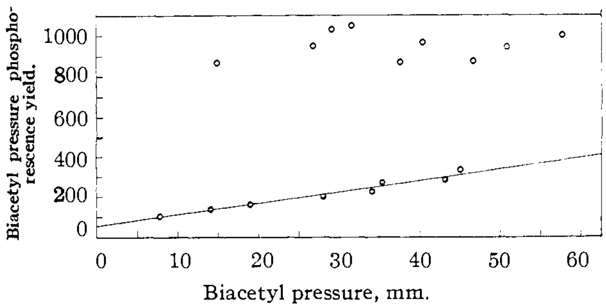

Fig. 2.—Plots of biacetyl pressure divided by the phosphorescence yield *versus* the biacetyl pressure. Biacetylpressure in mm. Temperature is 40°. For the upper points the incident radiation is 3340 Å. from BTH arc. For the lower points O, incident radiation is 3655 from Hanovia SH burner; for lower points X, incident radiation is 3655 from BTH arc.

(4) The steps leading to fluorescence, phosphorescence and dissociation are all demanded by the facts except that the effect of pressure on (10B) is somewhat doubtful.

The data on acetone are not susceptible to very quantitative kinetic treatment, largely because phosphorescence and fluorescence are so weak as to leave uncertainties in rate constants which would be derived. The mechanism fits both emission data and data on the photochemical primary quantum yield.[10]

If the probable assumption is made in biacetyl that methane is produced at 40° by

$$CH_3 + CH_3CO = CH_4 + CH_2CO \qquad (12)$$

rather than abstraction from biacetyl, the primary quantum yield can be calculated from the equation[8]

$$\phi = \Phi_{CO} - \Phi_{C_2H_6} + {}^1/_2\Phi_{CH_4} + \frac{(\Phi_{CO} - 2\Phi_{C_2H_6})^2}{K\Phi_{C_2H_6}} \qquad (13)$$

where K is $k_{14}{}^2/k_{15}k_{16}$ where k_{14}, k_{15} and k_{16} are, respectively, the rate constants for the reactions

$$CH_3 + CH_3CO = CH_3COCH_3 \qquad (14)$$

$$2CH_3 = C_2H_6 \qquad (15)$$

$$2CH_3CO = (CH_3CO)_2 \qquad (16)$$

Wijnen[11] recently has given 2.7 for K.

Figure 1 shows a plot of $1/\phi$ *vs.* biacetyl pressure (where ϕ is the primary quantum yield) at 28° and 3655 Å. The intercept is 3 and the ratio of slope to intercept is 2.7×10^3 liters per mole. The complete expression for the primary quantum yield is

$$\phi = \frac{k_{2B}}{k_{2B} + k_{3B} + k_{5B}\,(B)} + \frac{k_{10B}k_{7B}k_{5B}(B)}{(k_{10B} + k_{8B} + k_{9B})(k_{2B} + k_{3B} + k_{5B}(B))(k_{6B} + k_{7B} + k_{11B})} \qquad (17)$$

Hence $k_{3B}/k_{2B} = 2$ and $k_{5B}/(k_{2B} + k_{3B}) = 2.7 \times 10^3$ l./mole ($h_{10b} \simeq 0$ at 28°).

If one now turns to the phosphorescence, the assumption of the steady state leads to

$$\frac{(B)}{Q_3} = \frac{(k_{8B} + k_{9B})(k_{6B} + k_{7B} + k_{11B})(k_{2B} + k_{3B} + k_{5B}(B))}{k_{8B}k_{7B}k_{5B}} \qquad (18)$$

where Q_3 is the phosphorescence efficiency.

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(8) G. F. Sheats and W. A. Noyes, Jr., THIS JOURNAL, **77**, 1421, 4532 (1955).

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

(10) J. Heicklen and W. A. Noyes, Jr., THIS JOURNAL, **81**, 3858 (1959).

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

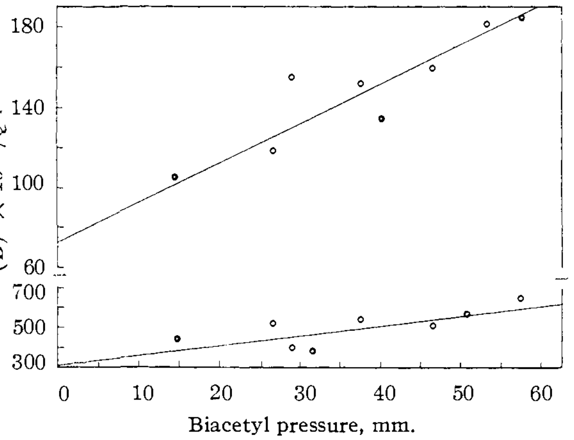

Fig. 3.—Plots of the biacetyl pressure squared times 10^{-3} divided by the phosphorescence yield *versus* the biacetyl pressure. Biacetyl pressure in mm. Temperature is 40°. Upper plot, incident radiation is 3130 Å. from BTH lamp; lower plot, 3020 Å. from BTH lamp.

