

decomposition of the azo compound in ethylbenzene was analyzed for deuterium. As shown in Table II, the atom % D in the product is the same, within 1.5%, as that in the starting material. From these results it can be concluded that the hydrogen abstraction reaction by a benzylic radical to produce the same benzylic radical does not occur to any measurable extent.

Similar observations have been made on other benzylic systems.^{29,30}

Acknowledgments.—I would like to express my thanks to Mrs. Mary Kresge for programming the kinetic data, to Dr. D. R. Christman for deuterium analysis to Dr. Aharon Lowenstein for preliminary n.m.r. determinations and to Dr. Max Wolfsberg for helpful discussions.

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The Photolysis and Fluorescence of Diethyl Ketone and Diethyl Ketone-Biacetyl Mixtures at 3130 and 2537 Å.¹

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The photolysis of diethyl ketone and the photolysis and phosphorescence of diethyl ketone-biacetyl mixtures have been studied at 3130 and 2537 Å. The addition of biacetyl at 3130 Å. decreases the photodecomposition of diethyl ketone and increases the phosphorescence of biacetyl. An energy transfer from excited triplet diethyl ketone to biacetyl is proposed and there is evidence that the propionyl radical formed from the singlet state at 3130 Å. is sufficiently "hot" to dissociate into an ethyl radical and carbon monoxide. At 2537 Å. dissociation appears to occur from the initially formed upper singlet state, and there is no evidence that the triplet state intervenes. A detailed mechanism is presented for the primary process in diethyl ketone and for the energy transfer between diethyl ketone and biacetyl.

Introduction

The vapor phase photodecomposition of diethyl ketone at 3130 Å. has been studied³⁻¹² extensively and a comprehensive review of the primary process in simple ketones published.¹³

The light emission from excited diethyl ketone has not been so well studied although Matheson and Zabor¹⁴ have recorded an emission from 4360 to 5460 Å. with a maximum around 5200 Å. Since the emission is similar to that observed with propionaldehyde, they have ascribed it to the diketone, bipropionyl, formed during radiation. This effect is similar to that observed in acetone where the green emission is due to biacetyl.

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(2) Postdoctoral Fellow 1958-1960 under a grant from the Camille and Henry Dreyfus Foundation, Inc.

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This paper presents the results obtained from an investigation of the primary process involved in the photodecomposition of diethyl ketone and of diethyl ketone-biacetyl mixtures and the energy interchange between excited diethyl ketone and biacetyl.

Experimental

Eastman Kodak diethyl ketone was used. The ketone was distilled under dry nitrogen through about thirty theoretical plates and a middle fraction, constant boiling at 102.7°, retained and stored over anhydrous copper sulfate. The fraction was thoroughly degassed at Dry-Ice temperature in a vacuum line and the middle fraction retained from a bulb-to-bulb distillation. No impurities could be detected in the mass spectrum and vapor phase chromatogram. Eastman white-label biacetyl was dried over Drierite, degassed and fractionated in a bulb-to-bulb distillation. A vapor phase chromatogram gave impurities of less than 1%. Spectro Grade Eastman acetone was dried over Drierite, degassed and distilled in a grease-free vacuum system. No impurities could be detected.

For 3130 Å. radiation, an Osram HBO Super Pressure mercury lamp operating at 76 volts direct current and 6.2 amps was used. A Hanovia S-100 Alpine Burner was used for wave lengths in the region of 2537 Å. The light was collimated and stray radiation prevented from entering the cell by a series of screens. For 3130 Å. the filter arrangement described by Kasha¹⁵ was used, supplemented by a Pyrex plate and a Corning 9700 filter. A filter combination of chlorine, cobalt sulfate-nickel sulfate solution and a Corning 9863 filter was used to give radiation of approximately 2537 Å. The quantum yields for diethyl ketone photolysis were corrected for biacetyl absorption and decomposition.

A T-shaped quartz reaction cell was used for photolysis and light emission measurements. The cell was 125 mm. long with a main window diameter of 38 mm. and a fluorescence window diameter of 23 mm.

