# The Photochemistry of Cyclopentanone in the Gaseous Phase

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The mechanism of the photochemical reactions of cyclopentanone has been investigated by obtaining quantum yields of products (CO,  $C_2H_5$ ,  $c-C_5H_5$ , 4-pentenal) as a function of pressure, of temperature, and to a lesser extent of wavelength. At 3130 Å the pentenal decreases with increase in temperature and increases with increase in pressure, thus showing in agreement with earlier work by others that this product is formed mainly from low vibrational levels of an excited state. The ratio  $C_2H_4/c-C_4H_5$  at 3130 Å is independent of all variables, but there may be a slight increase at low pressures at 2537-2654 Å. This latter point is not very definite. Ratios of rate constants for several steps in the proposed mechanism are given. There is no kinetic proof that the triplet state plays any part in this gas phase photolysis. 1,3-Pentadiene (*trans*) seems to exert no other effect than that of vibrational relaxation, and there seems to be no detectable *cis-trans* isomerization of the pentadiene. By analogy with other similar molecules one might expect those molecules which do not react in the singlet state to cross over to the triplet state. In the present case there is no proof that electronic relaxation to the ground state occurs *via* the triplet rather than directly by internal conversion, but steps must be included in the mechanism for destruction of the singlet state which are first order and do not lead to products.

### Introduction

The photochemistry of cyclopentanone has been the subject of active investigation since  $1935,^{2-11}$  and a summary up to 1963 has been given by Srinivasan.<sup>12</sup>

Upon irradiation with ultraviolet light gaseous cyclopentanone decomposes to give ethylene, cyclobutane, and carbon monoxide;<sup>3,4</sup> it also rearranges to form 4-pentenal<sup>5</sup>

$$\begin{array}{c} \overset{H}{\longrightarrow} CH_2 = CH - CH_2 CH_2 C = 0 \quad (3) \end{array}$$

It has been found<sup>6</sup> that at 3130 Å, while the yield of disappearance of the ketone remained roughly constant, process 3 becomes increasingly important at the expense of processes 1 and 2 with decreasing temperature and with increasing pressure, but the ratio of ethylene to cyclobutane shows little change. There may, however, be a slight increase in this ratio at pressures below about 5 Torr. Addition of oxygen up to 275 Torr shows effects comparable to those of other added gases commonly regarded as inert, and there was virtually no exchange with  $O^{18}-O^{18}$ . These results have been interpreted as indicating that all three processes 0 ccur from the excited singlet state, with processes 1 and 2 requiring higher vibrational energy than 3.<sup>6</sup>

On the other hand, a detailed analysis<sup>11</sup> of the results of the benzene sensitization of cyclopentanone photolysis indicates that the processes which yield CO may arise from the excited singlet state, but that pentenal may come from the triplet state. This does not prove, of course, that pentenal comes from the triplet state in the ordinary unsensitized photolysis. In the liquid phase photolysis<sup>10</sup> pentenal is the only major product, and its formation is significantly quenched by adding oxygen or pentadiene, an observation which is consistent with a mechanism involving the triplet state.

In agreement with the findings of the liquid phase photolysis, fluorescence as well as phosphorescence of cyclopentanone have been observed in condensed media, but only fluorescence could be detected in the gas phase<sup>13-15</sup> although the yield is very low.

It thus appears that the role of multiplicity in the photochemical processes during direct photolysis is not fully resolved.

In the present work, attempts have been made to establish the mechanism by which the various processes

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of excited cyclopentanone take place through the determination of quantum yields, and the study of effects of pressure, added gases, temperature, and wavelength of exciting light.

### **Experimental Section**

Material. Cyclopentanone was obtained from Matheson Coleman and Bell. It was purified with preparative gas chromatography. The final product was better than 99% pure, but contained an impurity which had a retention time slightly shorter than that of cyclohexanone with a capillary MBMA (mixture of *m*-bis-*m*-phenoxyphenoxybenzene and apiezon L) column. The compound was degassed by several freeze-pump-thaw cycles before being admitted to the photolysis cell.

trans-Pentadiene (Aldrich Chemical Co., Inc.) originally contained a trace of the *cis* isomer but after purification with preparative gc no *cis* isomer could be detected with a Perkin-Elmer F11 chromatograph. The *trans*-diene was degassed before use.

Spectrograde acetone (Eastman Kodak) was used without further purification but was degassed before use.

