Fluorescence Excitation Study of Cyclobutanone, Cyclopentanone, and Cyclohexanone in the Gas Phase[1]

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Abstract: The fluorescence excitation spectra for cyclobutanone, cyclopentanone, and cyclohexanone have been measured in the gas phase between 260 and 330 nm, and they are compared to the spectrum obtained for acetone. For the most part, little pressure effect is observed on the fluorescence excitation spectra. The quantum yield of fluorescence near 310 nm is ~0.002 for all three cyclic ketones, being equal to that for acetone. This finding is consistent with an interpretation that the $S_1 \rightsquigarrow T_1$ intersystem crossing rates for all of the four ketones are similar in magnitude at low excess vibrational energy of the S_1 species, and that much of the photochemical activity proceeds not on the S_1 manifold but most likely on the T_1 manifold.

Quantitative kinetic information obtained on the fluorescence and phosphorescence emission yields from the electronically excited molecules is invaluable for elucidating the photochemical mechanism and for understanding the reactivity of these excited states. However, the intramolecular, radiationless, electronic relaxation processes, such as intersystem crossing, internal conversion, dissociation, and chemical isomerization compete so overwhelmingly with the radiative process that the quantum yield of the luminescence is often very low in many photochemical systems of interest. Furthermore, a dilute gaseous sample of a simple carbonyl compound whose molar absorptivity in the $n \rightarrow \pi^*$ transition is low (<20 l. mol^{-1} cm^{-1}) absorbs so little that detection of luminescence with appropriate control of the experimental variables has been difficult to achieve. We have recently carried out a fluorescence emission study in which the measurements of the fluorescence excitation spectrum, the fluorescence emission spectrum, the fluorescence quantum yields (Φ_F) over the entire $S_0 \rightarrow S_1$ absorption band, and the pressure dependence of Φ_F were made easy by a photon-counting setup. We wish to briefly report the results obtained on the cyclic ketones and the mechanistic interpretation based on our fluorescence data, since the previous studies on the gas-phase fluorescence emission from cyclobutanone[3] and cyclopentanone[4] did not provide adequate information required for a satisfactory mechanistic understanding of their photochemical transformations, and since no such fluorescence study has been made on cyclohexanone to date.

Experimental Section

Chemicals used in the present experiment were satisfactory in terms of chemical and spectral purity, and the samples for the fluorescence measurements were prepared on a grease-free and mercury-free vacuum line as in earlier studies.[5] The optical arrangement used in this work was similar to the one employed earlier[5b] except for the following modifications: a Bausch and Lomb monochromator (high-intensity model, 3.2 nm/mm reciprocal dispersion) plus a DC-stabilized 150-W Xenon arc lamp (Osram, XBO-150/1) as the excitation source, and a Jarrell-Ash monochromator (3.5 nm/mm reciprocal dispersion, $f = 3.5$, 300-nm blaze) as the emission analyzer.

The emission intensity was monitored by the following modular electronic equipment working in series: a pulse preamplifier for the cooled photomultiplier tube (EMI 9526S, S-13), a pulse amplifier, a pulse-height discriminator, and a digital rate-meter capable of providing an analog output to a strip chart recorder or a digital output to a teletype. A typical count rate due to the photomultiplier noise (dark) under working conditions was ~15 counts/sec, while the count rate due to the "cell glow" from the scattered exciting light (λ_{ex} 265–320 nm) was about 10 counts/sec at the typical emission wavelength setting (λ_{em} 395 nm). This "cell-glow scattering" effect becomes a serious limiting factor below λ_{ex} 265 nm in the present work. All of the luminescence study was carried out at room temperature (~23°), using the spectral band widths of 1.6 nm for excitation and 8 nm for emission. In order to improve the counting statistics, the photon counts were often accumulated for a period as long as 1 min.

The distribution of the incident photon flux over the range of exciting wavelength was obtained by measuring the photoelectric output with a vacuum phototube (RCA 935) and then by correcting the observed output for its S-5 spectral response as specified by the manufacturer. The corrected fluorescence excitation spectra were obtained by dividing the observed fluorescence count rate by the relative number of the incident photons at each value of λ_{ex}. The probable error in the corrected intensity values is estimated as $\leqslant 30\%$ down to 260 nm. However, it was not feasible in our laboratory to calibrate the spectral response of the emission monochromator (plus photomultiplier tube), and thus the fluorescence emission spectra were uncorrected for their spectral response. As can be seen later, however, the uncorrected spectrum alone is sufficient for the present study.

