

concentrations. Various integers were substituted for  $n$  in the expression  $k' = k [\text{Et}_2\text{NH}]^n$  and  $k$  was calculated (see Table II). The constancy

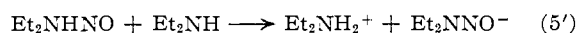
TABLE II<sup>a</sup>  
DETERMINATION OF THE ORDER OF DIETHYLAMINE

$[\text{Et}_2\text{NH}]_M$	$\frac{k'}{[\text{Et}_2\text{NH}]_n}$ (min. <sup>-1</sup> )	Various values of $k$ (min. <sup>-1</sup> )		
		$n = 1$	$n = 2$	$n = 1/2$
1.0	$4.05 \times 10^{-3}$	$4.05 \times 10^{-3}$	$4.05 \times 10^{-3}$	$4.05 \times 10^{-3}$
0.5	$2.48 \times 10^{-3}$	$4.96 \times 10^{-3}$	$9.9 \times 10^{-3}$	$3.51 \times 10^{-3}$
0.1	$5.14 \times 10^{-4}$	$5.14 \times 10^{-3}$	$51.4 \times 10^{-3}$	$1.61 \times 10^{-3}$

<sup>a</sup> Rate constants measured at 27°.

of  $k$  for  $n = 1$  supports a first order dependency of the rate on amine concentration. The resulting experimental rate expression  $d[\text{P}]/dt = k[\text{Et}_2\text{NH}] \cdot [\text{NO}]$  is in support of the mechanism II where the first step (equation 4) is slow and rate controlling.

An alternate mechanism 5' and 6' is possible instead of steps 5 and 6. This involves removal of the proton from  $\text{Et}_2\text{NHNO}$  before attack by NO



This sequence of reactions cannot be positively ruled out but is regarded as less likely for trimethylamine reacts with nitric oxide to produce  $(\text{CH}_3)_3\text{NN}_2\text{O}_2$ . This result indicates that formation of an anion is not necessary for the NO dimerization step.

The order of the reaction calculated by the differential procedure from the data in Table I and also from other sets yielded values for  $n = 1.0$  to 1.2.

The rate constant for this reaction was measured in the temperature range 18.5 to 35° by assuming that  $\epsilon_p$  and  $\epsilon_{\text{NO}}$  have constant values over this temperature range. The results are contained in Table III. From these data a value of  $12.0 \pm 3.8$  kcal. mole<sup>-1</sup> is calculated for the activation energy. The error is estimated at the 90% confidence level.

TABLE III

TEMPERATURE DEPENDENCE OF THE RATE CONSTANT

Temp., °C.	$[\text{Et}_2\text{NH}]$ , mole/l.	$k^a$
18.5	1.0	$2.3 \pm 0.2 \times 10^{-3}$
25	1.0	$4.2 \pm .2 \times 10^{-3}$
27	1.0	$4.05 \pm .2 \times 10^{-3}$
27	0.5	$4.96 \pm .2 \times 10^{-3}$
27	0.1	$5.1 \pm .2 \times 10^{-3}$
30	1.0	$4.4 \pm .2 \times 10^{-3}$
35	0.5	$8.8 \pm .2 \times 10^{-3}$
35	1.0	$7.8 \pm .2 \times 10^{-3}$

<sup>a</sup> Since the reaction is first order in  $\text{Et}_2\text{NH}$ , the  $k$  values can be calculated from  $k = k'/[\text{Et}_2\text{NH}]$ .

The kinetic data enable us to explain an interesting observation made in the synthesis<sup>1</sup> of the diethylammonium salt by the reaction of diethylamine and nitric oxide in ether at -78°. Even though the product is insoluble and precipitates from solution, the yield realized is only 11%. Additional product could be obtained by further reaction of the filtrate, demonstrating that an inhibitor was not formed. Evidently the reaction is very slow at -78°, and most of the product is obtained when the ether solution saturated at the low temperature is allowed to warm to room temperature in the work up. An increase in the amount of solid present in the reaction vessel is detected during the warm-up period. The yield obtained is determined by the amount of nitric oxide that has dissolved. When the reaction is carried out at room temperature, no compound is obtained. This probably is due to both the low solubility of nitric oxide in ether and the slow rate of absorption of nitric oxide in ether at room temperature. The product decomposes as fast as it is formed under these conditions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ARIZONA, TUCSON, ARIZONA]