The monatomic gases listed below were used without further treatment, except for degassing in the case of xenon: argon (Matheson, 99.98%); helium (Matheson 99.995%) krypton and xenon (Matheson research grade, 99.995%).

Apparatus. A grease-free, mercury-free Pyrex glass vacuum line equipped with Hoke 413 and 413-A metal valves in the manifold and large Veeco valves in the main line was employed. Two Wallace and Tiernan metal gauges were used for pressure reading: Model FA-160150 for the pressure range 0.1-20 Torr, and Model FA-160240 for 0 to 800 Torr. A cold cathode gauge in the main line provided assurance that the system pressure did not exceed  $10^{-4}$  Torr for all runs.

The photolysis cell was made of quartz and was cylindrical, 10 cm long with end windows of 45 mm i.d. Dead space was about 30% of the total volume up to the metal valve. The cell and the dead space were encased in an oven made of asbestos boards with heating tapes attached to the rear wall. The oven had two circular quartz windows for passage of the light beam. Fluctuations of temperature in the vicinity of the cell were usually less than 1°.

The light source was a Hanovia S-100 mercury lamp. A filter combination of 5 cm of  $CoSO_4$ -NiSO<sub>4</sub> mixed solution and 1 cm of potassium biphthalate solution was used to isolate light essentially of 3130 Å. Another filter system of 5 cm of the  $CoSO_4$ -NiSO<sub>4</sub> solution, 1 cm of KI<sub>3</sub> solution, and 5 cm of chlorine gas at atmospheric pressure provided a means for isolating the 2537-Å line, <sup>16,17</sup> but some 2654-Å light is also included. Usually the solutions were renewed after a run. The light was collimated with a quartz lens to form a beam

which filled the cell. Light intensity was monitored with an RCA 935 phototube connected to a Keithley 410 micromicroammeter. Before reaching the active surface of the phototube, the beam passed through a glass filter (Corning 9863) and then through a sodium salicylate plate, which fluoresced with intensity proportional to that of the beam.<sup>18,19</sup>

Actinometry. Acetone at  $130^{\circ}$  and 45 Torr was used as a chemical actinometer for photolysis at 3130 Å.<sup>16</sup> Under such conditions the quantum yield of carbon monoxide is unity. Condensables were trapped with liquid nitrogen, and CO was collected for analysis by mass spectrometry.

Mixing and Photolysis Procedure. Generally cyclopentanone was trapped in the cold finger; added gas was then either expanded to the cell or subsequently trapped in the cold finger. Thus mixing with less than 100 Torr Ar or He involved trapping cyclopentanone at liquid nitrogen temperature and expanding the inert gas to the cell. For higher pressures of Ar or of Kr, the ketone was trapped with a Dry Ice-acetone mixture. Xenon and pentadiene, as added gases, were condensed with the ketone at liquid nitrogen temperature. The components were then allowed to mix in the gas phase for several hours if the partial pressure of one gas was not more than ten times that of the other, otherwise mixing time was extended to about 10 hr (overnight).

Photolysis at 3130 Å usually lasted for 60 to 90 min and was carried out to 2-3% conversion.

Sampling and Analysis. Carbon monoxide was separated as a gas from other compounds at  $-196^{\circ}$ . It was analyzed with a CEC mass spectrometer, Model 21-110, by using known amounts of Ar as a reference. For most runs CO was not analyzed and was pumped off.

Ethylene and cyclobutane were isolated from 4-pentenal and the ketone by trapping the latter two compounds at the temperature of Dry Ice. Small amounts of isobutane at about 0.5 Torr were introduced to serve as a carrier, and the gas mixture was condensed at  $-196^{\circ}$  in a capillary tube which was inserted into a gas chromatograph (Aerograph Model 600-C) with a solid injector. A column of dimethylsulfolane on fire brick, 6.1 mm long and 2.5 mm i.d., gave good separation. The isobutane besides being a carrier was also a reference.

4-Pentenal was analyzed with a Perkin-Elmer F11 gas

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(19) The plate was prepared by spraying a solution of sodium salicylate in methanol on a Corning 7740 glass filter, until a uniform layer of about 2 mg/sq cm had deposited. See also the Ph.D. Thesis of F. S. Wettack, The University of Texas at Austin, 1968.

chromatograph. An MBMA capillary column, 17 m in length and 0.5 mm i.d., was employed.