Results

Fluorescence Emission. The fluorescence emission spectra of acetone[6] obtained in the presence of a few Torr of O_2 and about 50 Torr of c-C_6H_{12} are shown in Figure 1 as a reference,[6] since the fluorescence spectra for the cyclic ketones shown in Figures 1 and 2 should be compared to the acetone spectra. The emission spectra of all four ketones are similar as expected; they are broad with the emission maximum near 400 nm.

Fluorescence Excitation. The corrected fluorescence excitation spectra of acetone and cyclic ketones are shown in Figures 1 and 2 for comparison. With the exception of cyclobutanone, each of them resembles closely the shape of the first absorption band; the

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[1] This research has been supported by National Science Foundation Grant No. GP 11390.

[2] NDEA Predoctoral Fellow, 1967–1970.

[3] (a) R. J. Campbell, E. W. Schlag, and B. W. Ristow, *J. Amer. Chem. Soc.*, **89**, 5098 (1967); (b) R. J. Campbell, Ph.D. Thesis, Northwestern University, 1967.

[4] (a) S. R. La Paglia and B. C. Roquitte, *J. Phys. Chem.*, **66**, 1739 (1962); (b) *Can. J. Chem.*, **41**, 287 (1963).

[5] (a) E. K. C. Lee, M. W. Schmidt, R. G. Shortridge, Jr., and G. A. Haninger, Jr., *J. Phys. Chem.*, 73, 1805, (1969); (b) G. A. Haninger, Jr., and E. K. C. Lee, *ibid.*, 73, 1815 (1969).

[6] O_2 not only prevents the formation of biacetyl during the uv illumination but also quenches the phosphorescence from the acetone. If O_2 is not used, the emission from the biacetyl quickly complicates the system. Cyclohexane vibrationally relaxes the excited singlet acetone.

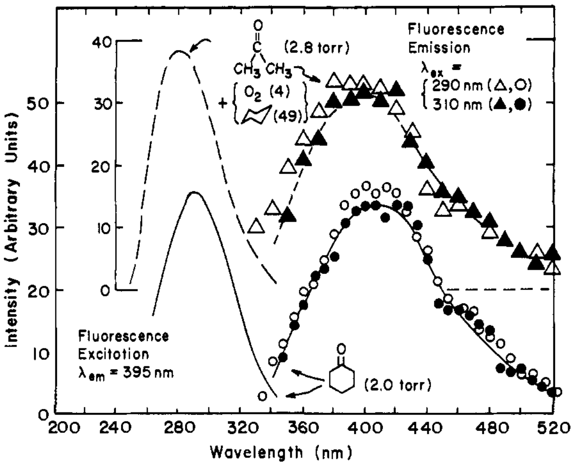

Figure 1. Fluorescence excitation spectra obtained at λ_{em} 395 nm (corrected for the exciting intensity variation) and fluorescence emission spectra obtained at λ_{ex} 290 and 310 nm (uncorrected for the spectral response) for acetone and cyclohexanone in the gas phase.

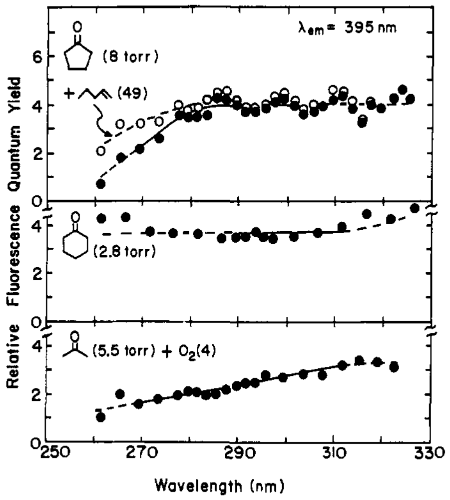

Figure 3. Relative fluorescence emission quantum yields in arbitary units for acetone, cyclopentanone, and cyclohexanone *vs.* the exciting wavelength. The scale factors for all three ketones are not identical.

