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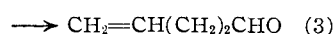
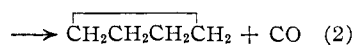
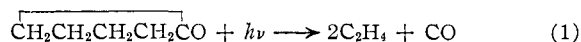
Photochemistry of Cyclopentanone. II. Transfer of Vibrational Energy from the Excited State^{1a}

BY R. SRINIVASAN^{1b}

RECEIVED MAY 25, 1961

The photochemical production of carbon monoxide, ethylene, cyclobutane and 4-pentenal from cyclopentanone at constant temperature, pressure and wave length (3130 Å.) have been studied as a function of the pressure of inert gases. Argon, hydrogen, methane, carbon dioxide, cyclopropane and cyclobutane have been used as inert gases. In all cases, over the pressure ranges used (10 to 400 mm.), the amount of ketone photolyzed, as determined by mass balance, was independent of the total pressure. The results have been interpreted to mean that the vibrational energy of the ketone molecule is lost gradually (one or a few quanta at a time). From a quantitative interpretation of the data, relative efficiencies for the inert gases for the transfer of vibrational energy from cyclopentanone have been obtained.

It has been shown² that in the vapor phase photochemistry of cyclopentanone three processes are important. These are



Evidence has been accumulated which indicates that all three processes occur from the same electronically excited state and that the vibrational energy possessed by the molecule at the instant of its decomposition may determine its mode of decomposition. It seemed of interest to study the collisional transfer of vibrational energy from excited cyclopentanone molecules to foreign molecules by observing the relative rates of the three decomposition processes at various pressures. In essence, the present work is similar to previous studies on the transfer of vibrational energy from electronically excited states in which the process was followed by competition between light emission and decomposition. In the present instance, since competition is between two modes of decomposition it appeared that the results may bear comparison to similar studies on thermally decomposing systems.

Experimental

The apparatus used has been described before.² Cyclopentanone was the same sample used before. Good commercial grades of the following gases were obtained from the sources given in parentheses and used without purification: Argon (Air Reduction Co); carbon dioxide (Air Reduction Co); cyclopropane (Ohio Chemical and Manufacturing Co); hydrogen (Air Reduction Co). The sample of cyclobutane was kindly supplied by Professor W. D. Walters of this Laboratory.

The analytical procedure has been described.² In cases in which the added gas could be pumped off at -195° , the amount of carbon monoxide was estimated from $\text{C}_2\text{H}_4/2 + \text{cyclobutane}$. When the added gas was not volatile at -195° , the C_2 and C_4 fractions were not measured.

Results

The results obtained with six inert gases are listed in Tables I and II. The data for methane which have been shown graphically² should also

(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)679. 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) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 4344 (1961).

be considered here. All the inert gases showed very similar effects.

TABLE I

EFFECT OF FOREIGN GAS ON THE PHOTOLYSIS OF CYCLOPENTANONE AT 3130 Å.

Ambient room temperature; medium pressure Hg arc; 2 mm. Pyrex filter; cell volume 114.5 ml.; dead space 35.3 ml.; time, 120 min.

Press., mm.	Ketone ^a ac- counted for			Pental CO ^b	C ₂ H ₄ / C ₄ H ₈	
	C ₂ H ₄	C ₄ H ₈	Pental μ mole			
Argon, average ketone pressure 10.1 mm.						
0	2.04	0.50	0.94	2.46	0.51	4.07
116.4	1.35	.34	1.38	2.40	1.35	3.95
219.3	0.96	.30	1.71	2.50	2.19	3.19
239.1	.81	.25	1.49	2.15	2.27	3.19
364.1	.64	.20	1.77	2.29	3.39	3.18
Hydrogen, average ketone pressure 11.7 mm.						
105.0	1.44	0.33	1.58	2.63	1.51	4.33
210.3	0.99	.24	1.96	2.70	2.65	4.12
257.6	.80	.24	1.78	2.42	2.78	3.38
378.0	.63	.17	2.03	2.52	4.14	3.73
Methane, average ketone pressure 11.6 mm.						
0	1.96	0.53	0.69	2.20	0.46	3.70
29.5	1.58	.46	1.22	2.47	.98	3.44
42.1	1.52	.39	1.06	2.21	.92	3.90
51.8	1.34	.40	1.23	2.30	1.15	3.35
107.6	0.92	.30	1.59	2.35	2.09	3.06
158.3	.66	.20	1.50	2.03	2.83	3.30
196.0	.64	.21	1.52	2.04	2.92	3.05

^a $\text{C}_2\text{H}_4/2 + \text{C}_4\text{H}_8 + \text{pental}$. ^b $\text{C}_2\text{H}_4/2 + \text{C}_4\text{H}_8$.

