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 supplement 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.

Photochemistry of Cyclopentanone. I. Details of the Primary Process[1a]
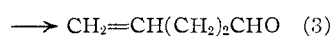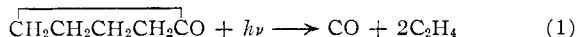
BY R. SRINIVASAN[1b]

In the photochemistry of cyclopentanone, three processes are known to be important. These lead to $CO + 2C_2H_4$ (1), $CO + \overline{CH_2CH_2CH_2CH_2}$ (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 $O_2{}^{18}$ does not lead to detectable amounts of cyclopentanone-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.[2-8] It was shown by Benson and Kistiakowsky[3] that the important products were carbon monoxide, ethylene and cyclobutane. Later work[6] 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

$$\overline{CH_2CH_2CH_2CH_2CO} + h\nu \longrightarrow CO + 2C_2H_4 \qquad (1)$$

$$\longrightarrow CO + \overline{CH_2CH_2CH_2CH_2} \qquad (2)$$

$$\longrightarrow CH_2{=}CH(CH_2)_2CHO \qquad (3)$$

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

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.[5]

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. $O_2{}^{18}$ was obtained from the Weizmann Institute of Science, Rehovoth, Israel.[10]

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[11] 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 C_2 and 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

(1) (a) This research was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 18(600) 1528 presently AF 49(638)079. Reproduction in whole or in part is permitted for any purpose by the United States Government. (b) IBM Research Center P. O. Box 218, Yorktown Heights, N. Y.

(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).

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

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

(10) For isotopic analysis see ref. 11.

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

of the peak in the trace made by the recorder. Analyses for 4-pentenal made in this fashion over a period were reliable to only ± 15% and constituted the least accurate part of the analysis.

Results

1. Light Emission.—Attempts were made to detect any radiation emitted by cyclopentanone on absorption of 3130 Å. light. In the vapor phase no light was detected visually at right angles to the incident beam. But this failure may be solely due to an insufficient concentration of molecules in the light path as the vapor pressure of cyclopentanone at room temperature is about 12 mm. Excitation of liquid cyclopentanone also failed to give a detectable amount of light. On illumination of a 1% solution of cyclopentanone in a glass composed of 5 parts of isopentane, 5 parts of ether and 2 parts of ethanol at 77°K. a weak afterglow was observed visually. Its lifetime as determined by a rotating sector phosphoroscope was less than 10^{-3} sec. The emitted light was not strong enough to be photographed with the f/11 spectrograph that was available, with reasonable exposures.[12]

2. Quantum Yields at 3130 Å. and 125°.—Since the value of Φ_{CO} at 125° and about 106 mm. pressure has been measured accurately by Blacet and Miller,[4,5] this may be used as the actinometer. The ratio of pentenal to carbon monoxide was found to be 1.08 under these conditions. Since Φ_{CO} was 0.33,[5] the quantum yield for the disappearance of cyclopentanone is 0.69. The actual value may be even higher as a satisfactory separation of pentenal from the unreacted ketone was not obtained on the chromatograph when high pressures of cyclopentanone were used.

3. Effect of Oxygen.—The effect of oxygen on the formation of ethylene, cyclobutane and pentenal is shown in Table I. Very little carbon dioxide and water, which may be expected as oxidation products, were to be found even at the highest oxygen pressure used.

TABLE I

EFFECT OF OXYGEN ON THE PHOTOLYSIS OF CYCLOPENTANONE AT 3130 Å.

Average ketone pressure 10.9 mm.; cell volume 114.5 ml.; room temperature

Oxygen pressure, mm.	Products in μ mole C_2H_4	C_4H_8	Pentenal	Cyclopentanone[a] accounted for, μ mole
0	1.78	0.42	0.84	2.15
10.7	1.83	.43	0.92	2.27
35.5	1.87	.37	1.06	2.36
80.3	1.20	.23	0.74	1.57
159.9	0.96	.18	.84	1.50
274.8	0.64	.12	.73	1.17

^{a} Calculated from $C_2H_4/2 + C_4H_8 +$ pentenal.

4. Exchange with O_2^{18}.—Photolysis of a mixture of 10.8 mm. of cyclopentanone and 27.1 mm. of O_2^{18} for 240 minutes did not lead to the formation of a detectable quantity of cyclopentanone-O^{18}. From the size of the mass 86 peak in the mass spectrum of the ketone after photolysis, the upper

(12) The author is grateful to Drs. Norman Blake and Conrad Houle of the Eastman Kodak Research Laboratories for carrying out these experiments.

limit for the quantum yield for the formation of cyclopentanone-O^{18} may be estimated to be 0.03. No dark reaction was observed and hence no correction for the formation of cyclopentanone-O^{18} in the dark had to be applied. The small amount of carbon dioxide found in the products was made up of $CO^{18}O^{18}(62\%)$, $CO^{16}O^{18}(30\%)$ and CO^{16}-$O^{16}(8\%)$.