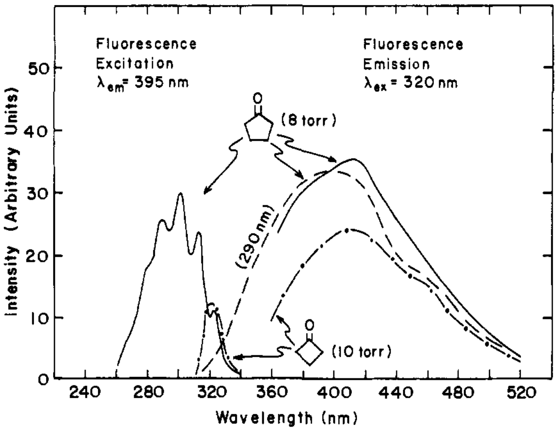

Figure 2. Fluorescence excitation spectra obtained at λ_{em} 395 nm (corrected for the exciting intensity variation) and fluorescence emission spectra obtained at λ_{ex} 320 nm (uncorrected for the spectral sensitivity) for cyclobutanone and cyclopentanone.

extinction of the fluorescence emission from cyclobutanone below λ_{ex} 310 nm is unusual and interesting. Most of the time, the fluorescence excitation spectra were recorded at λ_{em} 395 nm, where the signal to noise ratio was the greatest. These spectra and those recorded at λ_{em} 405 nm were the same.

Pressure Dependence. Within the experimental uncertainty, there was no significant pressure effect of the added foreign gases on the fluorescence excitation spectra between 275 and 325 nm, when 51, 102, 201, and 409 Torr of 1-pentene were added to 18.2 Torr of cyclobutanone. No significant pressure effect on the fluorescence excitation spectra of cyclohexanone (2.8 Torr) between λ_{ex} 325 and 275 nm was observed when 49 (or 10) Torr of c-C_6H_{12} or 50 Torr of 1-pentene was added. On the other hand, 50 Torr of 1-pentene added to 8 Torr of cyclopentanone significantly enhanced the emission yield below λ_{ex} 275 nm as shown in Figure 3, while no significant pressure effect was observed between λ_{ex} 325 and 275 nm when 49 Torr of c-C_6H_{12} or 50 Torr of 1-pentene was added. Furthermore, no pressure effect on the emission quantum yield was observed for cyclopentanone when its pressure was varied between 1 and 8 Torr. Since O_2 would be an efficient quencher of the phosphorescence, as much as 50 Torr of O_2 was added to the cyclic ketone samples, but it had no effect on the observed emission.

Wavelength Dependence. The relative fluorescence quantum yields ($\Phi_{F,rel}$) were calculated by dividing the corrected fluorescence excitation spectra shown in Figures 1 and 2 by the absorption intensity of the ketone.[5a,7] They are shown in Figure 3 for acetone, cyclopentanone, and cyclohexanone, but not for cyclobutanone emission, which suffers a rapid decline below λ_{ex} 320 nm.

Fluorescence Quantum Yield. Since the fluorescence quantum yield (Φ_F) of acetone in the gas phase is known to be 0.0021 at 313 nm,[8] we can estimate the values of Φ_F for the three cyclic ketones by comparing their emission yields to the emission from acetone as the standard. The values of Φ_F thus obtained are shown in Table I, and they are all nearly the same near λ_{ex} 310 nm within the precision of the experiment, ~20%. These values are similar in magnitude to the values of Φ_F obtained for other substituted methyl ketones.[9]

Discussion

The fate of the first excited singlet state (S_1) of a ketone following an $n \rightarrow \pi^*$ transition is determined by the unimolecular competition rates of fluorescence emission (k_F), internal conversion to the ground state (k_{IC}), intersystem crossing to the triplet state (k_{ISC}), and chemical decomposition or rearrangement on the S_1 surface (k_D), and also by the vibrational relaxation of the vibrationally hot S_1 through collisions. These transformations are shown in the equations below (eq I), where A, D, and M represent ketone, product, and collision partner, respectively, asterisks denote vibrational excitation, superscripts 1 and 3 denote the excited singlet and the triplet states, respectively, and ω(M) is the collisional relaxation rate.

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(7) The molar absorptivity values for acetone was taken from J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 377.

(8) J. Heicklen, *J. Amer. Chem. Soc.*, **81**, 3863 (1959).

(9) P. Ausloos and E. Murad, *J. Phys. Chem.*, **65**, 1519 (1961).