## Results

Since no evidence was found for polymer formation and no products other than those appearing in eq 1-3could be detected, the yield (in micromoles) of carbon monoxide should be equal to 0.5 the yield of ethylene plus the yield of cyclobutane. This relationship was found to be true, within experimental error, for a few runs for which the amounts of all the three products were determined. For most runs the amount of CO was calculated.

Table I shows the results for experiments where only cyclopentanone was present initially. The data indicate that the ratio pentenal/CO increases as the

Table I: Variation of Product Quantum Yields with Pressure and Temperature;  $\lambda$  3130 Å

Pressure of				
cyclopentanone,				
Torr	$\Phi_{pentenal}$	<b>₽</b> co <sup>a</sup>	$C_{2}H_{4}/\Box$	Pentenal/CO
	T	$emp = 26^{\circ}$		
2.46	0.22	0.23	3.40	0,98
4.44	0.21	0.19	3.26	1.13
6.39	0.24	0.18	2.96	1.28
7.77	0.26	0.17	3.07	1.50
9.31	0.27	0.16	2.86	1.68
	Т	emp = 65°		
2.10	0.17	0.37	3.07	0.46
2.23	0.16	0.39	3.28	0.42
2.66	0.20	0,38	3.11	0.52
3.99	0.18	0.35	2.83	0.52
5.18	0.19	0.32	2.87	0.58
5.19	0.20	0.34	2.98	0.57
7.14	0.21	0.29	2.74	0.73
7.21	0.20	0.27	3.01	0.73
9.72	0.21	0.24	3.23	0.85
10.28	0.22	0.27	2.91	0.81
11.05	0.18	0.25	3.13	0.70
14.7	0.24	0.24	3.2	1.03
27.3	0.26	0.17	2.90	1.52
37.4	0.34	0.15	3.10	2.28
38.4	0.31	0.16	2.79	2.01
53.1	0.36	0.11	3.08	3.15
69.0	0.35	0.086	3,63	4.06
	Te	mp = 106°		
3,34	0.18	0.52	2.86	0,34
8.88	0.18	0.47	2.80	0.38
14.52	0.22	0.41	3.03	0.54
27.0	0.24	0.37	3.08	0.64
" The world of	CO was cala	ulated from	these of C.H	and a C.H.

<sup>a</sup> The yield of CO was calculated from those of C<sub>2</sub>H<sub>4</sub> and c-C<sub>4</sub>H<sub>8</sub>, *i.e.*,  $\Phi_{CO} = \frac{1}{2}\Phi_{C_2H_4} + \Phi_{e-C_4H_8}$ .

temperature is lowered, or as the pressure is increased, in accord with previous results.<sup>6,7</sup> This ratio varies linearly with cyclopentanone pressure within experi-



Figure 1. Plot of  $1/\Phi$  (pentenal) vs. 1/P (cyclopentanone) at 25°.  $\odot$ , Cyclopentanone only;  $\triangle$ , added gas: 1,3-pentadiene;  $\times$ , points calculated by eq 6.

mental error and in the absence of foreign gas. Furthermore,  $1/\Phi_{\rm CO}$  vs. pressure of cyclopentanone is linear within experimental error. On the other hand, Figure 1 shows that  $1/\Phi$  (pentenal) vs. 1/P cyclopentanone shows a curvature but may become linear at high pressure.

The ratio of ethylene to cyclobutane is virtually invariant to changes in temperature and pressure except possibly at low pressures. The mean value is 3.05. The average deviation from the mean is 0.16, which is about 5%, and is about the magnitude of experimental error.

A check on the possibility of a dark reaction at  $65^{\circ}$  was made by heating 10.87 Torr of cyclopentanone at that temperature in the cell for a period of 208 min. No products were found.

Results of the added gas study are shown in Table II. The presence of relatively large amounts of foreign gas generated some difficulties in product sampling.<sup>20</sup> For this reason the data are more incomplete and less precise than those given in Table I. Nevertheless they indicate that the effects of pressure on product distribution and quantum yields are of the same nature as those manifested in Table I. This is further illustrated in Figures 2, 3, and 4.

The presence of *trans*-1,3-pentadiene during photolysis did not lead to the formation of any detectable amount of *cis* isomer, even though one part of *cis* in a thousand parts of the *trans* could have been readily determined. A run was made in which a mixture of 46.1 Torr of the ketone and 6.20 Torr of *trans*-diene was photolyzed at 3130 Å and 65° for 65 min. No *cis* isomer was formed.