Discussion

It is evident that addition of an inert gas does not change the amount of cyclopentanone that undergoes photolysis. At the same time the ratio of pental to carbon monoxide changes sharply. The ratio of ethylene to cyclobutane changes much less markedly but the change is outside of experimental uncertainties.

Any collision mechanism that is proposed to account for these observations must take into account the fact that at least three vibrational levels (for the three decomposition processes) must be visualized in the upper singlet state of the molecule, and provision must be made for the transfer of cyclopentanone molecules from the initially formed vibrational level to all three of these levels. Even if the initial vibrational level

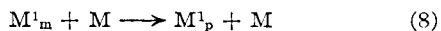
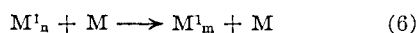
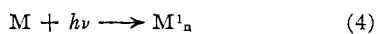
TABLE II
EFFECT OF FOREIGN GASES ON THE PHOTOLYSIS OF CYCLOPENTANONE AT 3130 Å.

Press., mm.	Conditions as listed in Table I		Ketone ^a accounted for	Pentalen CO
	CO	Pentalen μ mole		
Carbon dioxide, average ketone pressure 12.0 mm.				
0	2.13	0.98	3.11	0.46
56.6	1.42	1.59	3.01	1.12
90.9	1.13	1.68	2.80	1.49
128.9	1.05	1.64	2.69	1.56
137.0	0.92	1.84	2.76	2.00
205.1	.80	1.86	2.66	2.32
364.3	.51	2.20	2.71	4.10
Cyclopropane, average ketone pressure 10.0 mm.				
0	1.42	0.74	2.15	0.52
13.6	1.15	0.76	1.91	0.66
43.6	0.78	1.21	1.99	1.54
69.2	.70	1.24 ^b	..	1.78
129.3	.43	1.50	1.93	3.45
154.6	.45	1.49 ^b	..	3.31
Cyclobutane, average ketone pressure 9.6 mm.				
0	1.45	0.79	2.24	0.54
66.9	0.72	1.55	2.27	2.14
117.0	0.50	1.76 ^b	..	3.53

^a From CO + pentalen. ^b Estimated from average value of ketone accounted for minus CO.

is equated with one process and the zeroth level with a second process, at least one additional step must be provided in the "ladder" of vibrational levels for the third process. It would appear best to postulate that in this system vibrational energy is transferred during collisions at the rate of one or a few quanta per collision.

If for the sake of simplicity one considers only three vibrational levels from which (1), (2) and (3) take place, then the following mechanism can be set up (superscripts denote multiplicity and subscripts the vibrational level)



Since the amount of ketone found in the products is independent of pressure, a deactivation step from M^1_p is not required. With the usual steady-state assumptions, it can be derived that

$$\frac{\text{Rate of formation of A}}{\text{Rate of formation of C}} = \frac{k_2 k_7}{k_6 k_8 M^2} + \frac{k_5}{k_6 M} \quad (10)$$

It was found that a plot of pressure $\times \frac{C_2H_4}{\text{pentalen}}$ vs. 1/pressure for pure cyclopentanone at 124° was a satisfactory straight line, but the slope was extremely small. This suggested that the magnitudes of the rate constants for decomposition (k_5 and k_7) as compared to the rate constants for energy transfer (k_6 and k_8) were exceedingly small.