Table I. Fluorescence Quantum Yields in the Gas Phase

Ketone	Acetone	CB	CP	CH
Pressure, Torr	2.8[a]	18	8.0	2.8
$\Phi_{F,rel}$[b] 320 nm		14	10.7	17.3
310 nm	16.9	<1	11.0	14.2
300 nm	14.1	<0.2	9.9	12.8
Φ_F 320–310 nm[c]	(0.0021)	0.0019 ± 0.0005	0.0014 ± 0.0005	0.0018 ± 0.0005

[a] 4 Torr of O_2 and 50 Torr of c-C_6H_{12} present. [b] Gas-phase values of ϵ (l. mol^{-1} cm^{-1}) for acetone were taken from ref 7: 1.1 at 320 nm, 4.0 at 310 nm, and 7.6 at 300 nm. The values of ϵ for the cyclic ketones measured in n-C_6H_{14} were used directly.[5] [c] Φ_F of acetone in the gas phase was taken to be 0.0021 from Heicklen's measurement (ref 8).

$$\begin{array}{lll} A + h\nu \longrightarrow {}^1A^* & k_a & \\ \quad\;\; \longrightarrow A + h\nu_f & k_F & \\ \quad\;\; \longrightarrow A^{**} \text{ (or } A^*) & k_{IC} & \\ {}^1A^* \text{ (or } {}^1A) \longrightarrow {}^3A^{**} \text{ (or } {}^3A^*) & k_{ISC} & \text{(I)} \\ \quad\;\; \longrightarrow {}^1D^{**} \text{ (or } {}^1D^*) & k_D & \\ {}^1A^* + M \longrightarrow {}^1A + M & \omega(M) & \end{array}$$

The fluorescence lifetime of the S_1 state in the absence of collisional perturbation is the reciprocal of the sum of all the unimolecular rates

$$\tau_F = 1/(k_F + k_{IC} + k_{ISC} + k_D) \qquad (1)$$

while the quantum yield of fluorescence is

$$\Phi_F = k_F\tau_F \qquad (2)$$

and the quantum yield of intersystem crossing is

$$\Phi_{ISC} = k_{ISC}\tau_F \qquad (3)$$

Acetone. Φ_F for acetone in the gas phase has been measured in the wavelength range of 280–313 nm and in the pressure range of 25–200 Torr at 40°;[8] the fluorescence yield changed little with the variation in the exciting wavelength and the pressure. However, a slight but steady decline of $\Phi_F = 0.0021$ at λ_{ex} 313 nm to $\Phi_F = 0.0017$ at λ_{ex} 280 nm was observed, and our present measurement of $\Phi_{F,rel}$ over λ_{ex} 320–260 nm is consistent with the earlier findings.[8]

Φ_{ISC} for acetone in the gas phase has been shown to be 1.0, and the decomposition to methyl and acetyl radicals occurs from the triplet state.[10] Thus $(k_{IC} + k_D)$ is negligible compared to k_{ISC}. Since the fluorescence decay time of acetone excited at 313 ± 20 nm has been measured to be $\sim$2.7 nsec in the gas phase,[11] the k_{ISC} is $\sim 4 \times 10^8$ sec^{-1}. It is interesting to note that the value of $k_F \approx 7 \times 10^5$ sec^{-1} calculated on the basis of $\Phi_F = 0.002$ is much greater than the value of $k_F \approx 1.2 \times 10^5$ sec^{-1} which we calculated from the Strickler–Berg expression using integrated absorption coefficients,[12] and that our calculated value for acetone is equal to the value of k_F similarly calculated for 2-pentanone.[13] Since the value of k_F is known to be invariant over the wide range of the vibrational excitation energy in the excited singlet state (S_1) of hexafluoroacetone and β-naphthylamine,[14] one could expect it to remain constant for acetone and other simple ketones; consequently, the decline of the fluorescence quantum yield at low λ_{ex} values can be attributed to the increase in the nonradiative rates (k_{IC}, k_{ISC}, and k_D) with the increasing vibrational excitation energy.[15]