5. Effect of Pressure at 124°.—The yields of the various products as a function of pressure of cyclopentanone are shown in Table II. The values for $C_2H_4/2 + C_4H_8$ are given in order to compare these with the yields of carbon monoxide. To estimate the quantum yields for the disappearance of cyclopentanone, the fraction of light absorbed was obtained from the tables of Miller.[13]

TABLE II

EFFECT OF PRESSURE ON THE PHOTOLYSIS OF CYCLOPENTANONE AT 3130 Å.

Temp. 123.8°; time 60 min.; cell volume 114.5 ml.; dead space 35.3 ml.

Pressure (mm.)	106.0	75.6	53.3	31.5	12.2
Products (μmole)					
CO	2.49	2.39	2.42	2.12	1.18
C_2H_4	3.18	3.17	3.00	2.60	1.44
C_4H_8	0.90^a	0.77	0.68	0.63	0.39
4-Pentenal	2.70	2.28	1.82	0.69	0.18
$C_2H_4/2 + C_4H_8$	..	2.36	2.18	1.93	1.11
Pentenal/CO	1.08	0.95	0.75	0.33	0.16
$\Phi_{Cyclopentanone}{}^b$	0.69	0.72	0.78	0.73	0.71
C_2H_4/C_4H_8	3.53	4.12	4.41	4.12	3.67

^{a} Estimated assuming $CO = C_2H_4/2 + C_4H_8$. ^{b} $\Phi_{CO} + \Phi_{pentenal}$.

6. Addition of Methane.—The effect of the addition of methane on the disappearance of cyclopentanone and on the formation of the products at constant temperature and ketone pressure is illustrated in Fig. 1.
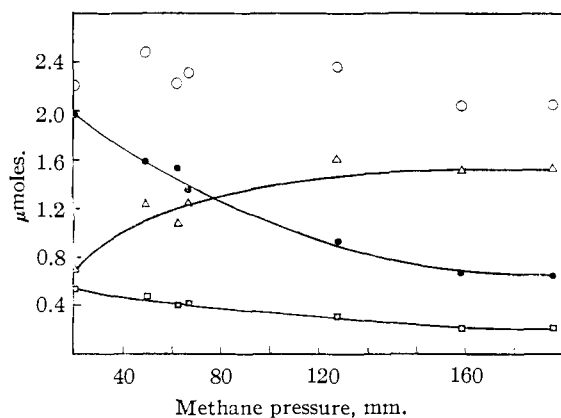

Fig. 1.—Effect of methane on the photolysis of cyclopentanone at 3130 Å: average ketone pressure 11.6 mm.; room temperature: □, cyclobutane; △, pentenal; ●, ethylene; ○, cyclopentanone accounted for in products.

7. Photolysis at 2537 Å.—The results of three runs are given in Table III. Since it is known[4,5] that Φ_{CO} at this wave length at about 125° is 0.73, it may be estimated from the present value for pentenal/CO that the quantum yield for the

(13) Ref. 4, p. 70.

disappearance of cyclopentanone is 0.85 ± 0.07 under these conditions.

Discussion

It is unfortunate that a detailed analysis of the ultraviolet spectrum of cyclopentanone has not been made. Qualitatively, the spectrum in the first absorption region appears to be similar to that of the simple aliphatic ketones.[14] On this basis it will be assumed here that initial excitation is to the upper singlet state and that the zero–zero band is near 3600 Å.

Nature of the Excited State(s).—Present attempts to look for a triplet state in the photochemistry of cyclopentanone fall under two categories. The experiments intended to detect any light emitted by the excited molecule gave negative results with the vapor and the liquid. The weak light emission observed in the glassy state could well have come from an impurity present in trace amounts. Even if the light did come from a triplet state of cyclopentanone, its low intensity even at 77°K. suggests a low concentration of molecules in this state.

TABLE III

PHOTOLYSIS OF CYCLOPENTANONE AT 2537 Å.