Transmitted intensities of the exciting radiation were measured on an R.C.A. 935 phototube connected to a Varian G. 10 Graphic Recorder. Quantum yields were calculated against the CO yield from diethyl ketone at 105° for 3130

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

Å. radiation and the CO yield from acetone at 120° for 2537 Å., both of which are unity under these conditions.^{5,16} Light emissions were photographed on a Hilger quartz prism spectrograph using Eastman Kodak 103a-B plates for the biacetyl emission and 103a-O for the diethyl ketone emission. The intensity of the biacetyl emission seen through a Corning filter was measured on an R.C.A. 1P21 photomultiplier tube connected to an R.C.A. WV-84A direct current microammeter.

A conventional vacuum line was used. The products from the photolysis of diethyl ketone—carbon monoxide, ethylene, ethane and butane—were collected and measured in a McLeod Gauge-Toepler pump arrangement.¹⁷ The products of photolysis were frozen in the cold finger of the reaction cell with liquid nitrogen for 15 minutes. The volatile products were then left in contact with a solid nitrogen trap for a further twenty minutes before the carbon monoxide was removed and measured. The nitrogen trap on the cell cold finger was replaced by a Dry-Ice-acetone trap and the two remaining fractions, ethylene-ethane and butane, were separated using a Ward still.¹⁸ The C₂ fraction came off at about -155° and the C₄ fraction at about -115°. Four hours were required for the full separation of the butane fraction from the residual diethyl ketone and involved repeated warming of the ketone from Dry-Ice-acetone temperature to room temperature.

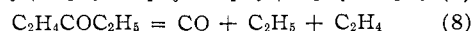
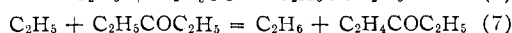
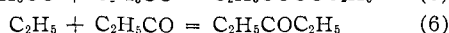
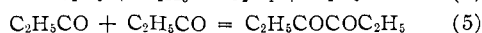
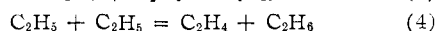
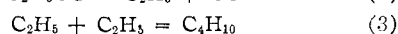
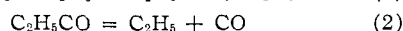
Results

The results were observed at two incident wave lengths, 3130 and 2537 Å. For the intensity measurements carried out at 3130 Å., the filter combination described above was replaced by a pyrex plate to obtain a larger variation in incident intensity. The absorbed intensity I_a is given in quanta/ml./sec. as calculated from the cell volume and the rate of absorption.

3130 Å.—The rate of formation of the total C₂ fraction (C₂H₄ + C₂H₆) was measured. Individual values for C₂H₄ and for C₂H₆ were not obtained. At this wave length it is to be expected that the rate of formation of C₂H₄ and of C₂H₆ will be the same at room temperature. If one-half of the total C₂ fraction is taken to represent the rate of formation of ethylene, then a value of 0.135 is obtained for the ratio of rate of C₂H₄ formation to rate of C₄H₁₀ formation. This value compares favorably with previous evaluations of this ratio.^{9,10,12}

The variation of biacetyl emission is given in microamps. This value is obtained from the difference in photomultiplier readings when the cell is empty and when the cell is full.

The primary quantum yields are obtained by considering the reaction scheme



Reactions 7 and 8 are not considered important under the conditions of the experiments. Reaction 8 is probably important only at low intensity and high temperature,¹⁹ and reaction 7 which does not

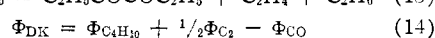
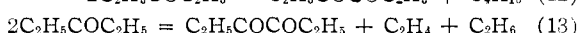
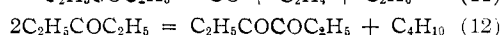
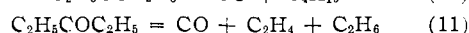
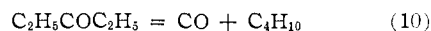
have a high activation energy⁹ should be important only at low intensities. The reaction between C₂H₅ and C₂H₄COC₂H₅ radicals which would be expected to give mainly C₄H₉COC₂H₅ is also considered negligible.

The primary quantum yields are estimated from the sum of the quantum yields of the radical-radical reactions

$$\phi = \Phi_{\text{C}_4\text{H}_{10}} + \frac{1}{2}\Phi_{\text{C}_2} + \Phi_{\text{DK}} + \Phi_{\text{K}} \quad (9)$$

where $\Phi_{\text{C}_4\text{H}_{10}}$, Φ_{C_2} , Φ_{DK} , Φ_{K} are the quantum yields of butane, ethylene + ethane, diketone formation and ketone formation, respectively, and ϕ is the calculated primary quantum yield.