Three runs were made for light which contained almost exclusively the two lines at 2537 and at 2654 Å.

<sup>(20)</sup> For instance if He, Ar, and Kr were removed by pumping at liquid nitrogen temperature after photolysis, significant amounts of  $C_2H_4$  and  $c-C_4H_8$  might be stripped off.

Pressure of cyclopentanone, Torr	Pressure of added gas, Torr	$\pmb{\Phi}_{ extsf{pentensl}}$	<b>Φ</b> CO	C2H4/c-C4H8	Pentenal/CO
	3	$\lambda$ 3130 Å, temp = 65°	•		
10.64	106 (He)	0.25	0.18	3.11	1.38
10.55	209 (He)	0.28	0.15	3.72	1.94
10.34	57 (Ar)	0.25	0.19	2.56	1.33
10.67	107 (Ar)	0.24	0.15	2.75	1.62
10.55	225 (Ar)	0.32	0.13	3.52	2.53
10.60	372 (Ar)	0.41	0.11	3.12	3.64
10.57	478 (Ar)	0.41	0.081	3.00	5.07
10.55	110 (Kr)	0.23	0.17	2.91	1.36
10.43	233 (Kr)	0.33			
10.55	113 (Xe)	0.26	0.15		1.73
10.60	454 (Xe)	0.36			
10.50	454 (Xe)	0.41			
10.70	11.9 (trans-pentadiene)	0.26	0.21	3.00	1.23
10.70	25.7 (trans-pentadiene)	0.28	0.17	2.83	1.65
10.75	41.2 (trans-pentadiene)		0.13		
10.55	83 (trans-pentadiene)	0.37			





Figure 2. Ratio of pentenal to carbon monoxide yields as a function of pressure at 25° during photolysis of cyclopentanone.



Figure 3. Reciprocal of carbon monoxide yield vs. pressure of added gas at 25° during photolysis of cyclopentanone.

Table III:Photolysis of Cyclopentanone at2537-2654 Å, 26°

Pressure of cyclopentanone,			
Torr	2.33	5.37	9.17
Time, min	1225	1272	1257
Relative incident light			
intensity	3.09	3.15	3.02
4-Pentenal, mol	0.072	0.17	
C <sub>2</sub> H <sub>4</sub> , mol	0.442	0.836	1.43
c-C4H8, mol	0.118	0.251	0.492
$C_2H_4/c$ - $C_4H_8$	3.75	3.33	2.91
Pentenal/CO <sup>a</sup>	0.21	0.26	
4-Pentenal, mol $C_2H_4$ , mol $c-C_4H_8$ , mol $C_2H_4/c-C_4H_8$ Pentenal/CO <sup>a</sup>	$\begin{array}{c} 0.072 \\ 0.442 \\ 0.118 \\ 3.75 \\ 0.21 \end{array}$	$\begin{array}{c} 0.17 \\ 0.836 \\ 0.251 \\ 3.33 \\ 0.26 \end{array}$	$1.43 \\ 0.492 \\ 2.91$

 $^{\alpha}$  The yield of CO was calculated from the amounts of  $\mathrm{C}_{2}\mathrm{H}_{4}$  and  $\mathit{c}\text{-}\mathrm{C}_{4}\mathrm{H}_{8}.$ 

A medium pressure mercury arc and filters were used. The results are shown in Table III.

### Discussion

It has been established that triplet-triplet energy transfer to olefin molecules may lead to *cis-trans* isomerization of the latter.<sup>21-23</sup> The energy transfer process is a very efficient one provided it is exothermic.<sup>22</sup> Thus conjugated dienes such as 1,3-pentadiene may be useful for mechanistic diagnosis in view of the fact that they have relatively low-lying triplets and are capable of geometrical isomerization. The lowest triplet state of cyclopentanone is situated at least a few kcal/mol above that of pentadiene,<sup>13,14,22</sup> and yet the

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Figure 4. Reciprocal of carbon monoxide yield vs. pressure of *trans*-1,3-pentadiene (Torr) at 25° during photolysis of cyclopentanone.

first excited singlet state of the ketone is roughly 44 kcal/mol lower than that of the diene.<sup>14,22</sup> This makes the triplet energy transfer from the ketone to the diene favorable. The absence of *cis* isomer when photolysis of gaseous cyclopentanone was carried out in the presence of *trans*-1,3-pentadiene indicates that intersystem crossing to the triplet is not important.