Cyclohexanone. Three important observations for cyclohexanone are: (1) Φ_F for cyclohexanone is nearly identical with Φ_F for acetone at λ_{ex} 310 nm; (2) Φ_F for cyclohexanone is independent of λ_{ex}; and (3) Φ_F for cyclohexanone is independent of the added gas (c-C_6H_{12} and 1-pentene) below 50 Torr. We estimate the value of τ_F for cyclohexanone in the gas phase to be 3 nsec.[16] In fact, $\tau_F \approx 3.2$ nsec obtained in the gas phase[11a] is very close to the liquid-phase lifetime of 2.5 nsec measured recently.[17] According to a recent photochemical study,[18] the intersystem crossing to the triplet state is the most important process for the excited singlet cyclohexanone. Thus, $k_{ISC} = (3\text{–}ca.\ 4) \times 10^8$ sec^{-1} for cyclohexanone is comparable to k_{ISC} for acetone.

It has been found earlier that c-C_6H_{12} added in the photolysis of cyclohexanone at λ_{ex} 297 nm quenches the 1-pentene yield with a half-quenching pressure of 8 Torr,[18] while Φ_F at λ_{ex} 300 nm is unaffected by as much as 50 Torr of cyclohexane. Therefore, the *immediate precursor* of 1-pentene cannot be the vibrationally hot cyclohexanone in its S_1 state. The present result is consistent with the following mechanistic interpretation based on photochemical product analysis; the degree of vibrational excitation of the triplet state determines the ratio of the C_5 hydrocarbon products (1-pentene and cyclopentane) to the C_6 isomerization product (5-hexenal), favoring a higher value of this ratio at a high excitation energy.[18] Furthermore, the present result is consistent with a mechanism in which the collisional deactivation of the vibrationally hot CH(S_1*) above 10 Torr becomes an important factor in the subsequent internal energy distribution of CH(T_1*), since $\tau_F = 3 \times 10^9$ sec for CH(S_1*) equals the mean collision time interval (ω^{-1}) between CH(S_1*) and added deactivator molecules (*e.g.*, c-C_6H_{12}) at $\sim$30 Torr. However, the present result does not necessarily prove that the CH(T_1*) is the *immediate precursor* of C_5 hydrocarbon products.[18]

Cyclopentanone. Three important observations for cyclopentanone are: (1) Φ_F for cyclopentanone is slightly lower than Φ_F for acetone at λ_{ex} 310 nm; (2) Φ_F for cyclopentanone drops slowly below λ_{ex} 280 nm;

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(10) See, for a review on the photochemistry of acetone, R. B. Cundall and A. S. Davies, *Progr. React. Kinet.*, **4**, 147 (1967).

(11) (a) The result of the unpublished work by G. M. Breuer in our laboratory; (b) a comparable result has been obtained recently by A. M. Halpern and W. R. Ware at University of Minnesota.

(12) S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, **37**, 814 (1962).

(13) F. S. Wettack and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **90**, 3901 (1968).

(14) (a) W. R. Ware and A. M. Halpern, *J. Chem. Phys.*, **53**, 1696 (1970); (b) E. W. Schlag and H. von Weissenhoff, *ibid.*, **51**, 2508 (1969).

(15) This interpretation is consistent with the measurement of the observed τ_F values at varying λ_{ex} for acetone.[11a]

(16) The value of k_F for cyclohexanone calculated by the Strickler–Berg expression[12] is 2.2×10^5 sec^{-1}. However, this value could be too low, since the value of k_F for acetone calculated by the same expression was too low by a factor of $\sim$3. Thus, if we take a value of $k_F = 7 \times 10^5$ sec^{-1} for cyclohexanone as an upper estimate, $\tau_F \approx 3$ nsec is estimated.

(17) J. C. Dalton, D. M. Pond, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 2173 (1970).

(18) R. G. Shortridge, Jr., and E. K. C. Lee, *ibid.*, **92**, 2228 (1970).

(3) Φ_F for cyclopentanone below λ_{ex} 280 nm can be enhanced somewhat by ~50 Torr of added 1-pentene. The earlier observation that the fluorescence yield of cyclopentanone at λ_{ex} 313 nm is unaffected by a large excess of added inert gases[4b] is consistent with our present observation. Again the value of k_F for cyclopentanone is $\geq 5 \times 10^5$ sec^{-1}, and τ_F is $\sim 2.6 \times 10^{-9}$ sec,[11a] corresponding to the collision frequency of CP(S_1) with 1-pentene at ≈30 Torr.