Figure 2 shows plots of $(B)/Q_3$ *vs.* (B) at 3340 Å. and 3655 Å. The ratio of slope to intercept at 3655 Å. is 2.4×10^3 liters/mole, in satisfactory agreement with the value found in Fig. 1 cited in the previous paragraph.

The intercepts show that $(k_{2B} + k_{3B})$ is about 19 times as large at 3340 Å. as at 3655 Å. At 3655 Å. $(k_{2B} + k_{3B}) << k_5(B)$ at sufficiently high pressures and the data in Table I show phosphorescence yields to become about the same as at 4047 and 4358 Å. at the highest pressures studied.

At 3020 and 3130 Å., the values of $(B)/Q_3$ diminish with increase in pressure (not shown). Since these two wave lengths lie beyond a minimum in the absorption curve of biacetyl, there is every reason to believe that a second upper singlet state is produced. To account for the data in this part of the spectrum some steps must be added as

$$B + h\nu = B_n^{II} \qquad (19)$$

$$B_n^{II} = D \qquad (20)$$

$$B_n^{II} + B = B_0^{II} + B \qquad (21)$$

$$B_0^{II}\,(+B) = B_n^{I}(+B) \qquad (22)$$

where the superscript II refers to the second upper singlet state. By assumption of the steady state one derives the expression

$$\frac{(B)^2}{Q_3} = \frac{(k_{8B} + k_{9B})(k_{2B} + k_{3B})(k_{6B} + k_{7B} + k_{11B})(k_{20} + k_{21}(B))}{k_{6B}k_{7B}k_{8B}k_{21}}$$

Figure 3 shows plots of $(B)^2/Q_3$ *vs.* (B) which are straight lines within experimental error. This gives support to but not proof of the mechanism.

The wave length 3340 Å. lies just about at the minimum between two absorption regions. It is difficult to say which upper level is involved at this wave length. Possibly there are two overlapping absorptions.

Thus it is possible to give a reasonably complete picture of emission and photochemical behavior of biacetyl and within the limits of the data, which are less extensive and more difficult to obtain, also for acetone.

Acknowledgment.—The author wishes to extend his sincere thanks to Professor W. A. Noyes, Jr., for many helpful suggestions and criticisms.

ROCHESTER, NEW YORK

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

Radiolysis of CH_3COOCH_3 and CH_3COOCD_3 by Cobalt-60 γ-Rays[1]

BY P. AUSLOOS AND C. N. TRUMBORE

RECEIVED DECEMBER 2, 1958

Results of studies on the radiolysis of liquid and gaseous CH_3COOCH_3 and CH_3COOCD_3 by cobalt-60 γ-radiation are reported. Yields of the volatile radiation decomposition products have been studied as a function of temperature, dose and the presence of added radical scavengers. A comparison of the isotopic hydrogen, methane, ethane and dimethyl ether species present in these products provides information about possible primary processes, hot radical effects and radical disproportionation and recombination reactions within the liquid "cage." Recombination of methyl radicals originating from the same parent molecule as well as abstraction reactions between radicals in the same cage are postulated to explain the non-statistical yields of CH_3CD_3 and the high yields of CH_3D and CH_3OCD_3 in the liquid phase.

Introduction

The vapor and liquid phase γ-radiolysis of CH_3COOCD_3 has been investigated in connection with recent photolysis and radiolysis studies of esters and ketones carried out in this Laboratory.[2] It was expected that a study of the partially deuterated methyl acetate would give more precise information about radical recombination and disproportionation reactions occurring in the electron track, spur or solvent cage arising from absorption of high energy electromagnetic radiation.

Vapor phase experiments were carried out to obtain some information on possible ion–molecule processes and on the influence of the solvent cage.

Scavengers have been added in both the vapor and liquid phase in order to ascertain the importance of hot radical reactions as well as to separate cage effects from thermal processes.

The vapor phase photolysis of CH_3COOCD_3 recently has been investigated over a wide temperature range,[3,4] and some of the conclusions drawn

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[1] This research was in part supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18 (600) 1528. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] P. Ausloos and J. Paulson, THIS JOURNAL, **80**, 5117 (1958).

[3] M. H. J. Wijnen, *J. Chem. Phys.*, **28**, 271 (1958).

[4] M. H. J. Wijnen, *ibid.*, **28**, 939 (1958).