Medium pressure Hg arc; chlorine gas filter

Pressure (mm.)	11.0	10.7	100.8
Temperature (°C.)	27.1	122.4	123.0
Time (min.)	120	203	120
Products (μmole)			
CO	0.86	1.06	3.71
C_2H_4	1.09	1.39	4.72
C_4H_8	0.25	0.24	1.03
Pentenal	.14	.12	0.62
$C_2H_4/2 + C_4H_8$	.80	.93	3.39
Pentenal/CO	.15	.12	0.17
C_2H_4/C_4H_8	4.36	5.71	4.58

The experiments on the decomposition of the ketone in the presence of oxygen strongly indicate that the formation of ethylene, cyclobutane (and by inference, carbon monoxide) and pentenal is not affected by even 35.5 mm. of oxygen. This may be compared with the rapid quenching of the triplet state of acetone by even a tenth of a mm. of oxygen.[15] The *gradual* decrease in the quantum yield for the disappearance of cyclopentanone in the pressure range of oxygen from 80 to 275 mm. may be due to the quenching of the electronic excitation energy of the upper singlet state. It should be pointed out here that the detailed effects of the addition of oxygen, *i.e.*, the relative yields of the three products that were measured, show a trend which is exactly similar to that exhibited in the presence of an inert gas such as methane.

The upper limit of 0.03 for the quantum yield for the formation of cyclopentanone-O^{18} in the photolysis of cyclopentanone in the presence of O_2^{18} may be compared with the quantum yield of 0.45 for acetone-O^{18} formation under identical conditions.[11] It is believed (but not established) that this reaction between acetone and O_2^{18} takes

place with the triplet state of the molecule. The low efficiency of a corresponding reaction in cyclopentanone also supports the idea that a triplet excited state is not important in the photochemistry of cyclopentanone.

The Decomposition Processes.—The present results show that at 3130 Å. and 123.8° the yield of carbon monoxide equals $C_2H_4/2 + C_4H_8$ at all pressures of the ketone from 12 to 106 mm. While Blacet and Miller[5] found such an equivalence to be true at 3130 Å. and 125°, at higher temperatures or at shorter wave lengths they found that Φ_{CO} was greater than $C_2H_4/2 + C_4H_8$. The present results at shorter wave lengths (Table III) and the results of Benson and Kistiakowsky[3] (polychromatic light; 181 to 300°) do not substantiate this. Further, neither Miller nor Benson and Kistiakowsky[3] were able to find any polymeric products. Since the yield of carbon monoxide can exceed $C_2H_4/2 + C_4H_8$ only if there are other products to account for the discrepancy, for the purpose of this discussion it may be accepted that $CO = C_2H_4/2 + C_4H_8$ under all conditions.

It has been shown already that the photolysis of cyclopentanone-2,2,5,5-d_4 leads to the formation $C_2H_2D_2$ and cyclobutane-1,1,2,2-d_4.[6] Since the *thermal* decomposition of the latter compound leads to C_2H_4, $C_2H_2D_2$ and C_2D_4 in the ratio of $1:2:1$,[16] it may be inferred that the formation of ethylene is not through a mechanism such as

$$\overline{CH_2(CH_2)_3CO} + h\nu \longrightarrow \overline{CH_2CH_2CH_2CH_2}^* + CO \quad (4)$$

$$\overline{CH_2CH_2CH_2CH_2}^* \longrightarrow 2C_2H_4 \quad (5)$$

in which the asterisk denotes a "hot" molecule. It is necessary to postulate (1), (2) and (3) as three independent processes.

Details of the Primary Process.—The effects on the product composition arising from change in the pressure of cyclopentanone or the addition of methane at constant ketone pressure appear to be very similar. It will be shown elsewhere[17] that other inert gases have qualitatively similar behavior. In general an increase in the total pressure appears to favor the formation of pentenal at the expense of the processes which lead to the formation of carbon monoxide.[18] At the same time the quantum yield for the ketone accounted for in the products is constant within experimental error at all pressures in the pressure range studied. Since it already has been demonstrated that only one excited state—a singlet—may be important in the photochemistry of cyclopentanone, it follows that (a) this excited state may survive long enough to undergo collisions with other molecules and (b) such collisions determine the course of its subsequent decomposition. From (b) it is proposed that *the vibrational energy possessed by the molecule in the upper electronic state at the instant of decomposition will determine its mode of photolysis.* In support of this view it may be pointed out that
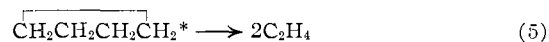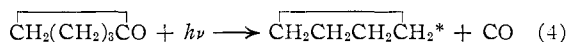
(14) Summarized by W. A. Noyes, Jr., G. B. Porter and J. E. Jolley, *Chem. Revs.*, **56**, 49 (1956).