From the over-all reactions



From equations 3, 4, 5 and 6 the Φ_{K} can be calculated from

$$\Phi_{\text{K}}^2 = \Phi_{\text{DK}} (\Phi_{\text{C}_4\text{H}_{10}} + \Phi_{\text{C}_2\text{H}_4}) \quad (15)$$

Two assumptions are necessary for the derivation of equation 15. First, that the collision diameter of the ethyl radical is approximately one-half that of the propionyl radical and secondly, that $S_b^2 = S_a S_c$ where S_a , S_b and S_c are the steric factors involved in the reaction of two ethyl radicals, an ethyl and a propionyl radical and two propionyl radicals, respectively. The first assumption cannot be greatly in error. The second assumption was tested using results obtained under conditions where the primary quantum yield is likely to be nearly unity, *i.e.* low intensity and high temperature. Since only Φ_{CO} and Φ_{C_2} were determined under these conditions, Φ_{C_4} was estimated from the previously determined relationship $\frac{1}{2}\Phi_{\text{C}_2} = 0.135\Phi_{\text{C}_4\text{H}_{10}}$. From equations 9 and 14 and assuming $\phi = 1$, Φ_{K} can be estimated. From Φ_{K} , $\Phi_{\text{C}_4\text{H}_{10}}$ and $\frac{1}{2}\Phi_{\text{C}_2}$ the ratio $S_b^2/S_a S_c$ can be calculated. The three values obtained for this ratio—0.76, 0.11 and 0.20—are within a factor of 10 of the assumed figure.

From 9, 14 and 15 the primary quantum yield can be estimated.

The principal results at 3130 Å. are:

1. Emission from Diethyl Ketone and Diethyl Ketone-Biacetyl Mixtures.—A weak emission from about 3850 to about 4700 Å. was observed from diethyl ketone. The emission was so weak that no structure could be observed. Oxygen appeared to decrease the intensity and to narrow slightly the emission from the long wave length end. Temperature did not affect the emission but pressure increased the intensity without affecting the spectrum. With a mixture of diethyl ketone and biacetyl a very strong emission was recorded. This emission consisted of three bands with maxima at 5120, 5600 and 6000 Å. Because of the low intensity of the diethyl ketone emission, it was impossible to tell whether the addition of biacetyl produced any effect on the intensity or the spectrum of this emission.

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(19) A. N. Strachan, Ph.D. Thesis, 1954, Rochester, N. Y.

2. Effect of Biacetyl on the Decomposition of Diethyl Ketone and on the Phosphorescence of Biacetyl.—These two effects are shown in Table I and Fig. 1, respectively. Table I shows the effect of biacetyl pressure on the Φ_{CO} , Φ_{C_2} and Φ_{C_4} at 25° and on Φ_{CO} at 57°. The effect on ϕ and ϕ^1 at 25° are also shown where ϕ is the primary quantum yield calculated by equation 9 and ϕ^1 is the same quantity less the contribution from reaction 6.

TABLE I
EFFECT OF BIACETYL ON THE PHOTOLYSIS OF DIETHYL
KETONE

$T = 25^\circ$ and 58° ; wave length, 3130Å.; diethyl ketone pressure = 25 mm.; I_a , the quanta absorbed/ml./sec. is 1.56×10^{12}

Biacetyl pressure, mm.	T , °C.	Φ_{CO}	Φ_{C_2}	Φ_{C_4}	$\frac{\Phi_{C_2}}{\Phi_{C_4}}$	ϕ	ϕ^1
0	25	0.71	0.18	0.65	0.28	0.919	0.77
0	25	.72	.18	.65	.28	.882	.76
0	25	.73	.19	.66	.29	.917	.78
0.3	25	.57	.14	.54	.26	.806	.65
0.5	25	.52	.14	.50	.28	.788	.62
0.6	25	.53	.14	.50	.28	.761	.61
1.25	25	.45	.11	.38	.29		
2.40	25	.45	.11	.40	.28	.507	.46
0.0	59	.91					
0.58	59.5	.82					
1.21	58.75	.77					
2.42	58.0	.73					
2.75	57.0	.72					
3.0	57.0	.73					