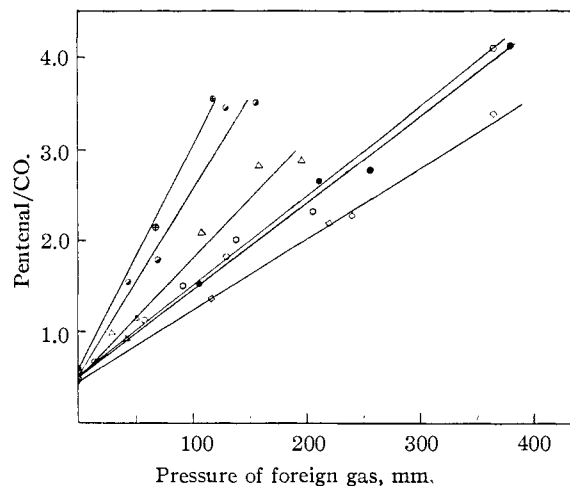


Fig. 1.—Plot of pentalen/CO vs. pressure of foreign gas: \diamond , argon; \bullet , hydrogen; \circ , carbon dioxide; Δ , methane; \ominus , cyclopropane; \oplus , cyclobutane.

Hence, within the accuracy of the data, a simpler interpretation was preferred. It was found reasonable to consider processes 1 and 2 as a single source of carbon monoxide. This approximation was based on the fact that the ratio of ethylene to cyclobutane changed by only 8/10th over the pressures used while the ratio of pentalen to CO changed six-fold.

When only two products are considered, a Stern-Volmer expression of the form

$$\frac{\text{pentalen}}{\text{CO}} = K + K'P \quad (11)$$

may be used. The constant K would include a function of the ketone pressure since this was kept constant.

Plots of pentalen/CO vs. pressure of added gas are shown in Fig. 1. The slopes of these straight lines which are proportional to the efficiencies of the inert gas molecules for transfer of vibrational energy were obtained by the method of least squares. The relative efficiencies of the various gases as obtained from the slopes are given in Table III. These values are estimated to be

TABLE III
EFFICIENCIES OF FOREIGN GASES FOR TRANSFER OF VIBRATIONAL ENERGY (PRESSURE BASIS)

Gas	Photolysis of cyclopentanone	Thermal decomposition Cyclopropane ^a	Cyclobutane ^b
Argon	0.21	0.05	0.17
Hydrogen	.25	.24	.28
Carbon dioxide	.26
Methane	.36	.27	.50
Cyclopropane	.55	1.00	..
Cyclobutane	.67	..	1.00

^a H. O. Pritchard, R. G. Sowden and A. F. Trotman-Dickenson, *Proc. Roy. Soc. (London)*, **A217**, 533 (1953).
^b H. O. Pritchard, R. G. Sowden and A. F. Trotman-Dickenson, *ibid.*, **A218**, 416 (1953).

reliable to $\pm 16\%$. For comparison, the relative efficiencies of these molecules in the thermal decomposition of cyclopropane and cyclobutane are

included. The relative efficiencies of the gases in the three systems seem to follow the same order. It is not possible to extend the comparison to a detailed picture of the transfer of energy with the order of accuracy obtainable at present.

Acknowledgments.—The author wishes to thank Professor W. Albert Noyes, Jr., for his advice and encouragement during the course of this work. He is also grateful to Professor D. J. Wilson for many illuminating discussions.

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY, EMERYVILLE, CALIFORNIA]

Solvent Effects on $n \rightarrow \sigma^*$ Transitions of the Bases, Water, Ammonia, Hydrogen Sulfide and Phosphine

BY D. P. STEVENSON, G. M. COPPINGER AND J. W. FORBES

RECEIVED JUNE 10, 1961

It is shown that the quartz and near vacuum ultraviolet absorption bands of water, ammonia, hydrogen sulfide and phosphine in water solution show a "blue shift" relative to the location of these absorption bands in the vapor or in aprototropic solvent solution spectra. The magnitudes of the blue shifts are approximately equal to the heats of solution at $\sim 25^\circ$ of these hydrides or bases in water. It is suggested that an upper limit to the concentration of such base molecules in water solution that are not engaged in hydrogen bond complexes with the water solvent can be estimated from the ratio of the absorptivity of the water solution to that of the vapor or aprototropic solvent solution at a particular wave length. It is shown that the effect of small concentrations of water on the spectrum of ammonia in otherwise dry diethyl ether are compatible with this suggestion.

