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

$$\mathrm{CB} + h\nu \longrightarrow \mathrm{C_2H_4} + \mathrm{CH_2CO} \quad \mathrm{C_2\ path} \qquad (1)$$

$$\phantom{\mathrm{CB} + h\nu} \longrightarrow c\text{-}\mathrm{C_3H_6} + \mathrm{CO} \quad \mathrm{C_3\ path} \qquad (2)$$

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

[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.

Table I. Photochemical Product Quantum Yields from the Liquid-Phase Photolysis of Cyclobutanone (23°)

λ_{ex}, nm	Solvent	Quantum yields[a] C_2H_4	c-C_3H_6	$(C_2 + C_3)$	(C_3/C_2)
326.1	0.19 M in n-C_7H_{16}	0.10	0.08	0.18	0.80
313	0.13 M in n-C_7H_{16}	0.12	0.09	0.22	0.75
313	0.13 M in *cis*-1,3-C_5H_8	0.12	0.07	0.20	0.57
313	0.20 M in CH_3OH	0.07	0.034	0.10	0.5

[a] 0.18 M cyclopentanone in n-C_7H_{16} was used to calibrate the intensity of the photolytic radiation, ~10^{16} photons/sec. The precision of the quantum yield measurement is ~10%.

Table II. Relative Photochemical Product Yields from the Gas-Phase Photolysis of Cyclobutanone (23°)

λ_{ex}, nm	Pressure, Torr: CB	1-C_5H_{10}	i-C_6H_{14}	Relative yields[a]: C_2H_4	c-C_3H_6	$(C_2 + C_3)$	(C_3/C_2)
334.3	15			6.5	22.4	28.9	3.4
334.3	15	100		6.0	20.8	26.8	3.4
334.3	15	200		6.3	18.7	25.0	3.0
334.3	15	505		6.5	16.5	23.0	2.6
326.1	15			40.8	55.4	96.2	1.35
326.1	15		10	43.6	58.4	102.0	1.34
326.1	15		15	41.2	65.1	106.3	1.42
326.1	15		50	39.8	58.4	98.2	1.47
326.1	15		100	34.6	52.6	87.2	1.52
326.1	15		150	32.3	48.1	80.4	1.49
326.1	15		189	30.3	45.4	75.7	1.50
326.1	15	200		26.6	40.8	67.4	1.53
326.1	15	500		25.4	45.1	70.5	1.77

[a] The precision of the relative yield measurement is ~5%.

Table III. Fluorescence Emission Quantum Yields in the Liquid Phase (c-C_6H_{12} Solvent)[a]

λ_{ex}, nm	Acetone	CB	CP	CH
302	(0.001)	$(0.8 \pm 0.3) \times 10^{-4}$	$(9 \pm 2) \times 10^{-4}$	$(9 \pm 2) \times 10^{-4}$
313	(0.001)	$(1.0 \pm 0.3) \times 10^{-4}$	$(6 \pm 2) \times 10^{-4}$	$(9 \pm 2) \times 10^{-4}$

[a] Taken without deaeration.

The quantum yield of the hydrocarbon products in the liquid-phase photolysis was measured, using the 4-pentenal yield ($\Phi = 0.37 \pm 0.01$)[7] in cyclopentanone photolysis as the reference.

Results

Ethylene and cyclopropane yields from the photolysis of cyclobutanone were determined by the usual gas chromatographic analysis. The results obtained in the liquid phase at λ_{ex} 326.1 and 313 nm are shown in Table I, and the results obtained in the gas phase at λ_{ex} 334.3 and 326.1 nm are shown in Table II. The total hydrocarbon product quantum yield obtained with the cyclopentanone actinometer in the liquid phase is probably accurate to ~30%. However, it was not possible to measure the quantum yields in the gas phase with any accuracy because the molar absorptivity at either wavelength used is quite low. We were only able to determine the molar extinction coefficient of CB for the 326.1-nm cadmium line to be ~0.3 l. mol^{-1} cm^{-1} at 30 Torr of CB. It was then estimated that the total product quantum yield at 326.1 nm was unity within a factor of 2.

It was desirable to observe the effect of a large excess of added gas on the fluorescence emission yields in the gas phase since the emission from CB is quite unusual.[5] As shown in Figure 1, 409 Torr of 1-pentene has virtually no effect upon the shape and the intensity of the fluorescence excitation spectra. There is a slight trend for a blue shift of ~2 nm when 201 (or 409) Torr of 1-pentene is added. Since the accuracy in the relative intensity measurement is ~10%, it is difficult to make any quantitative interpretation of this observation.

