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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, ROCHESTER 20, N. Y.]

The Photochemistry of Mixtures of 2-Pentanone and 2-Hexanone with Biacetyl¹

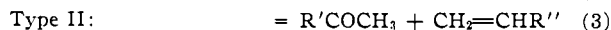
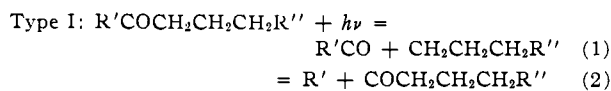
BY JUDITH LAKE MICHAEL AND W. ALBERT NOYES, JR.

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Energy transfer to biacetyl molecules occurs from 2-pentanone and from 2-hexanone molecules excited at 3130 Å. Evidence is found in sensitized biacetyl emission. The emission caused by pentanone is about twenty times as intense as that caused by hexanone. Biacetyl markedly reduces the non-free radical dissociation of 2-pentanone into ethylene and acetone at 3130 Å., but the yield of carbon monoxide increases although it is always low. The effect of biacetyl on the hexanone at 3130 Å. is negligible. Energy transfer to biacetyl and dissociation into ethylene and acetone both seem to come from the same state for the pentanone. There is a weak sensitized emission caused by 2-pentanone at 2537 Å. and a marked increase in carbon monoxide yield. For hexanone the effects are small, although there is some increase of carbon monoxide yield. The evidence indicates that the direct photochemical dissociation of 2-pentanone into ethylene and acetone occurs from an excited singlet state. Evidence herein presented is not sufficiently definite to permit conclusions about 2-hexanone.

Introduction

Ketones which have γ -hydrogen atoms in the alkyl groups attached to the carbonyl may undergo at least two and possibly more primary photochemical dissociations



The terms Type I and Type II seem first to have been used by Bamford and Norrish,² but the Type II process was first discovered by Norrish and Appleyard.³ Type II is a non-free radical reaction as proved by Norrish and his co-workers as well as by other investigators.⁴ It has been suggested that hydrogen bonding of the γ -carbon to the oxygen of the carbonyl might lead to a structure which could give acetone and an olefin in a single step.⁵ Evidence for this has been found⁶⁻⁸ as well as for the fact that this process occurs from a singlet state.⁹

Emission by 2-pentanone from an excited singlet state has been found,¹⁰ but emission from an excited triplet state is very small or zero. No emission from pure 2-hexanone has been reported. Nevertheless, there is sometimes evidence for appreciable concentrations of triplet state molecules even when emission from

such a state is not observed. The present study was undertaken to find evidence for triplet state molecules in 2-pentanone and in 2-hexanone when irradiated. Energy transfer problems related to the use of biacetyl to establish the existence of singlet and triplet state molecules proved to be interesting and are discussed.

Experimental

The 2-hexanone was from Matheson, Coleman and Bell or from K and K Laboratories. The results were the same in both cases. The 2-pentanone was from Matheson, Coleman and Bell. The ketones were distilled and a constant boiling middle fraction collected and stored over Drierite. This fraction was degassed at liquid nitrogen and at Dry Ice-acetone temperatures and a middle fraction retained from a bulb-to-bulb distillation. The purity of the samples was verified by mass spectra and by vapor phase chromatograms. Eastman Kodak Co. White Label biacetyl was introduced into the vacuum line, degassed, and purified by bulb-to-bulb distillation. A vapor phase chromatogram showed the sample to be better than 98% pure. Eastman Kodak Co. Spectro Grade acetone was purified as described above. No impurities were detected. *n*-Pentane (99.8% pure) and *n*-hexane (99.96% pure) from Phillips Petroleum Co. were used without further purification.

An Osram HBO super pressure mercury lamp operating at 76-82 volts and 6.8-7.2 d.c. amperes was used for 3130 Å. radiation. A Hanovia S-100 Alpine burner was used for wave lengths near 2537 Å. The light was collimated and stray radiation prevented from entering the cell by a series of shields. For 3130 Å. radiation a filter combination of cobalt sulfate-nickel sulfate solution¹¹ and a Corning 7740 filter was used. A filter combination of chlorine, cobalt sulfate-nickel sulfate solution and a Corning 9863 filter was used to give radiation of approximately 2537 Å.¹¹

A T-shaped quartz reaction cell, 11.5 cm. long, 5.0 cm. in diameter, with a fluorescence window of 2.5 cm. diameter was used.

The intensity of the transmitted light was measured periodically by a RCA 935 phototube connected to a Varian G-10 recorder. Quantum yields were calculated against the carbon monoxide yield from acetone at 125° at 3130 Å. and at 2537 Å. The carbon monoxide yield is unity under these conditions.¹² The intensity of the absorbed light was corrected at 2537 Å. for the light absorbed by biacetyl in the 2-pentanone-biacetyl and 2-hexanone-biacetyl mixtures. Absorption by biacetyl at 3130

(1) This work was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research under Contract AF 49(638)-679.

(2) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1504 (1935); 1531 (1938).