It has been shown by Rebbert and Ausloos<sup>24</sup> that 1,3-pentadiene is inefficient in quenching the triplet state of acetone, and the same could well be true for other simple ketones such as cyclopentanone. However, 1,3-pentadiene is effective in producing vibrational relaxation and in some instances in quenching singlet states even though direct electronic energy transfer by a simple collision of the second kind is impossible. Thus the use of 1,3-pentadiene to identify effects due to triplet states must always be studied very carefully. In the present instance since isomerization of the pentadiene does not occur the results may not be used either to prove or to disprove the role of the triplet state during photolysis of cyclopentanone.

If the intersystem crossing in cyclopentanone is collisionally induced, then it may be dependent on the mass of the colliding partner, due to the heavy atom effect on spin-orbital coupling.<sup>25,26</sup> Hence if any of the photodecomposition or photoisomerization processes occurred from the triplet state, introducing a heavy colliding partner might enhance that process. The data in Table II show that addition of the monatomic gases He, Ar, Kr, and Xe, with significant variance in mass, leads to little difference, if any, in the effects of added gas on product distribution.

Since noble gases even though inefficient cause some vibrational relaxation, the change in the ratio of pentenal to carbon monoxide could be due entirely to this factor, and xenon is no more effective than the others.

The present results therefore support the original assertion<sup>6</sup> that in direct photolysis, all three processes

take place from the singlet state, and that decarbonylation processes occur from upper vibrational levels as the data in the tables imply. However, although the ratio pentenal/CO increases linearly with pressure, there is no such relationship between  $1/\Phi$  (pentenal) and 1/P, as shown in Figure 1, the appearance of which can be anticipated if not all of the pentenal is formed from the thermally equilibrated vibrational levels of the excited singlet state.

The ratio  $C_2H_4/c-C_4H_8$  is virtually constant regardless of variations in pressure and temperature. The value of 3.05 is in good agreement with the values of 3.26 and about 3.10 obtained by Benson and Kistiakowsky,<sup>3</sup> and Lee,<sup>11</sup> respectively, but is lower than that obtained by Klemm, Gilderson, Morrison, and Blades.<sup>9</sup> The latter have observed a falloff in the ratio  $c-C_4H_8/C_2H_4$  at 100° at pressures below about 4 Torr. The data in Table III show a trend in qualitative agreement with this observation. Thus the possibility of some dissociation of a vibrationally "hot" cyclobutane may not be excluded.

At pressures above a few Torr, ethylene and cyclobutane seem to arise<sup>5</sup> from two concurrent processes. The present data, as well as previous ones,<sup>6,9</sup> indicate that both processes take place from upper vibrational levels of an excited (almost certainly singlet) state and that the ratio of their rate constants is independent of changes in pressure above pressures of 5 Torr, of temperature, and of exciting wavelength. A complete theory of this dissociation may not at present be given.

The results can therefore be explained in terms of the following simplified scheme

$$ep \xrightarrow{h_{\nu}} {}^{1}ep*$$
 (a)

$$\underset{k_{b_2}}{\overset{k_{b_1}}{\longrightarrow}} 2C_2H_4 + CO \qquad (b_1)$$

$$^{1*}cp \xrightarrow{\kappa c} 4$$
-pentenal (c)

$$\xrightarrow{kd} cp$$
 (d)

$$^{1}cp + M \xrightarrow{k_{e}} ^{1}cp + M$$
 (e)

$$^{1}cp \xrightarrow{ki} 4$$
-pentenal (f)

$$\xrightarrow{k_{g}}$$
 cp (g)

where cp denotes ground-state cyclopentanone, <sup>1</sup>cp<sup>\*</sup> and <sup>1</sup>cp denote the excited singlet ketone with and without excess vibrational energy, respectively, beyond that at thermal equilibrium. M is a colliding molecule,

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Temp, °C	ko/kb	$k_{ m d}/k_{ m b}$	$k_t/(k_t + k_g)$	ke/kb, Torr <sup>-1</sup>	Pentadiene, ke/kb, Torr <sup>-1</sup>	Ar, ke/kb, Torr <sup>-1</sup>
26	0.66	2.0	0.39	0.28		
65	0.36	1.2	0.38	0.12	0.10	0.017
106	0.28	0.5	0.43	0.035		

Table IV: Ratios of Rate Constants

either cyclopentanone or added gas.  $k_{\rm b} = k_{\rm b1} + k_{\rm b2}$ and  $k_{\rm b1}/k_{\rm b2} = 3.05/2$ .