In order to determine whether the fluorescence emission would be enhanced in the liquid phase as compared to that in the gas phase, the fluorescence emission and excitation spectra of acetone, cyclobutanone, cyclopentanone, and cyclohexanone were obtained using c-C_6H_{12} as solvent. The spectra are displayed for comparison in Figures 2 and 3. The concentrations of the ketones were so adjusted that the extent of the absorption at λ_{ex} 302 nm was nearly equal for all of them. It was found that the emission spectrum of CB obtained at high concentrations resembles the spectrum of acetone, though it is not shown in Figure 2. The fluorescence quantum yields of these ketones in c-C_6H_{12} obtained at λ_{ex} 302 nm are summarized in Table III. A value of $\Phi_F = 0.001$ for acetone reported by O'Sullivan and Testa[8] is used as the fluorescence yield standard.[9,10]

Discussion

Fluorescence Emission Yield in Solution. One of the most striking observations concerning the fluorescence emission from cyclobutanone is that Φ_F in the liquid phase near λ_{ex} 310 nm is 1×10^{-4}, only $^1/_{20}$th of that found in the gas phase. Furthermore, the fluorescence excitation spectrum in the liquid phase is not much wider

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[7] P. Dunion and C. N. Trumbore, *J. Amer. Chem. Soc.*, **87**, 4211 (1965).

[8] M. O'Sullivan and A. C. Testa, *ibid.*, **90**, 6245 (1968).

[9] We take the value of $\Phi_F = 0.001$ which was previously assigned as the "excimer" fluorescence yield by O'Sullivan and Testa,[8] because it has been shown subsequently [G. D. Renkes and F. S. Wettack, *J. Amer. Chem. Soc.*, **91**, 7514 (1969)] that the "excimer" emission is truly the acetone monomer fluorescence.[10]

[10] R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966); the value of Φ_F reported is 0.01 ± 0.003, an order of magnitude higher than that reported in ref 8. We do not understand the reason for the discrepancy, but we choose to use the lower value, since it appears more consistent with the gas-phase value.

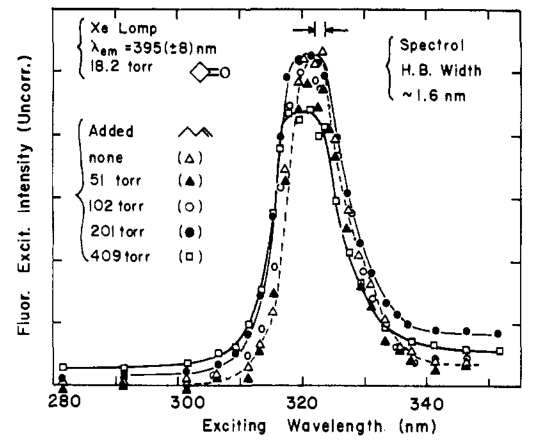

Figure 1. Effect of added 1-pentene gas on the fluorescence excitation spectrum of cyclobutanone.

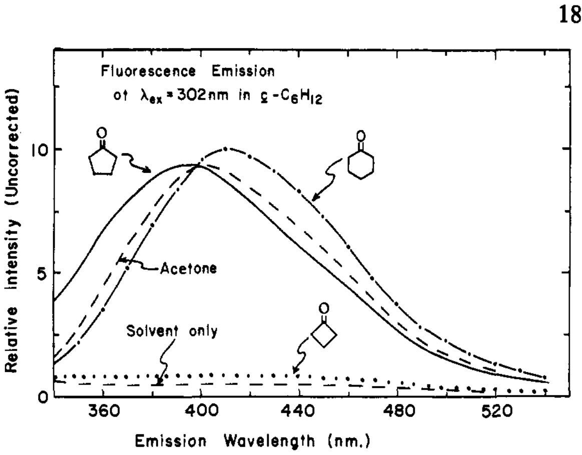

Figure 2. Fluorescence emission spectra obtained in *c*-C_6H_{12} solution (uncorrected for the spectral sensitivity) at λ_{ex} 302 nm: acetone, 0.24 *M;* cyclobutanone, 0.14 *M;* cyclopentanone, 0.097 *M;* cyclohexanone, 0.14 *M*.