(3) R. G. W. Norrish and M. E. S. Appleyard, *ibid.*, 874 (1934).

(4) For a review see J. N. Pitts, *J. Chem. Educ.*, **34**, 112 (1957).

(5) W. D. Davis, Jr., and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **69**, 2676 (1947).

(6) P. Ausloos and E. Murad, *ibid.*, **80**, 5929 (1958).

(7) See R. Srinivasan, *ibid.*, **81**, 5061 (1959).

(8) P. Ausloos and R. E. Rebbert, *ibid.*, **83**, 4897 (1961).

(9) V. Brunet and W. A. Noyes, Jr., *Bull. soc. chim. France*, 121 (1958); V. Brunet, M.S. Thesis, University of Rochester, 1957; P. Borrell and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **A262**, 19 (1961).

(10) P. Ausloos and E. Murad, *J. Phys. Chem.*, **65**, 1519 (1961).

(11) M. Kasha, *J. Opt. Soc. Am.*, **36**, 929 (1948).

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

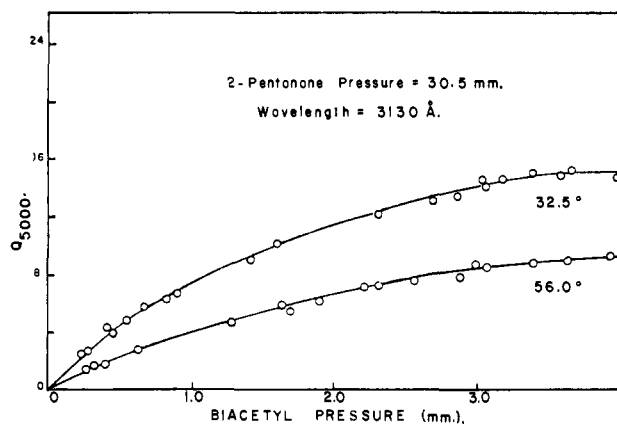


Fig. 1.—A plot of emission efficiency at wave lengths longer than 5000 Å., in arbitrary units, Q_{5000} vs. biacetyl pressure.

Å. was small. The relationship

$$\log (I_0/I_T(M)) = \log (I_0/I_T(B)) + \log (I_0/I_T(K)) \quad (4)$$

was tested for the two mixtures at constant ketone pressures at 2537 Å. where I_0 is the intensity of the light transmitted through the empty cell, $I_T(M)$ is the intensity of light transmitted through the cell filled with the ketone-biacetyl mixture, $I_T(B)$ is the intensity of the light transmitted through the cell filled with the pure biacetyl, and $I_T(K)$ is the intensity of light transmitted through the cell filled with pure ketone. Logarithms are to the base ten. This equation is valid only if loss at the windows is due to true absorption and none to reflection and if absorption by each type of molecule is not affected by the presence of the other type of molecule in the mixture. At low absorptions, reflection errors may be appreciable.¹³ Molar extinction coefficients were determined for 2-pentanone, for 2-hexanone and for mixtures of biacetyl with *n*-hexane and *n*-pentane. The relationship holds within 2% for the 2-pentanone-biacetyl mixtures but is not valid at high biacetyl pressures for the 2-hexanone-biacetyl mixtures. In this latter case, the intensity of the light absorbed by biacetyl was calculated in two ways, as

$$I_a(B) = \frac{(I_0 - I_T(M))}{V} \times \frac{\log (I_0/I_T(B))}{\log (I_0/I_T(M))} \quad (5)$$

$$I_a(B) = \frac{(I_0 - I_T(M))}{V} \times \frac{\log (I_0/I_T(M)) - \log (I_0/I_T(K))}{\log (I_0/I_T(M))} \quad (6)$$

where V is the volume of the cell. In this way, limiting intensity values were obtained.¹⁴

The light emitted passed through a Corning 3385 filter and was measured by a RCA 1P-21 photomultiplier tube connected to a RCA WV-84A direct current microammeter. The measured emission was of wave lengths greater than 5000 Å. The wave length distribution of the emitted light was determined by a Hilger quartz spectrograph with Eastman spectroscopic plates 103-D. The fluorescence was measured within 200 seconds after irradiation was begun.

A conventional vacuum line was used. The products of the photolysis of 2-pentanone (CO , CH_4 , C_2H_4 , C_2H_6 , C_3 + C_4 hydrocarbons, *n*- C_6H_{14} and CH_3COCH_3) were fractionated and measured in a McLeod gage-Toepler pump.¹⁵ Fractionation occurred by cooling three traps. The first two traps were cooled in liquid nitrogen and the third in solid nitrogen. The first trap was allowed to warm to room temperature after 20 minutes. After another 20 minutes, carbon monoxide and methane were collected and measured in the Toepler pump and then passed into a tube containing cupric oxide heated to 220°. After carbon monoxide was oxidized, methane was separated from carbon dioxide and measured. Liquid nitrogen was replaced by Dry Ice-acetone and the next two fractions, C_2H_4 - C_2H_6 and C_2H_6 - C_3H_8 -*n*- C_4H_{10} , were separated with a Ward still.¹⁶ The C_2 -fraction came off at approximately -170° and the C_3 + C_4 fraction at approximately -130°. The percentage of ethane in the C_2 -fraction from the photolysis at 2537 Å. was determined from the relative sensitivity of a Consolidated Electrodynamics Corporation mass spectrometer for ethane ($m/e = 30$)/ethylene ($m/e = 28$). The remaining products, principally acetone and 2-pentanone, were determined on a Perkin-Elmer vapor fractometer with a 2-meter column of dimethyl sulfolane carried on an

(13) R. E. Hunt and T. L. Hill, *J. Chem. Phys.*, **15**, 111 (1947).