## The Photolysis of Biacetyl Solutions<sup>1</sup>

BY STANLEY A. GREENBERG<sup>2</sup> AND LESLIE S. FORSTER

RECEIVED DECEMBER 8, 1960

Quantum yields of carbon monoxide, ethane and methane formation and biacetyl disappearance have been obtained for biacetyl dissolved in perfluoro-*n*-octane, FC-75, and mineral oil at 3660 and 4358 Å. as a function of concentration and temperature up to 100°. Only the mineral oil solutions were decomposed appreciably at 25°. In all solutions a 2nd order reaction between an excited biacetyl and an unexcited molecule occurs. In other respects, the 4358 Å. primary process is the same as that proposed by Sheats and Noyes. The carbon monoxide yield decreases markedly with biacetyl concentration at 3660 Å. but not at 4358 Å. The character of the reaction is therefore different at the two wave lengths. The primary process appears to be viscosity dependent at 3660 Å.

Although the gas-phase photochemistry of biacetyl has been the subject of numerous investi-

gations<sup>3</sup> and several reports on the luminescence of biacetyl solutions have appeared,<sup>4</sup> little infor-

(1) Based on a dissertation submitted by S. A. Greenberg in partial fulfillment of the requirements for the Ph.D. degree, University of Arizona. This research was supported by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) National Science Foundation Coöperative Graduate Fellow, 1959-1960.

(3) (a) G. F. Sheats and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **77**, 1421, 4532 (1955). (b) W. A. Noyes, Jr., G. B. Porter and J. E. Jolley, *Chem. Revs.*, **56**, 49 (1956). (c) H. Okabe and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **79**, 801 (1957).

(4) (a) L. S. Forster, S. A. Greenberg, R. J. Lyon and M. E. Smith, *Spectrochim. Acta*, **16**, 128 (1960). (b) H. L. J. Backstrom and K. Sandros, *Acta Chem. Scand.*, **12**, 3 (1958). (c) H. L. J. Backstrom and K. Sandros, *ibid.*, **14**, 48 (1960).

TABLE I  
 $\Phi_{B_2} = 1/2(\Phi_B - 1/2\Phi_{CO})$

Biacetyl concn. (mole/l.)	$\Phi_B$	$\Phi_{CO}$	$\Phi_{CH_4}$	$\Phi_{C_2H_6}$	$\Phi_{B_2}$
FC-75, 100°, 4358 Å., $\eta = 0.52$ cp.					
0.0098	0.00413	0.00046	0.000138	0.000048	0.0019
.0200	.00597	...	...	...	...
.0232	.00633	.00062	.000187	.000062	.0030
.0246	.00638	...	...	...	...
.0424	.00871	.00092	.000273	.000079	.0041
.0848	(.00328)	.00034	.000102	.000033	.0015
FC-75, 100°, 3660 Å.					
0.00196	0.0109	0.0205	0.0214	0	0.0004
.00330	.00992	.0161	.0154	0.000037	.0009
.0182	.0115	.00345	(.000644)	(.00144)	.0049
.0274	.00902	.00146	.000888	.00020	.0041
.0378	.0108	...	...	...	...
.0403	.0100	.00102	.000602	.00023	.0047
.0473	.0105	.00111	.000543	.00026	.0049
.143	.0143	.000204	.00042	.00007	.0069
.205	.164	.00057	0	(.00034)	.082
Perfluoro- <i>n</i> -octane, 100°, 4358 Å., $\eta = 0.63$ cp.					
0.00467	0.000635	0.00037	0	0.00014	0.00025
.0107	.000950	.00044	0	.00022	.00037
.0244	.00136	.00034	0	.00017	.00058
.0692	.00208	.00058	0	.00028	.00090
Perfluoro- <i>n</i> -octane, 100°, 3660 Å.					
0.00773	0.00240	0.00368	0	0.00184	0.00028
.0251	.00263	.00277	0	.00139	.00062
.0389	.00226	.00145	0	.00073	.00077
.0719	.00247	.00126	0	.00063	.00090
.180	.00260	.00061	0.00002	.00030	.00115
Mineral oil, 25°, 3660 Å., $\eta = 34.1$ cp.					
0.00916	0.00153	0.00230	0	0.00114	0.00017
.0097	.00151	...	...	...	...
.0126	.00151	.00211	(0.00132)	(.00039)	.00022
.0672	.00156	.00159	0	.00080	.00038
.110	.00162	.00156	0	.00078	.00042
Mineral oil, 100°, 3660 Å., $\eta = 4.27$ cp.					
0.00528	0.00558	0.00877	0.00099	0.0038	0.00060
.00929	.00570	.00738	0.00009	.0037	.00075
.0187	.00565	.00408	0	.0020	.0032
.0328	.00528	.00277	0	.0014	.0035

mation about the photodecomposition of biacetyl in solution is available. In the only published work concerned with the solution photolysis,<sup>5</sup> the reaction observed was undoubtedly between traces of oxygen and biacetyl molecules in the long-lived triplet state.<sup>4a</sup> Liquid phase photolytic studies of acetone<sup>6</sup> and other ketones<sup>7</sup> have indicated the difficulties to be expected as well as the potentialities for useful information. The present work was initiated with the aim of filling in the remaining gap in the knowledge of biacetyl photochemistry.