Increase in the biacetyl pressure has these effects: (a) At 25° and 58° there is a decrease in Φ_{CO} , in $\Phi_{C_2H_4 + C_2H_6}$ and in $\Phi_{C_4H_{10}}$. At 25° limiting values of 0.45 for CO, 0.11 for $(C_2H_4 + C_2H_6)$ and 0.40 for C_4H_{10} are reached at a biacetyl pressure of 1.2 mm. At 58° a limiting value of 0.73 is obtained for Φ_{CO} at a biacetyl pressure of 2.0mm. No value for Φ_{C_2} and Φ_{C_4} were obtained at this temperature. The calculated values of ϕ and ϕ^1 also drop with increase of biacetyl pressure.

(b) At both temperatures the decrease in quantum yields is paralleled by an increase in biacetyl phosphorescence which reaches a limiting value at a biacetyl pressure of 1.2 mm. at 25° and 2.5 mm at 58°. At 25° the limiting value is 24.2 microamps compared to 10.7 microamps at 58°.

(c) At 25° the ratio $\Phi_{C_2}/\Phi_{C_4H_{10}}$ remains constant. No figures were obtained for this ratio at 58°.

3. The Effect of Temperature on the CO Quantum Yield and Biacetyl Phosphorescence at High Biacetyl Pressure.—These effects are shown in Table II. An increase in temperature produces an

TABLE II
THE EFFECT OF TEMPERATURE ON THE CO QUANTUM YIELD
AND BIACETYL PHOSPHORESCENCE AT HIGH BIACETYL
PRESSURE

Diethyl ketone pressure, 25 mm.; wave length, 3130Å.; biacetyl pressure, 2.45 mm.

Temp., °C.	Φ_{CO}	Phosphorescence of biacetyl, μ amp.
27.5	0.45	24.2
33.25	.51	20.75
41.5	.58	16.2
57.0	.72	10.1

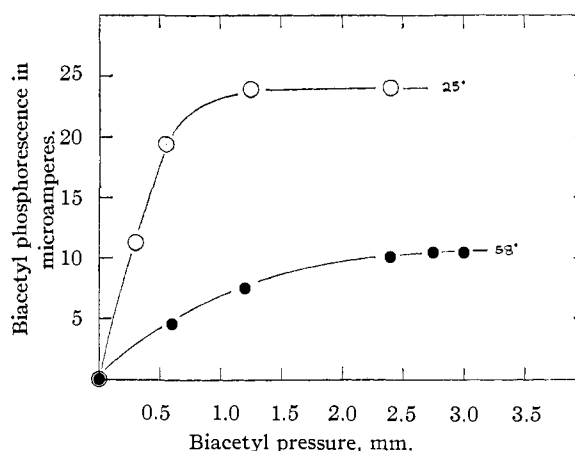


Fig. 1.—Plot of biacetyl phosphorescence versus biacetyl pressure at 25° and 58° and 3130 Å.

increase in Φ_{CO} and a decrease in biacetyl phosphorescence in the region where Φ_{CO} and phosphorescence have reached a limiting value with respect to biacetyl pressure.

4. Effect of Quanta Absorbed Per Ml. Per Second on the CO Quantum Yield.—Table III shows that at 25 and 60° a decrease in the rate of absorption per ml. increases the Φ_{CO} .

TABLE III
EFFECT OF QUANTA ABSORBED PER ML. PER SECOND ON
THE CO QUANTUM YIELD

$T = 25^\circ$ and 60° . Diethyl ketone pressure = 25 mm. Wave length = 3130Å.

Temp., °C.	$I_a \times 10^{11}$, quanta/ml./sec.	Φ_{CO}	Φ_{C_2}
25	99	0.56	
25	25	.71	
25	15.6	.72	0.18
25	12.5	.76	
25	1.79	.83	.21
60	99	.87	.21
60	25	.94	.22
60	15.6	.93	
60	1.79	.93	

2537 Å.—The results obtained at this wave length are:

1. Variation of Φ_{CO} , $\Phi_{C_2H_4 + C_2H_6}$, $\Phi_{C_4H_{10}}$ and Biacetyl Phosphorescence with Biacetyl Pressure in Diethyl Ketone-Biacetyl Mixtures.—The above variations are recorded in Table IV. The effects observed are:

TABLE IV
EFFECT OF BIACETYL PRESSURE ON THE CO, $C_2H_4 + C_2H_6$,
 C_4H_{10} QUANTUM YIELDS AND ON THE BIACETYL PHOSPHORESCENCE

$T = 25^\circ$. Diethyl ketone pressure = 25 mm. Quanta absorbed = 2.97×10^{10} quanta/ml./sec. Wavelength = 2537Å. Phosphorescence = 0.