Since the intersystem crossing rates (k_{ISC}) for acetone and the cyclic ketones are expected to be similar, due to the spin-orbit coupling, the values of Φ_F are also expected to be similar, unless the internal conversion and the chemical decomposition are very effective in competing with the intersystem crossing. The present study does not confirm the earlier interpretation that ethylene, cyclobutane, and CO are the *decomposition products of* and 4-pentenal is the *collisionally stablized isomeric product of* vibrationally hot, excited singlet cyclopentanone (S_1*) produced at λ_{ex} 313 nm.[19] However, it is consistent with the recent interpretations involving the triplet state and diradical precursors.[20-22]

We will consider two possible mechanisms for the photochemical transformation of cyclopentanone.

Mechanism A

$$\begin{aligned}
&S_1^* && \xrightarrow{k_1{}^*{}_f} S_0 + h\nu \text{ (fluorescence)}\\
&S_1^* && \xrightarrow{k_1{}^*{}_d} c\text{-}C_4H_8 \text{ (or } 2C_2H_4) + CO\\
&S_1^* + M && \xrightarrow{\omega_1{}^*(M)} S_1 + M\\
&S_1 && \xrightarrow{k_{1\,f}} S_0 + h\nu \text{ (fluorescence)}\\
&S_1 && \xrightarrow{k_{1,i}} \text{4-pentenal } (=\text{PA})
\end{aligned}$$

Mechanism B

$$\begin{aligned}
&S_1^* && \xrightarrow{k_1{}^*{}_f} S_0 + h\nu \text{ (fluorescence)}\\
&S_1^* && \xrightarrow{k_{ISC}{}^*} T_1^{**} \xrightarrow{\text{fast}} c\text{-}C_4H_8 \text{ (or } 2C_2H_4) + CO\\
&S_1^* + M && \xrightarrow{\omega_1{}^*(M)} S_1 + M\\
&T_1^{**} + M && \xrightarrow{\omega_3{}^*(M)} T_1^* + M\\
&S_1 && \xrightarrow{k_{1,f}} S_0 + h\nu \text{ (fluorescence)}\\
&S_1 && \xrightarrow{k_{ISC}} T_1^* \xrightarrow{\text{fast}} \text{4-pentenal } (=\text{PA})
\end{aligned}$$

A mechanism similar to mechanism A has been previously proposed by Srinivasan[19] and considered probable by La Paglia and Roquitte.[4] The latter workers who studied the fluorescence emission at λ_{ex} 313 nm only concluded that the mechanism A was consistent with the experimental observation that Φ_F is independent of the ω(M) if $k_1{}^*{}_f/k_{1,f} = k_1{}^*{}_d/k_{1,i}$ were maintained. The observed product ratio of CO/PA is known to be 0.10 at λ_{ex} 326 nm, 0.7 at 313 nm, 1.0 at 307 nm, and ~50 at 254 nm.[22] It is unlikely that $k_1{}^*{}_f/k_{1,f}$ can be as much as 500 as required by mechanism A, in view of the observation that k_F is nearly independent of the excess vibrational energy.[14] Furthermore, our fluorescence quantum yield measurement does not support any mechanism which requires a rate enhancement of nearly two orders of magnitude in the chemical decomposition ($k_1{}^*{}_d$) on the S_1 manifold when λ_{ex} is 254 nm.

We believe that mechanism B instead is consistent with all of the experimental observations: (1) the product ratio of CO/PA is suppressed at higher pressure of M owing to the vibrational relaxation prior to the intersystem crossing; (2) the ratio of CO/PA is enhanced at higher photoexcitation energy, since T_1** should decompose more rapidly than T_1*, according to the theory of unimolecular rate processes; (3) the value of Φ_F is *nearly* independent of the exciting wavelength (270–320 nm) because $k_1{}^*{}_f/k_{1,f} \approx k_{ISC}{}^*/k_{ISC}$, while $k_1{}^*{}_f \approx k_{1,f}$. According to the present fluorescence data, the decomposition process on the S_1 manifold cannot be competitive with the intersystem crossing process above λ_{ex} 270 nm. But it is conceivable that a significant fraction of the decarbonylation products observed below λ_{ex} 270 nm (*e.g.*, 253.7 nm)[19,20,22] is due to the singlet decomposition.