A complete elucidation of the mechanism would require data on the nature and quantities of all

the products formed in the photolysis. In this study the only quantum yields measured were those of biacetyl disappearance and methane, ethane and carbon monoxide formation. These quantities were determined as a function of solvent, temperature, excitation wave length and intensity and biacetyl concentration. The solvents employed were a perfluoroether (FC-75), perfluoro-*n*-octane and mineral oil.

### Experimental

Biacetyl, a Lucidol product, was distilled under reduced pressure in a Todd column, further purified by bulb to bulb distillation, and stored *in vacuo* at  $-78^\circ$ . FC-75, a fluorinated ether manufactured by Minnesota Mining and Mfg. Co., was purified by refluxing with acid  $KMnO_4$  and passing through silica gel. On one occasion an explosion resulted from this procedure. A highly purified sample of perfluoro-*n*-octane was generously supplied by the same company and was used without further purification. N. F. mineral oil of viscosity 100-110 was used without purification.

(5) E. J. Bowen and A. T. Horton, *J. Chem. Soc.*, 1505 (1934).

(6) (a) D. B. Peterson and G. J. Mains, *J. Am. Chem. Soc.*, **81**, 3510 (1959). (b) R. Pieck and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1304 (1955). (c) P. E. Frankenburg and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **75**, 2847 (1953).

(7) P. Ausloos, *Can. J. Chem.*, **36**, 400 (1958).

Samples were prepared by thoroughly degassing the solvent, distilling the biacetyl into a 1 cm. cell of about 5 ml. volume and sealing this off under vacuum. The extent of oxygen removal was checked by the determination of the lifetime of biacetyl phosphorescence.<sup>4a,b</sup> No thermal reaction was observed at 100° in any of the systems employed. 3660 or 4358 Å. radiation from an AH-6 or an AH-4 mercury lamp was allowed to pass through the sample cell which was mounted in a brass block furnace. The excitation intensity was monitored by a phototube-galvanometer system which also served as a simple photometer to determine the number of quanta absorbed by the sample. This quantity, which varied from 10<sup>12</sup>–10<sup>16</sup> quanta/cc./sec., was determined by uranyl oxalate actinometry. The initial and final concentrations were determined by the use of a Beckman DU Spectrophotometer. The extent of decomposition was usually kept below 5%. Irradiation times ranged from one to 117 hr.

After irradiation, the sample cell was sealed into an analytical system equipped with mercury cutoffs. The break-seal was broken and the gaseous products removed by refluxing the solvent into contact with a cold finger kept at -78°. This gas was drawn by means of a Toepler pump through a -150° trap to remove traces of solvent and through a -196° trap to condense ethane. The carbon monoxide was oxidized in a Cu-CuO furnace. Carbon dioxide, methane and ethane were successively toepled into a calibrated volume and the pressures recorded.

In many runs, small amounts of a brown oil, insoluble in the solvent, were formed. This material did not absorb appreciably at  $\lambda > 400 \text{ m}\mu$ .

### Results

The results are presented in Table I. In several cases, the cell cracked before the analysis. Data that are questionable are enclosed in parentheses.  $\Phi_B$  represents the quantum yield of biacetyl disappearance.

$\Phi_B$  may not be as reliable as  $\Phi_{CO}$ ,  $\Phi_{CH_4}$  and  $\Phi_{C_2H_6}$ . Should any of the products absorb appreciably at 418 m $\mu$ , the wave length used to follow the biacetyl disappearance, the calculated values of  $\Phi_B$  would be too low. To check this point we determined the spectrum of a sample before and after photolysis, with a Cary Spectrophotometer. The number of moles of biacetyl decomposed was kept rather high to magnify the effect. A slight change in spectrum did occur. Although the apparent concentration independence of  $\Phi_B$  at 3660 Å. may be illusory, the difference in the 4358 and 3660 Å. behavior is meaningful. The approach of  $\Phi_{CO}/\Phi_B$  to two at low concentration indicates that the results here are reliable.