(14) H. Ishikawa, Ph.D. Thesis, University of Rochester, 1962; H. Ishikawa and W. A. Noyes, Jr., *J. Chem. Phys.*, **37**, 583 (1962).

(15) A. N. Strachan and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **76**, 3258 (1954).

(16) D. J. LeRoy, *Can. J. Res.*, **B28**, 492 (1950).

inert support. The acetone yield was determined by comparing the peak areas with that obtained with mixtures of the parent ketone with acetone at known concentrations. The absolute yields of *n*- C_6H_{14} were not determined, but trends were observed from the change in peak height with changes in experimental conditions.

1-Methylcyclobutanol has been reported among the products of the liquid phase photolysis of 2-pentanone¹⁷ and also during its vapor phase photolysis.⁸ The quantum yield of formation of 1-methylcyclobutanol is low. It was not identified in the present work and the presence of this additional reaction product would not alter the conclusions which are drawn.

The products of the photolysis of 2-hexanone (CO , CH_4 , C_2H_6 , C_3H_8 and CH_3COCH_3) were determined similarly. The acetone yield at 3130 Å. was determined in the fractometer with a Perkin-Elmer Column A. The yields at 3130 Å. are less accurate than those at 2537 Å. due to the presence of another peak at a similar retention time. The usefulness of the dimethyl sulfolane column, which eliminated this difficulty, was not discovered until after the results at 3130 Å. had been obtained.

The products of the photolysis of biacetyl (CO and C_2H_6) were determined in a similar manner. Biacetyl was photolyzed in the presence of *n*-pentane or *n*-hexane to compensate for any effect which the high pressure of the ketones, in the ketone-biacetyl mixtures, might have on the dissociation and fluorescence of biacetyl.

Results

(a) 3130 Å.: 2-Pentanone and 2-Pentanone-Biacetyl Mixtures.—The addition of biacetyl to the photolysis of 2-pentanone at 3130 Å., at 32.5° and 56.0°, results in sensitized emission of biacetyl and in a change in the decomposition yields from 2-pentanone.

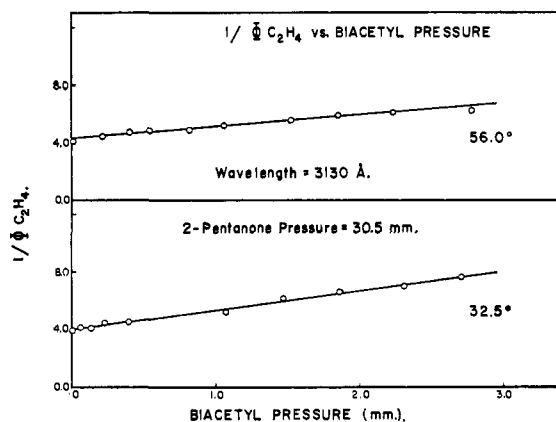
The sensitized biacetyl emission (long-lived, in the green) increases with increasing biacetyl pressure, as is shown in Fig. 1, and appears to become constant at biacetyl pressures greater than 3 mm. The yield decreases with increasing temperature and is unaffected by the addition of up to 30 mm. of *n*-pentane. Exposure of mixtures of biacetyl and *n*-pentane at 3130 Å. results in no observable emission. A comparison of the sensitized emission with that obtained from acetone-biacetyl mixtures was made under identical experimental conditions. The maximum emission yields were obtained with addition of less than 0.2 mm. of biacetyl and of about 2.7 mm. of biacetyl with acetone and with 2-pentanone, respectively. Maximum values were in the ratio of about 2.5:1. A rough estimate of the quantum yield for biacetyl formation was obtained at 32.5° by comparing the emission from the 2-pentanone-biacetyl mixtures with the emission from prepared mixtures at known biacetyl concentrations. A yield per quantum absorbed of approximately 0.06 was obtained.

No emission at wave lengths longer than 5000 Å. other than that ascribable to the sensitized emission of biacetyl was observed.