Since the lifetime of the CP(S_1*) above λ_{ex} 270 nm is 2–*ca.* 3 nsec,[11a] the vibrational relaxation of this species above 10–100 Torr is expected to determine the internal energy distribution of CP(T_1*). Thus the degree of the vibrational excitation in the triplet state can account for the observed pressure-dependent behavior of the ratio of the C_2–C_4 hydrocarbon products (ethylene and cyclobutane) to the isomerization product (4-pentenal),[19] favoring a low value of this ratio at a high pressure.

Cyclobutanone. One can regard the values of Φ_F and τ_F for CB near λ_{ex} 320 nm to be quite normal as in CH and CP. However, below λ_{ex} 310 nm, it is most likely that Φ_F is $<10^{-4}$ and τ_F $<10^{-10}$ sec. Since a detailed account of the photochemistry of the predissociating CB appears in a separate paper which follows,[23] no further discussion is given here.

Conclusions

The fluorescence emissions from the three cyclic ketones are unambiguously identified. The observed fluorescence quantum yields strongly indicate a common value of the $S_1 \rightsquigarrow T_1$ intersystem crossing rate of 1–4 $\times 10^8$ sec^{-1} for these ketones at low vibrational excitation levels of the S_1 state; furthermore, the $S_1 \rightsquigarrow T_1$ intersystem crossing quantum yield is most probably unity for these ketones as it is for acetone.

The wavelength dependence of the fluorescence quantum yields suggests that the threshold energy needed for an effective competition of the "predissociation" with the intersystem crossing from the S_1 state is ~4 kcal/mol for cyclobutanone, ~15 kcal/mol for cyclopentanone, and >25 kcal/mol for cyclohexanone. This trend is entirely consistent with the expectation from unimolecular decomposition rate theory, since the rate of the "predissociation" process is significantly reduced by the increased number of oscillators. Only above this threshold energy, then, does the decomposition process from the S_1 manifold become important, while below this threshold energy the observed product distribution is largely affected by the internal excitation energy of

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(19) (a) R. Srinivasan, *ibid.*, **83**, 4344, 4348 (1961); (b) C. Y. Mok, *J. Phys. Chem.*, **74**, 1432 (1970).

(20) E. K. C. Lee, *ibid.*, 71, 2805 (1967), and references therein.

(21) (a) P. Dunion and C. N. Trumbore, *J. Amer. Chem. Soc.*, **87** 4211 (1965); (b) R. Simonaitis, G. W. Cowell, and J. N. Pitts, Jr., *Tetrahedron Lett.*, 3751 (1967); (c) P. J. Wagner and R. W. Spoerke, *J. Amer. Chem. Soc.*, **91**, 4437 (1969).

(22) A. T. Blades, work on cyclopentanone, to be published.

(23) J. C. Hemminger, C. F. Rusbult, and E. K. C. Lee, *J. Amer. Chem. Soc.*, **93**, 1867 (1971).

the T_1 state. Thus, the triplet state plays an important role in the photochemistry of these cyclic ketones.

It is well demonstrated here that the fluorescence excitation study made at low and high pressures can provide kinetic information essential for the mechanistic elucidation of photochemical transformations. Since the sensitivity of the present experimental measurement is very high, a similar study can be extended to other photochemical systems of interest with an extremely low-level luminescence.

Unusual Photochemistry of Cyclobutanone near Its Predissociation Threshold[1]

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Abstract: The fluorescence excitation and emission spectra have been measured in the gas phase as well as in the liquid phase. Furthermore, quantum yields of fluorescence in both phases have been measured. The very unusual feature of the fluorescence excitation spectra, together with photodecomposition studies near its absorption threshold (326.1 and 334.3 nm) and the recent study of its high-resolution absorption spectroscopy made in the gas phase, provides strong evidence for the onset of a *predissociation* above ~3 kcal/mol vibrational excitation in the first excited singlet (n, π^*) state. The photodecomposition study was also carried out in the liquid phase, and the mechanism of the decomposition in the liquid phase is discussed in light of the predissociative behavior in the S_1 manifold.