**Temperature Dependence.**—In neither the FC-75 nor the perfluoro-*n*-octane systems did prolonged irradiation result in appreciable decomposition at 25°.  $\Phi_B$  is about one-hundredth as large at 25° as at 100°. One run at 75° in FC-75 at 3660 Å. (biacetyl concentration = 0.0825 *M*) resulted in  $\Phi_B = 0.0083$ .

**Intensity Dependence.**—A 10-fold intensity variation did not result in significant changes in  $\Phi_B$ ,  $\Phi_{CO}$ ,  $\Phi_{CH_4}$  or  $\Phi_{C_2H_6}$ .

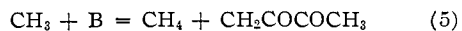
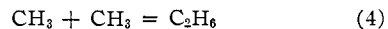
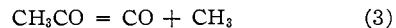
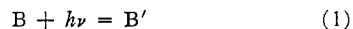
**Lifetime Dependence.**—The lifetime of the triplet state decreased from about 1000  $\mu\text{sec.}$  before irradiation to the neighborhood of 70  $\mu\text{sec.}$  after irradiation. Both the initial and final lifetimes varied considerably from run to run and the trends described below hold despite this random lifetime fluctuation. However, the lifetimes were measured at 25° while most of the photolyses were made at 100° and the lifetime decreases by a factor of six in this interval because of thermal quench-

ing. The participation of the lowest triplet state in the decomposition cannot be conclusively eliminated on this basis.

**Dependence on Extent of Decomposition.**—The fraction of biacetyl decomposed was varied by a factor of two while the initial concentration was kept nearly constant. No meaningful variation in any of the quantum yields was observed.

### Discussion

Several of the steps in the generally accepted gas-phase mechanisms are<sup>3a</sup>



In terms of the gas-phase mechanism, the results lead to a number of conclusions.

(i) At 3660 Å.  $B'$  corresponds to a high vibrational level of the 1st excited singlet state.<sup>8</sup> The absence of appreciable decomposition at 3660 Å. and 25° in FC-75 and perfluoro-*n*-octane indicates that the removal of the vibrational energy by the solvent is so rapid that predissociation cannot take place and that only internal conversion to the lowest triplet state is of importance. The mineral oil results will be considered below.

(ii) With the exception of FC-75 solutions at 4358 Å. ( $\Phi_{CH_4} + \frac{1}{2}\Phi_{C_2H_6}$ )/ $\Phi_{CO}$  is close to unity. This means that (6) is unimportant. The absence of  $\text{CH}_4$  in perfluoro-*n*-octane and mineral oil precludes (5). The formation of  $\text{CH}_4$  in FC-75 will be considered below.

(iii) If steps 5 and 6 are excluded, then the above mechanism predicts that  $\Phi_B = \frac{1}{2}\Phi_{CO}$ . It can be seen in Fig. 1 that this is true only as  $(B)$  approaches zero. A reaction of the type



must consequently be added.  $B''$  indicates some relatively long-lived species. For the moment further specification of this species is not essential. If biacetyl disappears by (1) – (4) and (7) – (8) then  $\Phi_{B_2} = \frac{1}{2}(\Phi_B - \frac{1}{2}\Phi_{CO})$ . The values of  $\Phi_{B_2}$  are included in Table I. At very low concentration the rate of step 8 will be negligible, the reaction will be most "gas-like," and  $\frac{1}{2}\Phi_{CO}$  should be a measure of the primary dissociation yield less geminate ("cage") recombination. The high pressure gas-phase<sup>3a</sup> and these low concentration limiting solution  $\Phi_{CO}$  (Fig. 3) are listed in Table II. The gas-phase  $\Phi_{CO}$  are also roughly twice the primary yield.