At 3130 Å the ratio  $C_2H_4/c$ - $C_4H_8$  is essentially independent of temperature and of pressure. This must mean that small changes in vibrational level are unimportant. There may be a slight increase in this ratio at 2537 Å at low pressures, and thus one must reserve judgment as to the role which may be played by large amounts of vibrational energy.

Steps d and g are unimolecular processes which can be either fluorescence or internal conversion, possibly a combination of both. Data for most molecules of this type indicate that internal conversion from a first excited singlet state into the ground singlet state does not occur, but in the present instance it is impossible on kinetic evidence to draw such a positive conclusion. One may only say that (d) and (g) do not give recognizable products. In the case of cyclobutanone the preferred mechanism does not need to include internal conversion.<sup>27</sup>

Fluorescence of cyclopentanone has been studied in the gas phase,<sup>14,15</sup> but the yield is very low. An attempt was made in this work to observe fluorescence but without success. The lower limit of sensitivity would be a yield of about 0.01.

The following equations can be derived

$$1/\Phi_{\rm CO} = 1 + \frac{k_{\rm e} + k_{\rm d}}{k_{\rm b}} + \frac{k_{\rm e}({\rm ep})}{k_{\rm b}} + \frac{k_{\rm e}^{\rm A}({\rm A})}{k_{\rm b}}$$
 (4)

and

$$\frac{\Phi_{\text{pentenal}}}{\Phi_{\text{CO}}} = \frac{k_{\text{e}}}{k_{\text{b}}} + \frac{k_{\text{f}}}{k_{\text{b}}(k_{\text{f}} + k_{\text{g}})} \left(k_{\text{e}}(\text{cp}) + k_{\text{e}}^{\text{A}}(\text{A})\right) \quad (5)$$

where A represents an added gas.

Ratios of rate constants can be calculated from slopes and intercepts of plots of  $1/\Phi_{CO}$  and of (pentenal)/ (CO) vs. P, respectively. The results are in Table IV.

As can be anticipated,  $k_{\rm c} \geq k_{\rm e}^{\rm diene} > k_{\rm e}^{\rm Ar}$ , since in general the efficiency to remove vibrational energy increases with complexity of colliding molecules. The fact that the ratio  $k_{\rm f}/(k_{\rm f} + k_{\rm g})$  is independent of temperature is to be expected if both processes f and g require very small or similar energies of activation. The ratios  $k_{\rm c}/k_{\rm b}$ ,  $k_{\rm d}/k_{\rm b}$ , and  $k_{\rm e}/k_{\rm b}$  all decrease with increasing temperature, indicating that the dissociative processes require higher energies of activation than the other processes. The data are not precise enough to warrant a detailed discussion in terms of activation parameters.

From the ratios given in Table IV, the quantum yield of 4-pentenal can be calculated at different pressures. Since

$$\Phi_{\text{pentenal}} = \left[ k_{\text{c}} + \frac{k_{\text{f}}k_{\text{e}}(M)}{k_{\text{f}} + k_{\text{g}}} \right] \frac{1}{k_{\text{b}} + k_{\text{c}} + k_{\text{d}} + k_{\text{e}}(M)} \quad (6)$$

The calculation was performed by using the ratios at 65°, for the case where no added gas is present. The calculated values agree well with those obtained experimentally, as shown in Figure 1, in which the line was drawn according to the calculated values. This is not in reality an independent check of the data.

The results of the present work are thus consistent with a mechanism by which all three chemical processes take place from the excited singlet state. This of course does not mean that these processes cannot occur from the triplet state.

Although some previous results seem to indicate that exothermic triplet energy transfer occurs on every collision between a triplet molecule and a molecule such as pentadiene,<sup>22</sup> more recent work indicates that this may not be true.<sup>24</sup> In the liquid phase it has been shown that the formation of 4-pentenal takes place from the triplet state,  $^{10,28}$  with a rate constant of  $1.1 \times 10^8$  $\sec^{-1}$ . It can be anticipated that in the gas phase the rate constant probably is of the same order of magnitude, yet no quenching was observed. The benzenesensitized photolysis<sup>11</sup> of cyclopentanone showed that only 40% of the triplet state cyclopentanone molecules undergo rearrangement to pentenal. The remainder probably return to the ground state through intersystem crossing, since no phosphorescence has been observed in the gas phase. If rearrangement is so fast as to avoid quenching, so must be intersystem crossing. The present data indicate that the excited singlet lives long enough to experience collisional relaxation of vibrational energy, implying that intersystem crossing from excited singlet to triplet if it occurs should not be too much faster than the collision frequency.