(15) G. W. Luckey and W. A. Noyes, Jr., *J. Chem. Phys.*, **19**, 227 (1951); J. Heicklen, *J. Am. Chem. Soc.*, **81**, 3863 (1959).

(16) R. Srinivasan and S. M. E. Kellner, *ibid.*, **81**, 5891 (1959).

(17) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 4348 (1961).

(18) In solution it has been observed that very little ethylene and cyclobutane are formed while pentenal is a major product. M. S. Kharasch, J. Kuderna and W. Nudenberg, *J. Org. Chem.*, **18**, 1225 (1953).

an increase in temperature[6] or a decrease in wave length (both at constant pressure) affect the ratio of pentenal/CO in the same way as a decrease in pressure at constant temperature and wave length. It is possible to obtain a measure of the energy difference separating the process which leads to carbon monoxide from the isomerization process, from a plot of log CO/pentenal vs. $1/T$. Such a plot is shown in Fig. 2. The data from ref. 6 are also included in this figure. It is seen that a satisfactory straight line is obtained. The slope of this line corresponds to an activation energy of 2.5 kcal./ mole. This energy may be interpreted to be the difference which separates the lowest vibrational level (in the upper singlet state) at which carbon monoxide production via (1) and (2) is predominant over (3), from the zeroth level in the same electronic state. The relationship of process 1 to 2 in this picture is not clear. Since the ratio of ethylene to cyclobutane changes very little with changes in pressure or temperature or wave length, the lower limit (in the vibrational energy "ladder") for (2) must be close to that for (1). But the exact position can be fixed only if the changes in C_2H_4/C_4H_8 can be determined more accurately than hitherto known. It is also not clear why 2.5 kcal./mole of vibrational energy should influence the reaction path so profoundly. From the ground state the enthalpies of processes 1 and 2 differ by 19 kcal. at 25° while (2) and (3) may be estimated to differ by 15 to 20 kcal. An explanation to this phenomenon should await a clear understanding of the excited state of the molecule. It is puzzling that an almost constant fraction (between $^2/_{10}$ and $^3/_{10}$) of the initially excited molecules return to the ground state without decomposition, by a route that is virtually unaffected by pressure. It may be worthwhile to recheck the absolute value of the quantum yield for decomposition.

The Diradical Mechanism.—Since the addition of even 35.5 mm. of oxygen does not prevent the formation of ethylene, cyclobutane or pentenal, it may be inferred that either (i) free radicals are not involved in the formation of these products or (ii) that a free radical intermediate is involved and that
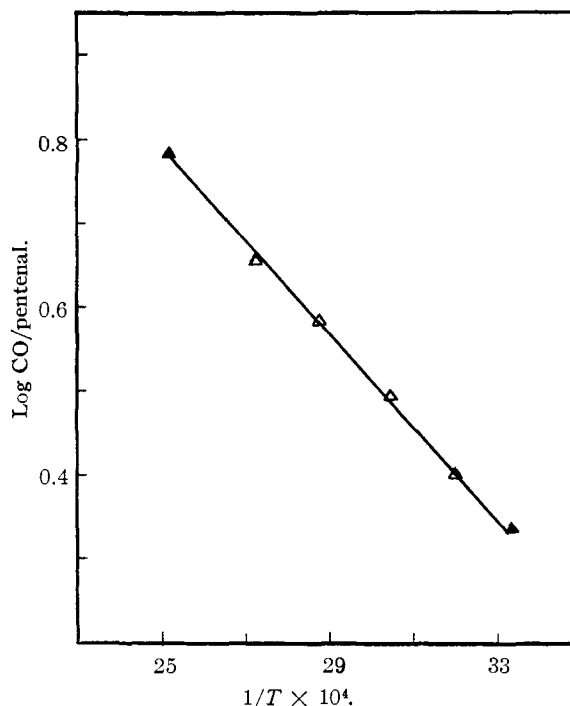

Fig. 2.—Log CO/pentenal vs. $1/T$: average ketone pressure 11.5 mm.: ▲, this study; △, ref. 6.

its lifetime is less than the time between two collisions (ca. 10^{-8} sec. at the pressures used). It may also be observed that such hypothetical radical intermediates behave quite differently from simple mono radicals such as methyl in that they do not seem to recombine with each other or abstract hydrogen atoms.[19] It seems simpler to accept the first possibility and conclude that (1), (2) and (3) are concerted processes, until positive evidence for the diradical hypothesis is discovered.