TABLE II  
LIMITING  $\Phi_{CO}$  AT 100°

Excitation wave length, Å.	Gas <sup>3a</sup>	Perfluoro- <i>n</i> -octane	FC-75	Mineral oil
3660	0.21	0.005	0.10	0.016
4358	0.06	0.0002	0.0003	

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

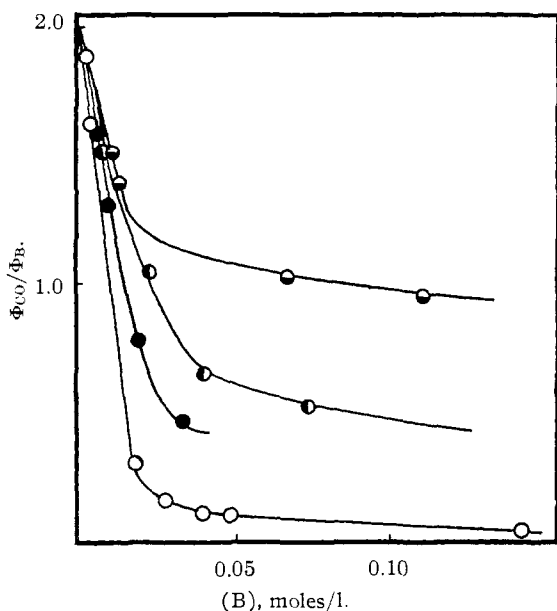


Fig. 1.— $\Phi_{CO}/\Phi_B$  vs. biacetyl concentration at 3660 Å. Solvents are: ○, FC-75 (100°); ●, mineral oil (100°); ◐, mineral oil (25°); ●, perfluoro-*n*-octane (100°).

The low quantum yields in solution might be ascribed to the high probability of geminate recombination.<sup>9,10</sup> It has been suggested<sup>6a,b</sup> that solvent deactivation may also be of importance in liquid systems. The much higher  $\Phi_{CO}$  in FC-75 than in perfluoro-*n*-octane parallels the results found by Peterson and Mains<sup>6a</sup> for the liquid-phase photolysis of acetone.

The photolysis appears to follow a different path at the two wave lengths employed in this study. The following differences merit consideration.

(iv) The limiting  $\Phi_{CO}$  are *much* larger at 3660 Å. than at 4358 Å.

(v) As (B) is increased  $\Phi_{CO}$  decreases markedly at 3660 Å. but remains constant or increases slightly at 4358 Å.

(vi)  $\Phi_B$  increases more rapidly with (B) at 4358 Å. than at 3660 Å. The results at the two wave lengths will be considered separately.

**4358 Å.**—The primary process at 4358 Å. in the liquid phase may be the same as that proposed by Sheats and Noyes<sup>3a</sup> for the gas-phase reaction at 100°, *i.e.*, dissociation occurs thermally from  $B'$ , the low vibrational levels of the initially excited  $^1A_u$  state. An activation energy for step 2 is required to explain the temperature dependence of the primary yield. It has been observed<sup>11</sup> that the gas-phase fluorescence yield is temperature independent. The same temperature independence is observed in solution. Due to the large (~99%) internal conversion from the  $^1A_u$  state to the lowest triplet state, a dissociation yield as large as 0.05 would not affect the fluorescence yield (0.003) appreciably. The possibility that dissociation occurs from the triplet state cannot be excluded.

In perfluoro-*n*-octane the  $\Phi_{CO}$  yields scatter somewhat but no substantial dependence on (B)

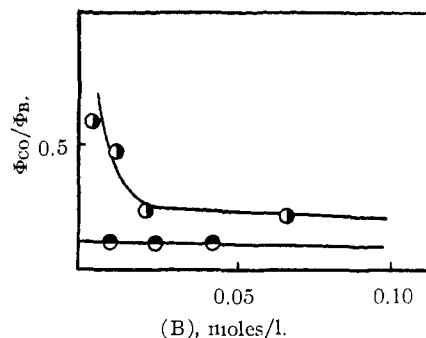


Fig. 2.— $\Phi_{CO}/\Phi_B$  vs. biacetyl concentration at 4358 Å. and 100°. Solvents are: ○, FC-75; ●, perfluoro-*n*-octane.

is observed for this quantity. The increase in  $\Phi_{CO}$  with (B) in FC-75 is difficult to explain. However some reaction of  $B'$  (or  $B''$ ) or  $CH_3CO$  with FC-75 is required to explain the constancy of  $\Phi_{CO}/\Phi_B$  at about 0.1 (Fig. 2) in this solvent and the much larger  $\Phi_B$  in FC-75 than in perfluoro-*n*-octane. In the latter solvent the data are not conclusive but  $\Phi_{CO}/\Phi_B$  does increase as (B) is diminished, and appears to approach two.