The effect of added biacetyl on the quantum yields of CO , $\text{CO} + \text{CH}_4$, C_2H_4 and CH_3COCH_3 is shown in Table I. An increase in biacetyl pressure results in a decrease in the yields of C_2H_4 and CH_3COCH_3 . The effects are comparable at the two temperatures. Addition of biacetyl causes an increase in the carbon monoxide yield at 32.5° and has no observable effect at 56.0°. The photolysis of 3.28 mm. of biacetyl in the presence of 30 mm. of *n*-pentane yielded 0.056×10^{-12} mole/liter of $\text{CO} + \text{CH}_4$. The same intensity of incident radiation was used in this run as is reported in Table I. Quantum yields were not obtainable at this low pressure. In the ketone-biacetyl mixtures, 2-pentanone absorbs 20% of the incident radiation so that this same rate would not be expected even if the two compounds decomposed independently. A sensitized decomposition of biacetyl would explain the results.

Plots of $1/\Phi_{\text{C}_2\text{H}_4}$ and (biacetyl pressure)/ Q_{5000} against biacetyl pressure are shown in Fig. 2 and 3; Q_{5000} is

(17) N. C. Yang and D-D. H. Yang, *J. Am. Chem. Soc.*, **80**, 2913 (1958).

Fig. 2.—Plots of $1/\Phi_{C_2H_4}$ vs. P_B for 2-pentanone.

proportional to the absolute emission yield at wavelengths greater than 5000 Å. The slope/intercept ratios for the two plots are 0.034 and 0.038 mm^{-1} at 32.5° and 0.016 and 0.026 mm^{-1} at 56.0°. The slopes of the plots of the photolysis data are 0.135 and 0.071 at the two temperatures and the intercepts are 4.0 and 4.4 at 32.5° and at 56.0°, respectively.

TABLE I

EFFECT OF BIACETYL ON THE PHOTOLYSIS OF 2-PENTANONE AT 3130 Å.

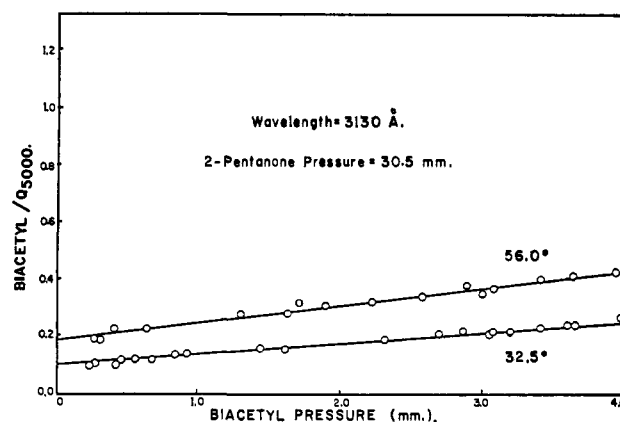
$I_a = 1.4 \times 10^{13}$ quanta/ml. sec., 2-pentanone pressure = 30.5 mm., time = 3000 sec.

Biacetyl press., mm.	Φ_{CO}	$\Phi_{CO + CH_4}$	$\Phi_{C_2H_4}$	$\Phi_{CH_3COCH_3}$
$T = 32.5^\circ$				
0	0.011	0.012 ± 0.001	0.25 ± 0.01	0.24 ± 0.01
0.06	.012	.014	.24	.23
.14	.012	.014	.24	.24
.23			.22	.21
.40	.013	.014	.22	.21
.78		.016	.17	.16
1.08			.19	
1.48	.016	.017	.16	.14
1.87	.016	.017	.15	
2.32	.017	.019	.14	.13
2.72		.019	.13	.13
$T = 56.0^\circ$				
0	0.046	0.050	0.24	0.22
0.22	.045	.048	.22	
.41	.044	.048	.21	
.55	.046	.050	.20	0.21
.83	.046	.050	.20	.21
1.06	.045	.049	.19	.20
1.53		.049	.18	.20
1.86		.048	.17	.16
2.24	.045	.049	.16	.16
2.79 ^a	.050	.053	.16	.16

^a All values high.

(b) 3130 Å.: 2-Hexanone and 2-Hexanone-Biacetyl Mixtures.—The addition of biacetyl to the photolysis of 2-hexanone at 3130 Å. at 35.0° results in extremely weak sensitized emission of biacetyl. At a biacetyl pressure of 2.7 mm., with equal pressures of 2-pentanone and of 2-hexanone, the emission yields are in the ratio of 20:1. Irradiation of mixtures of biacetyl and *n*-hexane, at comparable pressures, results in no observable emission.

There is no definite effect of added biacetyl on the photodecomposition of 2-hexanone. At 35.0°, with $I_a = 1.5 \times 10^{13}$ quanta/ml. sec., $\Phi_{(CO + CH_4 + C_2H_6)} = 0.0076 \pm 0.0002$, $\Phi_{C_2H_6} = 0.41 \pm 0.01$, and $\Phi_{CH_3COCH_3} =$

Fig. 3.—Plots of P_B/Q_{5000} vs. P_B for 2-pentanone; Q_{5000} is in arbitrary units.