Pressure biacetyl, mm.	Φ_{CO}	Φ_{C_2}	Φ_{C_4}	Φ_{C_2}/Φ_{C_4}
0	0.91	0.30	0.86	0.35
0.58	.89	.29	.81	.36
1.2	.91	.28	.81	.35

1. Increase in the biacetyl pressure does not affect the Φ_{CO} , Φ_{C_2} , Φ_{C_4} nor the biacetyl phosphorescence which was not observed.

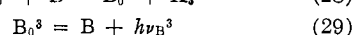
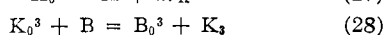
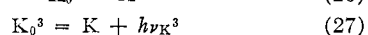
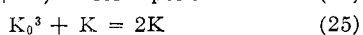
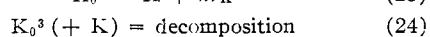
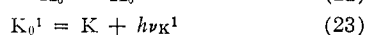
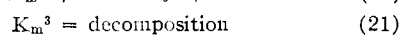
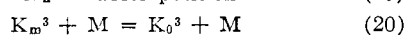
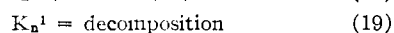
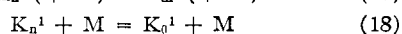
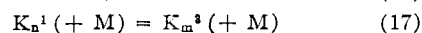
2. The ratio Φ_{C_2}/Φ_{C_1} remains constant but shows an increase over the values obtained at 3130 Å.

3. The Φ_{CO} , Φ_C , and Φ_{C_2} increase with decreasing wave length.

Discussion

Recent work²⁰ has led to the proposition of a detailed mechanism of the primary process in acetone which fits the broad outline visualized by Noyes, Porter and Jolley¹³ to cover simple ketones. The proposed process involves: (1) absorption producing an upper singlet state with a vibrational energy depending on the exciting wave length. The upper singlet can either decompose, pass over to an upper triplet or suffer collisional loss of vibrational energy followed by fluorescence to the ground state or internal conversion to the triplet state; (2) molecules in the triplet state can either decompose with an activation energy, phosphoresce or undergo internal conversion to the ground state. The addition of molecules such as oxygen or biacetyl would presumably remove this triplet state either in an energy transfer mechanism as suggested by Okabe and Noyes²¹ or by direct reaction.²²

Results obtained in the present work indicate that a similar mechanism may be involved in diethyl ketone. The proposed mechanism for diethyl ketone is:



where K is a normal diethyl ketone molecule, K_n^1 is a diethyl ketone molecule in the upper vibrational level of the excited singlet state, K_m^3 is a diethyl ketone molecule in the upper vibrational levels of the triplet state, K_0^1 is a diethyl ketone molecule in the low vibrational levels of the excited singlet state, K_0^3 is a diethyl ketone in the lower vibrational levels of the triplet state, B is a normal biacetyl molecule, B_0^3 is a biacetyl molecule in the low levels of the triplet state.

As in acetone²³⁻²⁷ a weak blue emission is pro-

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(22) G. B. Porter, *J. Chem. Phys.*, **32**, 1587 (1960).

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(27) H. J. Groh, Jr., G. W. Luckey and W. A. Noyes, Jr., *ibid.*, **21**, 115 (1953).

duced by light of wave length 3130 Å. The diethyl ketone emission occurs in the same region as the acetone emission but is much weaker. The addition of oxygen reduces the intensity slightly and appears to shorten the emission spectrum from the long wave length end. This suggests the removal of some triplet state diethyl ketone but the effect is small and indefinite.

When excited by 3130 Å. a mixture of diethyl ketone and biacetyl shows a very strong green emission with maxima at 5120, 5600 and 6000 Å. This is undoubtedly the biacetyl phosphorescence, thus indicating that the mechanism suggested by Okabe and Noyes,²¹ involving the energy transfer step 28 followed by step 29, is important. Corresponding energy transfer by the singlet state can be neither proved nor disproved.