**3660 Å.**—The diminution in  $\Phi_{CO}$  with (B) would be expected if the primary dissociation is



The competition between steps 8 and 9 would then lower  $\Phi_{CO}$  as (B) increases.  $B''$  cannot correspond to  $B'$ , the high vibrational level of  $^1A_u$  reached by 3660 Å. excitation, because the lifetime of this state would be too short. In addition, no reaction was observed at 25°. Neither can  $B''$  be the lowest vibrational level of  $^1A_u$  or the lowest triplet state because the mechanism would then be the same at both wave lengths, contrary to our results. We suggest that  $B''$  is formed from  $B'$  by



The mathematical formalism will not depend upon the identity of  $B''$ . A steady state treatment gives

$$\frac{1}{\Phi_{CO}} = \frac{k_9 + k_{13}}{2k_8\alpha} + \frac{k_8(B)}{2k_8\alpha} \quad (11)$$

$$\frac{1}{\Phi_{B_2}} = \frac{1}{\alpha} + \frac{k_9 + k_{13}}{k_8\alpha(B)} \quad (12)$$

where  $\alpha$  represents the fraction of initially excited molecules that reach  $B''$  by step 10 and  $k_{13}$  is the aggregate rate constant for all the radiationless processes of  $B''$  that compete with steps 8 and 9. That equations 11 and 12 are consistent with the results can be seen in Figs. 3 and 4. It is possible to evaluate  $\alpha$  from the slopes and intercepts in Fig. 4. In the case of perfluoro-*n*-octane we find that  $\alpha = 0.0013$ . If all the  $B''$  react by either (8) or (9) then the limiting  $\Phi_{CO}$  would be twice as large as  $\alpha$ , or 0.0026. In accord with the preceding discussion we expect that the calculated  $\Phi_{B_2}$  may be too low because of interference in the analysis by the products. This would make the agreement better. The corresponding agreement for FC-75 and mineral oil solution is much poorer. Of additional interest is the comparison of  $(k_9 + k_{13})/k_8$  obtained from equations 11 and 12. These agree well (within 10%) for the perfluoro-*n*-octane solu-

(9) R. M. Noyes, *J. Phys. Chem.*, **63**, 19 (1959).

(10) R. M. Noyes, *J. Am. Chem. Soc.*, **82**, 1868, 1872 (1960).

(11) H. Okabe and W. A. Noyes, Jr., *ibid.*, **79**, 801 (1957).

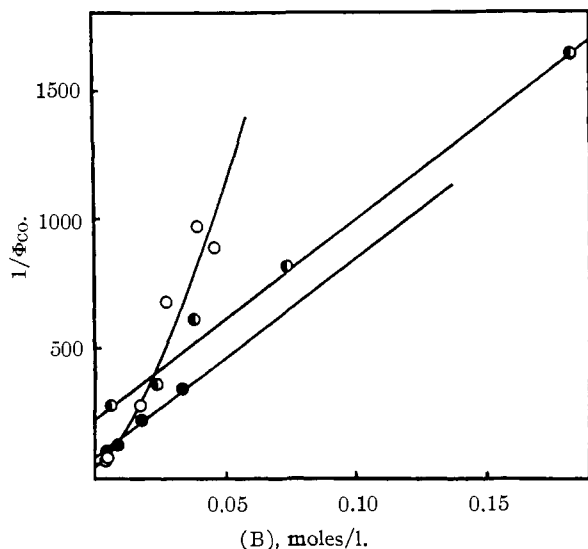


Fig. 3.— $1/\Phi_{CO}$  vs. biacetyl concentration at 3660 Å. and 100°. Solvents are: ○, FC-75; ◐, perfluoro-*n*-octane; ●, mineral oil.

tions. We do not claim that these calculations confirm the proposed mechanism. Any mechanism in which a long-lived species produces CO and/or reacts with normal biacetyl molecules will lead to the same type of numerical concordance and this treatment is merely illustrative of the results to be expected.

It is desirable to consider the physical meaning and plausibility of step 10. If such a reaction is important, the absence of decomposition at 25° can only be interpreted as meaning that the removal of vibrational energy by solvent molecules is so efficient that (10) does not occur to an appreciable extent at 25° but that at 100° this vibrational deactivation is less efficient. The gas phase results of Sheats and Noyes<sup>3a</sup> do show that the primary yield is diminished with increasing pressure and that this pressure effect is more pronounced as the temperature is decreased. This implies that vibration deactivation is much more efficient at 25° than at 100°. We might speculate that B'' is a tautomer of biacetyl or a second triplet state. The difference in the behavior at the two wave lengths precludes the participation of the lowest triplet at 3660 Å. in the major part of the primary dissociation because this state would be populated to an equal extent at both wave lengths.

The mineral oil results may be considered in terms of this deactivation hypothesis. The very high viscosity of mineral oil at 25° might so inhibit the removal of vibrational energy that (10) can occur. Further work with solvents of different viscosities, at both wave lengths, would be useful in testing this suggestion.