It is generally accepted that the lowest energy (longest wave length) electronic excitation process of such substances as ammonia, water, phosphine, hydrogen sulfide, hydrogen chloride and the alkyl derivatives of these substances is associated with the promotion of a non-bonding electron from a 2p or 3p level of the most electronegative atom to an anti-bonding orbital, *i.e.*, the transition is of the type $n \rightarrow \sigma^*$.^{1,2} Stated in other terms, the optical electron for the longest wave length ultraviolet absorption band of such substances is one of the unshared electron pair with which the base properties of these substances are associated. Rather naive considerations³ suggest that if an unshared electron pair of a base is involved in hydrogen bond formation there should be a significant blue shift of the associated electronic absorption band. That is, hydrogen bonding should markedly lower the energy level of the non-bonding electrons while having relatively small effect on the energy level of the anti-bonding orbital. To the extent that this conclusion is valid, one may further conclude that spectrophotometric observations of the $n \rightarrow \sigma^*$ absorption band of such bases in various solvents should provide a means of distinguishing the degree of specific solvation of bases in prototropic solvents from the non-specific solvation as Brealey and Kasha³ have suggested for the solvent effects on $n \rightarrow \pi^*$ transitions.

Direct evidence of the general validity of the concept of a dramatic blue shift of $n \rightarrow \sigma^*$ absorption bands accompanying solution of a base in a prototropic solvent is provided by a comparison of the spectrophotometric behavior of water vapor with that of liquid water. Wilkinson and Johnston⁴ have described the absorption spectrum

(1) R. S. Mulliken, *J. Chem. Phys.*, **3**, 506 (1935).

(2) A. D. Walsh, *J. Chem. Soc.*, 2260, 2296 (1953).

(3) Based on the discussion of the effect of solvent polarity on the location of $n \rightarrow \pi^*$ absorption bands. H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952); G. J. Brealey and M. Kasha, *J. Am. Chem. Soc.*, **77**, 4462 (1955).

(4) R. G. Wilkinson and H. L. Johnston, *J. Chem. Phys.*, **18**, 190 (1950).

of water vapor for wave lengths in the range of 1450 to 1850 Å. From their Fig. 3 one finds the absorptivity of water vapor to be 162 and 22 l./mole cm. at 1800 and 1850 Å., respectively. Ley and Arends⁵ reported measurements on the absorption spectrum of liquid water in the range 1820–1985 Å.; at 1824 Å. and 1850 Å. they report $A = 0.11$ and 0.04 l./mole cm., respectively. This decrease in the absorptivity of water that accompanies its condensation corresponds to a ~ 150 Å. blue shift of the long wave length edge of the absorption band. Such a wave length shift in the vicinity of 1800 Å. corresponds to ~ 13 kcal./mole stabilization in the liquid phase of the orbital carrying the optical electron.

Ley and Arends⁶ reported on the absorption spectrum of ammonia in hexane ($1900 \leq \lambda \leq 2100$ Å.) and ammonia in water ($1820 \leq \lambda \leq 2020$ Å.) where the absorptivities are in the range from 2000 to 50 l./mole cm. Their results for the hexane solution spectrum of NH_3 coincide with the envelope of the minima of the vibronic bands of the ammonia vapor spectrum reported by Tannenbaum, *et al.*,⁷ while the *aqua* ammonia absorption band is displaced about 120 Å. to the *blue* from that of the hexane solution.

The present authors have measured the absorptivities of solutions of ammonia in water and in dry diethyl ether with the results shown as curves I and II of Fig. 1. In the region of overlap between our measurements of the *aqua* ammonia spectrum and those of Ley and Arends,⁶ the absorptivities agree to about 50% corresponding to a difference of 10 to 20 Å. at constant absorptivity. The ether solution spectrum coincides more or less with the smooth curve through the ammonia vapor band spectrum.⁷ In the region of overlap between our ether solution observations and those of Ley and Arends on hexane solutions, we find perhaps a 10

(5) H. Ley and B. Arends, *Z. Physik. Chem.*, **B6**, 240 (1929).

(6) H. Ley and B. Arends, *ibid.*, **B17**, 177 (1932).

(7) E. Tannenbaum, E. M. Coffin and A. J. Harrison, *J. Chem. Phys.*, **21**, 311 (1953).