As indicated in Table I and Fig. 1, the addition of biacetyl at 3130 Å. reduces Φ_{CO} , Φ_C , and Φ_{C_2} , and, increases the biacetyl phosphorescence. Both effects reach a limiting value at the same biacetyl pressure. This would indicate the removal by the biacetyl of the triplet diethyl ketone thereby causing a reduction in the decomposition products and an increase in the triplet state biacetyl. An increase in the phosphorescence is therefore produced. If this is the case, it would appear that in the limiting condition where further addition of biacetyl causes no further effect, decomposition comes solely from the singlet state and the decrease in primary quantum yield is a measure of the removal of the triplet state. This conclusion is supported by the parallel increase in phosphorescence.

From the above mechanism it can be shown that

$$\frac{1}{\phi_S} = 1 + \frac{(k_{17} + k_{18})(K)}{k_{19}} \quad (30)$$

$$\frac{1}{\phi_T} = X + Y(B) \quad (31)$$

$$\frac{(B)}{Q} = X^1 + Y^1(B) \quad (32)$$

where ϕ_S and ϕ_T are the primary quantum yields for the singlet and triplet states respectively, (K) is the diethyl ketone concentration, (B) is the biacetyl concentration, Q is the phosphorescence efficiency (a purely arbitrary number obtained by dividing the phosphorescence in microamps by the quanta absorbed per ml. per second) and X, X¹, Y, Y¹ are groups of constants. Equation 30 could not be verified due to experimental difficulty in obtaining the effect of diethyl ketone pressure on the product yield. The data in Figs. 2 and 3 show that relationships 31 and 32, respectively, are reasonably well obeyed.

The propionyl radical formed from the singlet state at 3130 Å. seems sufficiently "hot" to dissociate into an ethyl radical and carbon monoxide. Thus this part of the primary process leads to 2 C₂H₅ + CO. Evidence for this is found in the fact that the extrapolated value of Φ_{CO} at infinite intensity is virtually identical with the limiting value of Φ_{CO} when biacetyl is added. From the simplified reaction scheme 1, 2, 3, 4 and 6 and assuming (Et) = I_a^{1/2} C, where C is a constant and (Et) is the ethyl radical concentration, it can be shown that $\Phi_{CO} = \alpha + C^1 I_a^{-1/2}$ where α is the fraction of

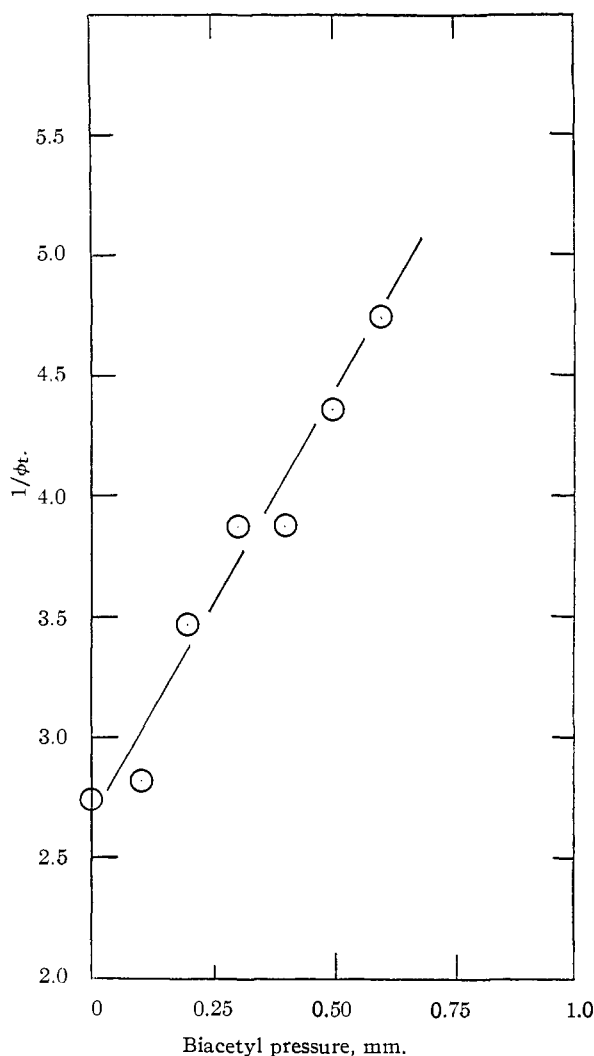


Fig. 2.—Plot of $1/\phi_t$ versus biacetyl pressure.