0.44 ± 0.04 . The yield of $CO + CH_4 + C_2H_6$ is unaffected by the addition of up to 4.0 mm. of biacetyl. There appeared to be a slight decrease in $\Phi_{C_2H_6}$. However, the change was almost within experimental error. The scatter in the acetone data obscured any small changes. At 100°, $\Phi_{CO} = 0.065 \pm 0.005$, $\Phi_{CH_4} = 0.008 \pm 0.001$, $\Phi_{C_2H_6} = 0.007 \pm 0.001$, $\Phi_{C_2H_4} = 0.42 \pm 0.12$, and $\Phi_{CH_3COCH_3} = 0.43 \pm 0.02$. The addition of biacetyl had no effect on the product quantum yields. It should be emphasized that when yields are wavelength dependent good reproducibility from one lamp-filter combination to another supposedly to give the same wave length is not to be expected. Even lamps of the same type may differ markedly.

(c) 2537 Å.: 2-Pentanone and 2-Pentanone-Biacetyl Mixtures.—The photolysis of 2-pentanone at 2537 Å. was studied as a function of temperature at 2537 Å. in order to compare the present work with previously reported data. The results are given in Table II. There is no obvious explanation for the great difference in the reported yield¹⁹ of carbon monoxide at 125° as compared with that found in the present work.

In order to see whether the increase in Φ_{CO} at 2537 Å. was due to a wave length or to an intensity dependence, one run was made at 3130 Å. with $I_a = 1.25 \times 10^{12}$ quanta/ml. sec. The CO yield was 0.051.

The effects of added biacetyl on the photolysis of 2-pentanone at 33.0° are given in Table III. No time dependence was observed. Intensities are for light absorbed only by 2-pentanone, as calculated with Beer's law for mixtures. The calculated rates of formation of CO and of the C_2 -fraction were obtained from the calculated fraction of light absorbed by biacetyl and experimentally determined quantum yields for CO and for C_2H_6 from the photolysis of biacetyl. These quantum yields are: $\Phi_{CO} = 0.84 \pm 0.03$; $\Phi_{C_2H_6} = 0.24$ for a maximum $I_a = 0.22 \times 10^{12}$ quanta/ml. sec. The yields are somewhat intensity dependent. The variation in the rate of production of the $C_3 + C_4$ fraction with intensity was studied in only one run. The rate increased slightly. The $n-C_6H_{14}$ yields are given in arbitrary units and are proportional to the true quantum yields.

The yield of ethylene is independent of biacetyl pressure. The acetone yield increases since acetone is a product of biacetyl decomposition. Carbon monoxide quantum yields were determined from the experimentally determined rates less the calculated rate of carbon monoxide formation from biacetyl photolysis with the part of the light absorbed by the biacetyl. This calculation assumes no radical-radical reactions

TABLE II
PHOTOLYSIS OF 2-PENTANONE AS A FUNCTION OF TEMPERATURE
Wave length, 2537 Å.; 2-pentanone pressure, 25.0 mm.

Temp., °C.	$I_a \times 10^{-12}$, quanta ml. sec.	Φ_{CO}	Φ_{CH_4}	$\Phi_{C_2H_6}$	$\Phi_{C_2H_4}$	$\Phi_{C_3 + C_4}$	$\Phi_{CH_3COCH_3}$	$\alpha \Phi_{n-C_6H_{14}}$
33 ^a	1.30	0.049	0.008	0.006	0.36	0.029	0.36	0.012
67.5	1.08	.13	.038	.020	.36		.40	
125 ^b	1.03	.20	.12	.014	.40	.074	.38	.007
160	0.95	.21	.18	.017	.40	.11		
165 ^c	.92	.22	.17	.008	.40	.10	.42	.006
200	.88	.25	.22	.008	.40	.14	.39	.001

^a Average of four runs. ^b Average of two runs except for $C_3 + C_4$ and CH_3COCH_3 , which are averages of three runs. ^c Average of two runs except for CH_3COCH_3 and $n-C_6H_{14}$.

TABLE III
EFFECT OF BIACETYL ON THE PHOTOLYSIS OF 2-PENTANONE AT 2537 Å.
 $T = 33.0^\circ$; 2-pentanone pressure = 25.0 mm.

P_B , mm.	I_a , ^b	Total R_{CO}	Total R_{C_2}	Total $R_{CH_3COCH_3}$	Calcd. ^a Φ_{CO}	$\Phi_{C_2H_4}$	Calcd. ^a Φ_{C_2}	$\alpha \Phi_{C_6H_{14}}$
0	1.23	0.104	0.744	0.74	0.051	0.36		0.010
0.41	1.35	.135	.839	.84	.045		0.37	.009
0.75	1.28	.198	.807		.062		.37	
1.14	1.29	.230		.84	.062			.008
1.44	1.29	.264 (.19)	.839	.72	.067	.375	.38	.006
1.82	1.29	.365	.864	.89	.098		.38	.006
2.36	1.28	.462	.869	.92	.124		.38	.003
3.2	1.30	.623 (.41)	.887		.161	.36	.37	