The importance of step 10 in the gas-phase mechanism is questionable. The 3660 Å. primary yield is less dependent on temperature in the gas than in solution and perhaps the only effect of collision is to prevent predissociation. It should be remembered that in the gas-phase the decrease in primary dissociation is accompanied by

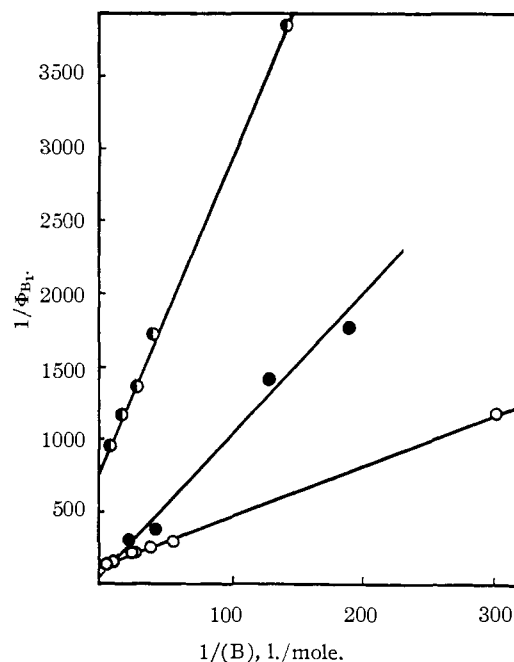


Fig. 4.— $1/\Phi_{B_2}$  vs. reciprocal of biacetyl concentration at 3660 Å. and 100°. Solvents are: ○, FC-75; ◐, perfluoro-*n*-octane; ●, mineral oil.

an increase in fluorescence. The fluorescence and phosphorescence yields are nearly the same in solution and in the gas-phase and are independent of solvent (including FC-75).<sup>4a</sup>

**The Mechanism of C<sub>2</sub>H<sub>6</sub> Formation.**—Only at very high concentrations is methane produced in perfluoro-*n*-octane solutions. When the intensity and concentration are comparable to those employed in the gas-phase work, no methane is produced, although in the gas-phase, methane and ethane are formed in roughly equivalent amounts. If the ethane is produced by recombination of methyl radicals originating from different biacetyl molecules then the only explanation for the absence of methane would be a smaller steric factor for methyl abstraction of hydrogen from biacetyl in solution than in the gas. There is some evidence that this may be the case.<sup>12</sup> The possibility that "cage" recombination is responsible for the ethane cannot be excluded. Experiments with mixtures of (CH<sub>3</sub>CO) and (CD<sub>3</sub>CO)<sub>2</sub> would remove this doubt.

The formation CH<sub>4</sub> in FC-75 solutions is to be expected because of the demonstrated presence of considerable quantities of reactive hydrogen in the solvent.<sup>6a</sup> The corresponding absence of methane in mineral oil solutions is somewhat surprising, especially in view of some results in heptane solutions. In the latter case considerable methane is produced. Evidently the activation energy for hydrogen abstraction by methyl radicals is greater for mineral oil than for heptane.

**Conclusion.**—It is a truism that a kinetic mechanism cannot be established unambiguously. We must emphasize, however, that the limited data

(12) C. Walling, "Free Radicals in Solution," John Wiley and Sons, New York, N. Y., 1957, p. 495.

that have been collected in this study require that we exercise more than the usual caution in the interpretation. The reproducibility of the results and the trends obtained do indicate the usefulness of liquid phase photochemical studies as a supple-

ment to the more fundamental work in the gas-phase. A study of the solution photolysis at 4047 Å. and at wave lengths shorter than 3660 Å. would be very helpful in testing the proposed mechanism.

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## Photochemistry of Cyclopentanone. I. Details of the Primary Process<sup>1a</sup>

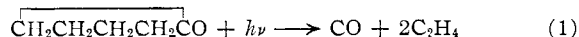
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In the photochemistry of cyclopentanone, three processes are known to be important. These lead to  $\text{CO} + 2\text{C}_2\text{H}_4$  (1),  $\text{CO} + \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$  (2) and 4-pentenal (3), respectively. Evidence is now presented to show that since there is no detectable light emission from cyclopentanone when excited at 3130 Å., and since oxygen does not suppress any of the processes, these processes probably do not arise from a triplet state. Photolysis of cyclopentanone in the presence of  $\text{O}_2^{18}$  does not lead to detectable amounts of cyclopentanone- $\text{O}^{18}$ . The effect of pressure or of the addition of a foreign gas on the distribution of the products has been interpreted to mean that the relative importance of the three photochemical processes (which probably occur from the same upper singlet state) is dependent on the vibrational energy possessed by the molecule at the instant of decomposition. It is estimated that the lowest vibrational level at which the processes leading to carbon monoxide, *i.e.*, (1) and (2) can still occur differ by 2.5 kcal. from the lowest vibrational level from which process (3) can occur. The lack of a scavenging effect on the products through the addition of even 35.5 mm. of oxygen suggests that the previously postulated diradical hypothesis for (1) and (2) should be reconsidered.