propionyl radicals which are "hot" and C^1 is a constant. At infinite intensity the intercept α tends to 0.44 at 25°, and although only two points are available on the straight line portion at 60°, a value near 0.78 is indicated at infinite intensity. While the singlet dissociation leads seemingly to $2 C_2H_5 + CO$, there seems to be some time lag in the formation of the second C_2H_5 and of the CO. In acetone²⁸ this is indicated by the fact that addition of I_2 nearly completely suppresses CO formation even at 2537 Å.

If the addition of biacetyl suppresses dissociation from the triplet state equally effectively at all temperatures, one is forced to the conclusion that the primary dissociation yield from the singlet state into ethyl and "hot" propionyl radicals increases with temperature and has an "apparent" activation energy of about 7.4 kcal. The meaning of this "apparent" activation energy is not clear but the following possibilities may be suggested: (a) molecules with more vibration energy in the ground state absorb 3130 Å to dissociate much more rapidly than do molecules with less vibration energy; (b)

(28) J. N. Pitts and F. E. Blacet, *J. Am. Chem. Soc.*, **74**, 455 (1952).

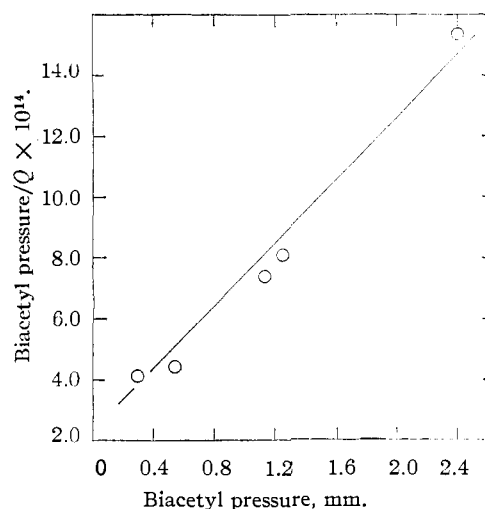


Fig. 3.—Plot of biacetyl pressure/ Q versus biacetyl pressure.

the upper singlet state may last long enough before having its vibration energy equilibrated with the surroundings to suffer a dissociation with a true activation energy. We are here confronted with unknowns but from the meager knowledge we have concerning loss of vibration energy and the lifetime of the upper singlet state, such a unimolecular dissociation of the singlet state may not be excluded. In the case of acetone²⁴ the small change of fluorescence with temperature argues against this possibility; (c) the triplet state biacetyl molecules may dissociate enough to yield carbon monoxide in adequate amounts at 60° to give the observed effect. Here again we are faced with an inadequate knowledge of the exact amount of energy transferred to the biacetyl. All of the evidence²⁹ from the behavior of pure biacetyl is against this explanation. Thus (a) is the most probable but neither (b) nor (c) may be excluded. It might be pointed out in passing that the CO from the singlet state should rapidly become negligibly small as the temperature is lowered. Measurements of this effect would be difficult because of the low vapor pressure of diethyl ketone.

At 2537 Å addition of biacetyl produces no effect on Φ_{CO} , Φ_C , or Φ_{C^1} , and no biacetyl phosphorescence was observed. Dissociation must occur from the initially formed upper state and there is no evidence that the triplet state intervenes at all. The process again is essentially a split into an ethyl radical and a "hot" propionyl radical, the latter always dissociating to give carbon monoxide and a second ethyl radical probably after a finite time interval. Insufficient data were available to calculate ϕ which however must be at least equal to Φ_{CO} . The high ratio of Φ_{C^1} to Φ_C is certainly due to the formation of C_2H_5 according to reaction 7. At the low intensities used, abstraction would be expected to be important. There is no evidence for or against "hot" ethyl radicals.

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(29) G. F. Sheats and W. A. Noyes, Jr., *ibid.*, **77**, 1421 (1955).