Rates (R) are in moles/ml. sec. $\times 10^{12}$; those rates in parentheses are calculated on the assumption of independent photochemical decomposition of the 2-pentanone and biacetyl. ^a Total rate less rate calculated for biacetyl alone. ^b Quanta/ml. sec. $\times 10^{-12}$.

resulting from the presence of two simultaneous primary processes but should be valid within experimental error. These residual yields increase with increasing biacetyl pressure, possibly due to a sensitized decom-

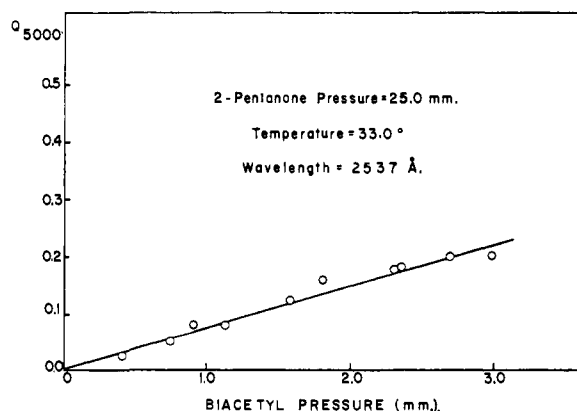


Fig. 4. —A plot of Q_{5000} vs. P_B , for 2-pentanone at 2537 Å. (Q_{5000} is in arbitrary units).

position of biacetyl. Since the calculations are only approximate, this conclusion is not definite. The decrease in the yield of $n-C_6H_{14}$ is presumably due to a change in the steady state concentration of propyl radicals as evidenced by the slight increase in the $C_3 + C_4$ yield.

One run was made at 2537 Å., at 33.0°, with the addition of 47.0 mm. of n -pentane to 25 mm. of 2-pentanone. The yield of ethylene decreased slightly from 0.38 ± 0.02 to 0.34 ± 0.02 under these conditions.

Sensitized biacetyl emission excited at 2537 Å. was weak compared to that excited at 3130 Å. The increase with increasing biacetyl pressure is shown in Fig. 4. Exposure of even 6 mm. of biacetyl in the presence of 20 mm. of n -pentane results in no observable emission.

(d) 2537 Å.: 2-Hexanone and 2-Hexanone-Biacetyl Mixtures.—In contrast to 2-pentanone, the

quantum yield of the Type II process from 2-hexanone apparently decreases with decreasing wave length. The reported Type II quantum yield at 3130 Å. is 0.45.⁵ The propylene quantum yields obtained in the present work are 0.41 ± 0.02 at 3130 Å. and 0.29 ± 0.01 at 2537 Å. from 36° to 125°. The carbon monoxide yield at 2537 Å. increases from 0.028 at 36° to 0.080 at 125°. Carbon monoxide yields are intensity dependent and appear to be essentially wave-length independent. At 125°, $\Phi_{CH_4} = 0.014$ and $\Phi_{C_2H_6} = 0.037$. Some propane was also formed, but the amount never exceeded 3% of the total C_3 yield.

Only two runs were made with added biacetyl since its effect was zero within experimental error. The results are given in Table IV. The intensity values are

TABLE IV
EFFECT OF BIACETYL ON THE PHOTOLYSIS OF 2-HEXANONE AT 2537 Å.

Temp., 36.0 ± 1.0°; 2-hexanone pressure, 10.5 ± 0.5 mm.				
P_B , mm.	0.0	0.0	2.6	4.1
$I_a \times 10^{-12}$, quanta/ml. sec.	.97	.71	0.66	0.64–0.74
R_{CO}	.034	.027	.33	.54
R_{CH_4}013	.018
$R_{C_2H_6}$085	.14
$R_{C_2H_4}$			(.06)	(.07–0.04)
$R_{C_3H_8}$.47	.32	.29	.28
$R_{CH_3COCH_3}$.48	.37	.39	...
$\Phi_{C_2H_6}$.29	.28	.27	.27–0.22
$\Phi_{CH_3COCH_3}$.30	.31	.36	...

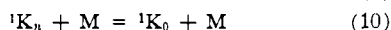
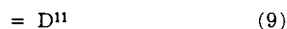
Rates (R) are in moles/ml. sec. Those in parentheses are calculated on the assumption of independent photochemical decompositions of the hexanone and of biacetyl.

for the part of the light absorbed by 2-hexanone alone. At higher biacetyl pressures there may or may not be a sensitized decomposition of biacetyl and the effect on the Type II process is also inconclusive.

There was no evidence for a sensitized emission of biacetyl at 2537 Å.