### Introduction

The photolysis of cyclopentanone in the vapor phase has been the subject of several investigations over the past 25 years.<sup>2-8</sup> It was shown by Benson and Kistiakowsky<sup>3</sup> that the important products were carbon monoxide, ethylene and cyclobutane. Later work<sup>6</sup> showed that 4-pentenal was also an important product under certain conditions. From a consideration of the mass balance, three photochemical processes have been postulated



Quantum yields for the first two processes have been obtained by Blacet and Miller<sup>5</sup> and for the third process by Srinivasan.<sup>6</sup> It was suggested<sup>3</sup> that the first two processes involved a diradical intermediate. Miller<sup>4</sup> has emphasized that this is an *a priori* hypothesis which needs to be tested by the addition of radical scavengers to the system.<sup>9</sup>

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(2) O. D. Saltmarsh and R. G. W. Norrish, *J. Chem. Soc.*, 455 (1935).

(3) S. W. Benson and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **64**, 80 (1942).

(4) A. Miller, Thesis, University of California at Los Angeles (1952).

(5) F. E. Blacet and A. Miller, *J. Am. Chem. Soc.*, **79**, 4327 (1957).

(6) R. Srinivasan, *ibid.*, **81**, 1546 (1959).

(7) J. Janak, M. Rusek and A. Lazarov, *Chem. listy*, **49**, 780 (1955).

(8) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3953 (1959).

(9) Attempts<sup>4</sup> to use iodine as such a scavenger failed as cyclic ketones reacted with this element even in the dark.

In this work attempts were made to study the intermediate state(s) involved in the photochemistry of cyclopentanone by the addition of a radical scavenger, inert gases and by variations in temperature. Most of the results reported here have been obtained at 3130 Å. and at temperatures less than 130°. Under these conditions reactions 1 to 3 account for all the cyclopentanone that disappears.<sup>5</sup>

### Experimental

**Materials.**—Cyclopentanone (Eastman Kodak White Label) was fractionated on a spinning-band column of 23 plates at a reflux ratio of 20:1. A middle cut which boiled over a 0.7° range was collected and used. It was admitted to the vacuum line, degassed at -78° and stored at that temperature.

Methane (Phillips Petroleum Co.) and oxygen (Linde Co.) were commercial grades. They were used without purification.  $\text{O}_2^{18}$  was obtained from the Weizmann Institute of Science, Rehovoth, Israel.<sup>10</sup>

**Apparatus.**—A conventional vacuum system in which the ketone did not come in contact with stopcock grease was used. Photolyses were carried out in a quartz cell 20 cm. × 2.7 cm. It was enclosed in an aluminum block furnace. The light source was a Hanovia type SH medium pressure mercury arc filtered by 2 mm. of Pyrex glass. The useful radiation was mainly 3130 Å. Three runs were made with a chlorine gas filter 5 cm. long and filled to a pressure of 460 mm. which transmitted light in the region 2300 to 2800 Å. These results are reported as obtained at 2537 Å. In experiments in which a foreign gas was added, a mixing device similar to the one already described<sup>11</sup> was used.

**Analysis.**—The fraction removed at liquid nitrogen temperature consisted of carbon monoxide. The fraction removed at Dry Ice-acetone temperature was a mixture of ethylene and cyclobutane. It was analyzed on a Consolidated Engineering Co. type 21-620 mass spectrometer. Data presented in each of the tables were obtained from analyses made at the same time after a calibration. The residue after the removal of  $\text{C}_2$  and  $\text{C}_4$  hydrocarbons was introduced into a Perkin-Elmer 154-D vapor fractometer fitted with a diisodecyl phthalate column (2 meters) heated to 98°. 4-Pentenal (retention time, 14 min.) was estimated from the area

(10) For isotopic analysis see ref. 11.

(11) R. Srinivasan and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **82**, 5591 (1960).