Two principal photochemical decomposition processes of cyclobutanone (CB) in the gas phase, as shown in eq 1 and 2, have been recently studied in

$$\mathrm{CB} + h\nu \begin{cases} \longrightarrow C_2H_4 + CH_2CO \quad C_2\ \text{path} & (1) \\ \longrightarrow c\text{-}C_3H_6 + CO \quad C_3\ \text{path} & (2) \end{cases}$$

great detail.[2] It was shown that the precursor of C_2H_4 and CH_2CO (C_2 products) was a vibrationally hot, ground electronic state of cyclobutanone (S_0^*), and that S_0^* was produced by the $S_1 \rightsquigarrow S_0$ internal conversion process.[2b] Furthermore, it was proposed, on the basis of the triplet-benzene-photosensitized decomposition study of cyclobutanone, that the precursor of cyclopropane and CO (C_3 products) was the lowest triplet state of cyclobutanone (T_1).[2a] These photochemical studies in the gas phase led us to extend our investigation to the liquid phase, since it was desirable to test the above simple mechanism in the liquid phase where the vibrational relaxation is much more rapid than in the gas phase at a few atmospheres. It was expected that no C_2 product would be observed in the liquid-phase photolysis at 313 nm if the vibrationally hot S_0^* were the only precursor of the C_2 product. On the contrary, an appreciable yield of C_2H_4 was observed, and our observation confirmed earlier liquid-phase studies in which CH_2CO was indirectly observed.[3]

This surprising result prompted us to study the photodecomposition of cyclobutanone in the gas phase in the exciting wavelength (λ_{ex}) region longer than 313 nm, because the CB(S_1^*) produced at λ_{ex} 313 nm has ~5 kcal/mol of excess vibrational energy. It was thought that the results obtained in the liquid-phase photolysis at 313 nm could be rationalized on the basis of the results obtained in gas-phase photolysis near the O–O absorption band, since the vibrational energy transfer process involving S_1^* and the solvent molecule should be extremely fast, $\sim 10^{-11}$ sec, in the liquid phase. Whether or not such a simple mechanistic convergence can be realizable in the photochemistry of cyclobutanone is examined in this paper.

Experimental Section

The gas-phase experiments were carried out as usual in the earlier studies.[2] The liquid phase photolysis was carried out in *n*-heptane, methanol, or *cis*-1,3-pentadiene solution under O_2-free nitrogen pressure, using a silica cell of 0.6-cm optical path. The concentration of cyclobutanone was adjusted so that 0.8–0.9 of the photolytic radiation was absorbed. A high intensity Bausch and Lomb monochromator was used in isolating the 313-nm line from a 200-W mercury arc lamp and the 334.3-nm line[4] from a 500-W mercury arc lamp, while a Corning CS 0-54 filter was used with an 18-W Cd lamp for the 326.1-nm photolysis. All of the experiments were carried out at room temperature (23°).

The fluorescence in the gas phase was measured with a highly sensitive photon-counting setup,[5] while the fluorescence in the liquid phase was measured with a Hitachi Perkin-Elmer MPF-2A spectrophotofluorometer using a thin front-face cell (1-mm optical path).[6] The spectrofluorometer was equipped with a Hamamatzu R106 photomultiplier tube with S-19 spectral response. Since the exciting light intensity from the xenon arc decreases smoothly from 340 to 260 nm by a factor of 7, the uncorrected excitation spectra are greatly distorted; however, the present study does not require correction.

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[2] (a) H. O. Denschlag and E. K. C. Lee, *J. Amer. Chem. Soc.*, **89**, 4795 (1967); (b) N. E. Lee and E. K. C. Lee, *J. Chem. Phys.*, **50**, 2094 (1969).

[3] (a) N. J. Turro and R. M. Southam, *Tetrahedron Lett.*, 545 (1967); (b) D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 4349 (1970).

[4] A 1.0-cm thick aqueous solution of 0.4 *M* KNO_3 and a CS 0-54 filter were placed between the monochromator and the photolysis cell in order to cut out the impurity radiation below 320 nm: C. A. Parker, "Photoluminescence in Solutions," Elsevier, New York, N. Y., 1968, p 187.

[5] R. G. Shortridge, Jr., C. F. Rusbult, and E. K. C. Lee, *J. Amer. Chem. Soc.*, **93**, 1863 (1971).

[6] See F. Wilkinson in "Fluorescence," G. G. Guilbault, Ed., Marcel Dekker, New York, N. Y., 1967, p 1.