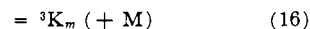
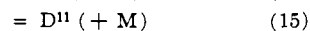
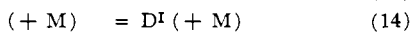
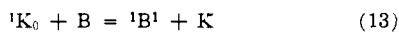
Discussion

The possible reactions may be listed

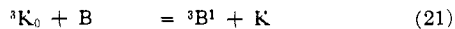
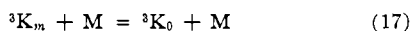


K is a normal ketone molecule (2-pentanone or 2-hexanone), 1K_n is a ketone molecule in the n th vibration level of the excited singlet state, 1K_0 is one with vibration energy equilibrated with the surrounding, D^I represents dissociation products of the Type I process (radicals), and D^{II} dissociation products of the Type II process (acetone plus olefin); B is a biacetyl molecule in the ground state, ${}^1B^I$ is a biacetyl molecule in the first excited singlet state, ${}^1B^{II}$ is a biacetyl molecule in the second excited singlet state.

It is probable from earlier work that the majority of ${}^1B^I$ molecules at sufficient pressure go over to the triplet state.^{19,20} Of these, about 15% emit radiation²¹ at room temperature, but they may dissociate with an activation energy of about 15 kcal.²²



where 3K_m is a ketone molecule in the m th vibration level of an excited triplet state. Crossover from 1K_n to the triplet state is also a possibility.



where ${}^3B^I$ is a biacetyl molecule in an excited triplet state.



where D represents dissociation products of biacetyl. Emission by 22 lies mainly in the green at wave lengths longer than 5000 Å. and was measured in the present work.

1K_n will possess electronic plus vibration energy dependent on the absorbing wave length, about 4.0 e.v. at 3130 Å. and 4.88 e.v. at 2537 Å; 1K_0 by analogy with other ketones has about 3.6 e.v. of electronic energy.²³ The 0,0 bands for $B \rightarrow {}^1B^I$ and $B \rightarrow {}^1B^{II}$ lie at about 2.8 and 3.9 e.v., respectively.^{23,24} The triplet state energies in each case are lower than the corresponding singlet state energies.

We may now discuss several different cases: (a) 2-Pentanone, 3130 Å.: 2-Pentanone at this wave length will have relatively little vibration energy in the state 1K_n . Yields of methane, ethane and carbon monoxide

(19) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

(20) G. P. Porter, *J. Chem. Phys.*, **32**, 1587 (1960).

(21) G. M. Almy and P. R. Gillette, *ibid.*, **11**, 188 (1943).

(22) Cf. W. A. Noyes, Jr., W. A. Mulac and M. S. Matheson, *ibid.*, **36**, 880 (1962).

(23) J. W. Sidman and D. S. McClure, *J. Am. Chem. Soc.*, **77**, 6461 (1955).

(24) J. W. Sidman, *Chem. Rev.*, **58**, 689 (1958).

are all rather low in spite of the low intensities used. Hence 8 and 14 are of minor importance.

From the intercepts in Fig. 2 one may calculate the ratio of the rate constant for the reaction (or reactions) which destroy the state which gives Type II dissociation to the rate constant of the Type II reaction. This ratio is 3.2 ± 0.2 and is nearly the same at 32.5° and at 56°.

Again one notes from Fig. 2 that the slopes of $1/\Phi_{C_2H_4}$, vs. P_B decrease with increase in temperature. This corresponds to a greater activation energy by 5 to 6 kcal. for the denominator than for the numerator of the expression for $1/\Phi_{C_2H_4}$. In a general way the denominator will contain the terms which lead to Type II reaction and the numerator will contain the terms which involve reactions which destroy the state from which Type II arises, including energy transfer and the Type II reaction itself. This apparently indicates a slightly greater activation energy for Type II than for energy transfer. The latter would be expected to be small or even zero.

Superficially these conclusions agree with the conclusions of Ausloos and Rebbert⁸ that the Type II process in 2-pentanone apparently has a small activation energy. However, if this is so, the conclusions from the intercepts must be that the Type II and the other processes which destroy the state leading to Type II, excluding energy transfer to biacetyl, have nearly the same activation energy (within 1.5 to 2 kcal.) and that both are several kilocalories. Thus the other main process for destroying the excited singlet state (presumably intersystem crossover to the triplet state) may have a small activation energy. This conclusion is purely tentative.

It should be pointed out in passing that at 3130 Å. biacetyl is also one of the products of 2-pentanone photolysis and has a quantum yield of about 0.06. Since biacetyl formation will decrease with increase in temperature because of the instability of the acetyl radical, a small apparent activation energy for the Type II process may be fortuitous. In the present experiments the effect of biacetyl formation is probably not great enough to account for these small apparent activation energies.

It is important to note that within experimental error the ratios of slope/intercept for Fig. 2 and 3 are identical (0.034 and 0.038 mm.⁻¹, respectively) at 32.5°.