While benzene triplet energy transfer to cyclopentanone gave rise to formation of the aldehyde,<sup>11</sup> triplet mercury-sensitized photolysis of 2-methylcyclohexa-

<sup>(27)</sup> T. H. McGee, J. Phys. Chem., 72, 1621 (1968).

<sup>(28)</sup> P. J. Wagner and R. W. Spoerkes, J. Amer. Chem. Soc., 91, 4437 (1969).

none<sup>29</sup> and 2-ethylcyclopentanone<sup>30</sup> produces largely decarbonylated products. It has been pointed out<sup>11,30</sup> that this difference in behavior may be connected with the fact that triplet mercury possesses about 1 eV of transferable energy more than triplet benzene and that the factor that determines the mode of reaction therefore appears to be the "energy content,"<sup>20,6</sup> rather than the "multiplicity" of the species. The results of the present work are in line with this view.

It is impossible to state with certainty whether or not triplet state molecules play an important role in the direct, unsensitized photolysis of cyclopentanone but if they do their mean lifetimes must be very short. Acknowledgment. The author wishes to express his appreciation to Dr. A. T. Blades of the Research Council of Alberta, Edmonton, Alberta, and to Dr. E. K. C. Lee of the University of California at Irvine for helpful discussions and suggestions. The guidance offered by Professor W. A. Noyes, Jr., and financial support for this work provided by The Robert A. Welch Foundation are gratefully acknowledged.

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# Interaction of the Benzene Molecule with Liquid Solvents.

# Fluorescence Quenching Parallels (0-0) Ultraviolet Absorption Intensity

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The fluorescence yield and uv absorption of benzene have been measured in 40 polar and nonpolar liquids. At  $25^{\circ}$  the total rate of all nonradiative transitions from the fluorescent state of benzene is found to increase systematically with increasing intensity in the solvent-induced (0–0) component of the 2600-Å absorption band.

### Introduction

When benzene is dissolved in liquids the fluorescence is thermally quenched with an activation energy of about 2000 cm<sup>-1.1</sup> Also at a given temperature the yield depends on the solvent, and the Debye reorientation rate of the solvent is not the determining factor.<sup>1</sup> In attempting to find out why the yield depends on the particular liquid used as solvent, we have measured the uv absorption and fluorescence yield of benzene dissolved in 40 different liquids, both polar and nonpolar.

### **Experimental Section**

The benzene used in this experiment was a zone-refined product (purity greater than 99.9%) obtained from James Hinton (358 Chicago Ave., Valparaiso, Fla. 32580). The solvents used were all of research grade, purity of 99.5 + mol %, and of Spectrograde. All solutions were prepared under nitrogen. References to the experimental methods are given in Table I.

#### Results

Integrated Uv Absorption Intensity. Absorptivities,  $\epsilon_{\max}$ , at the uv absorption maximum,  $\lambda_{\max}$ , and oscillator

strengths for the 2600-Å transition of benzene dissolved in various solvents are given in Table I. Oscillator strengths, f, are calculated as

$$f = 4.32 \times 10^9 \int \epsilon d\nu$$

where  $\epsilon$  is the molar absorptivity in  $(M \text{ cm})^{-1}$  and the frequency  $\nu$  is in reciprocal centimeters. The absorptivities reported here are an average of 20% above those of Bayliss and Hulme,<sup>2</sup> but this may be caused by our using narrower slit widths, since the integrated intensities of the present work agree with theirs.

Except when benzene is dissolved in carbon tetrachloride (ref 2) and chloroform (this work and ref 2), the oscillator strength of the 2600-Å band is independent of solvent (precision  $\pm 5\%$ , absolute magnitude  $\pm 10\%$  in this work). The present measurements coincide with those of Bayliss and Hulme.<sup>2</sup>

The oscillator strengths, as well as the peak absorptivities, of benzene in carbon tetrachloride and chloroform are anomalously high. The peaks are especially

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