It should now be noted that in the mechanism there are three reactions which may undergo the Type II reaction: 9, 15, and 20. One can derive the complete expressions for $1/\Phi^{II}$ and for $(B)/Q_{5000}$. The numerators are identical and each is the product of three linear terms in (B), one for the state 1K_n , one for the state 1K_0 , and one for the state 3K_0 . Thus there are at least three possibilities for slope/intercept for both graphs

$$(I) \quad \begin{array}{ll} (k_{11} + k_{12})/(k_8 + k_9 + k_{10}(M)) & \text{for } (B)/Q_{5000} \\ k_{12}/(k_8 + k_9 + k_{10}(M)) & \text{for } 1/\phi^{II} \end{array}$$

$$(II) \quad k_{13}/(k_{14} + k_{15} + k_{16}) \quad \text{for both equations}$$

$$(III) \quad k_{21}/(k_{18} + k_{19} + k_{20}) \quad \text{for both equations}$$

These are based on the reasonable assumption that only 1K_n at 3130 Å. at 32.5° has enough energy to undergo radical dissociation. There seems to be no *a priori* reason for accepting any one of the three states as the one on which to place full responsibility for the equality of slope/intercept ratios at 32.5°. However, two facts should be noted: (a) the ratios are not identical at 56°; (b) at 2537 Å. (see below) there is no slope to either graph so that the ratio of slope to intercept is zero in both cases.

The first of these facts indicates that relative rate constants have changed with temperature in such a way that some new step has become rate controlling. The second fact indicates strongly that the amount of vibration energy in the excited singlet state makes a decided change in behavior even though ϕ^{II} has changed only from about 0.25 to 0.40 with the change in wave length.

Thus one is inclined to conclude tentatively that the singlet state is the one which transfers energy to biacetyl and that this same state gives rise to the Type II decomposition. As previously recorded, there is some support for the conclusion as regards 2-hexanone that the singlet state is responsible for the Type II reaction.

This conclusion differs from that for acetone²⁵ and for 3-pentanone.²⁶ In neither of these molecules was it necessary to assume transfer of energy from excited singlet state molecules to biacetyl, although a small amount of such transfer is not excluded by the data. However, energy transfer to biacetyl from acetone was essentially complete at biacetyl pressures of a few tenths of a millimeter. In 3-pentanone a pressure of more than a millimeter was required and with 2-pentanone a pressure of about 3 millimeters is required. With 2-hexanone there is no transfer within experimental error. These facts suggest that these various ketones do not all behave in the same way.

(b) 2-Pentanone, 2537 Å.: The Type II yield increases from about 0.25 at 3130 Å. to about 0.40 at 2537 Å. At this wave length there is little variation with temperature and a negligible effect of total pressure.

The amount of vibration energy in the excited singlet formed at 2537 Å. is large and any thermal contribution would be small by small changes in temperature. Thus one would expect a small effect of temperature and of pressure on ϕ^{II} provided the Type II reaction occurs very rapidly after absorption. However, since the Type II yield is small and yields of other products do not bring the total near unity, there must be a rapid competing first-order process, presumably either inter-system crossover to the triplet state followed by another crossover to the ground state or even internal conversion to the ground state. In some way the

ability to undergo a Type II process and rapid internal degradation of electronic to thermal energy seem to be associated. It is probable that triplet state 2-pentanone molecules would be deactivated by biacetyl if they were present in sufficient concentration.^{14,27,28}

The availability of vibration energy for transfer of electronic energy is an interesting question. In biacetyl-2-pentanone mixtures the carbon monoxide yield increases more than one would expect from absorption by the biacetyl. This indicates that some biacetyl is raised to the second excited singlet state. In that event electronic and vibrational energy must both be transferred to biacetyl. Since there is also a small but definite biacetyl emission excited in the mixture at 2537 Å., there must also be some formation of the first excited state of biacetyl. Both processes are relatively inefficient since biacetyl has a very small effect on the Type II yield at 2537 Å.

(c) 2-Hexanone: Biacetyl has a negligible effect on the Type II yield from 2-hexanone. In this respect it parallels the lack of effect of oxygen. There is a very small but probably definite emission from 2-hexanone-biacetyl mixtures, thus indicating a small amount of energy transfer. The Type II yield from 2-hexanone is slightly lower at 2537 Å. than at 3130 Å.

The present study provides no new information about excited states of 2-hexanone.

The possibility of a concerted formation of 1-methylcyclobutanol rich in energy in a single step^{8,17} must be considered. Such a "hot" molecule could either split off ethylene (the Type II reaction) or lose vibrational energy to degrade either to the parent 2-pentanone or to the stable 1-methylcyclobutanol. A concerted formation of 1-methylcyclobutanol might mean temporarily two four-membered rings (including one by hydrogen bonding) rather than one six-membered ring. That four-membered rings may be of great importance is suggested by many lines of evidence.²⁹

The present work provides no evidence for or against the existence of appreciable concentrations of triplet state molecules during photolysis of 2-pentanone and of 2-hexanone. Such evidence as there is would lead one to believe that if triplet state molecules are formed they have very short lives and do not undergo easily energy transfer reactions. More work on this point is needed.

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(26) D. S. Weir, *ibid.*, **83**, 2629 (1961).

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(28) G. Porter and F. Wilkinson, *Proc. Roy. Soc. (London)*, **A264**, 1 (1961).

(29) Cf. R. Srinivasan, *J. Am. Chem. Soc.*, **81**, 1546 (1959).