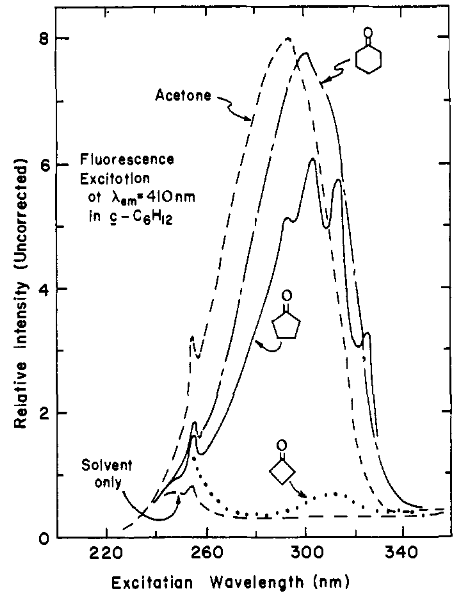

Figure 3. Fluorescence excitation spectra obtained in *c*-C_6H_{12} solution (uncorrected for the exciting intensity variation) at λ_{em} 410 nm. A sharp peak at 254 nm is the mercury impurity emission in the xenon continuum.

than that found in the gas phase, and it extends to λ_{ex} $\approx$290 nm. On the contrary, the fluorescence quantum yields of acetone, cyclopentanone, and cyclohexanone measured in the liquid phase[9,10] are comparable to that in the gas phase. We would interpret these results to mean that the fluorescence emission quantum yields for acetone, cyclopentanone, and cyclohexanone are essentially unchanged going from the gas phase to the liquid phase, since there is a significant discrepancy in the measurement made in the liquid phase.[8-10] Furthermore, the similarity of the fluorescence quantum yields and the fluorescence lifetimes of these ketones (except CB) in the liquid and in the gas phase implies that the rate of the $S_1 \rightsquigarrow T_1$ intersystem crossing (k_{ISC}) is nearly the same, (3-4) × 10^8 sec^{-1}.[5] This is consistent with the interpretation that k_{ISC} for acetone is *intrinsic*[10] and is determined chiefly by the *spin-orbit coupling.*[11] The fluorescence lifetime of the vibrationally relaxed CB in solution could be as short as ~0.2 nsec, while the vibrationally hot CB(S_1) in solution produced below λ_{ex} 290 nm must be much shorter than that, since there is practically no emission below λ_{ex} 290 nm. Therefore, the vibrational relaxation time of the excited singlet CB(S_1) with more than ~10 kcal/mol of vibrational excitation energy must be much slower than the competing "chemical decomposition" processes.[12] Since the vibrational relaxation time in an organic fluid solution is known to be ~7 × 10^{-12} sec,[13] the highly vibrationally excited CB(S_1) can have a short lifetime of ~10^{-12} sec.

"Predissociation." An electronically excited species undergoing "predissociation" can have such a short lifetime.[14] There are three criteria for predissociation, *e.g.*, (a) efficient photodecomposition originating from the predissociative level, (b) broadening of the absorption lines for the transitions to the predissociative level, and (c) weakening of the emission lines from the "diffuse" upper level. From our work, (a) and (c) are satisfied, while (b) is satisfied by the recent study of the cyclobutanone absorption at high resolution; it has been shown that a diffuseness of the $S_0 \rightarrow S_1$ absorption lines begins to develop when S_1* has more than ~3 kcal/mol vibrational excitation energy.[15] In the present work, a dramatic change in the photolytic product distribution obtained in the gas phase near λ_{ex} 315 nm, where the fluorescence yield suddenly begins to decline, is well illustrated in Figure 4.

In light of the foregoing discussion, it is obvious that a detailed study of this extremely interesting case of predissociation must be made. While such an experimental study is in progress, a few pertinent conclusions of immediate concern can be given. (1) The photochemistry of CB(S_1) below its predissociation threshold (λ_{ex} >320 nm) can be regarded as *normal* as found for

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(11) It is interesting to note that the values of τ_F for cyclohexanone and alkyl-substituted cyclohexanone range from 2.5 to 4.0 nsec in solution [see J. C. Dalton, D. M. Pond, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 2173 (1970)].

(12) It has been recently postulated that the radiationless relaxation of an electronically excited species can be achieved through an *isomer* formation [see D. Phillips, J. Lemaire, C. S. Burton, and W. A. Noyes, Jr., *Advan. Photochem.*, **5**, 329 (1968)].

(13) P. Rentzepis, *Chem. Phys. Lett.*, **2**, 117 (1968).

(14) See G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. 3, Van Nostrand, Princeton, N. J., 1966, p 455.

(15) (a) D. C. Moule, *Can. J. Phys.*, **47**, 1235 (1969); (b) D. C. Moule, private communication, unpublished work: the absorption line width should be greater than 0.1 cm^{-1}, according to the uncertainty principle, if the lifetime of CB(S_1*) is less than 0.5 × 10^{-10} sec.

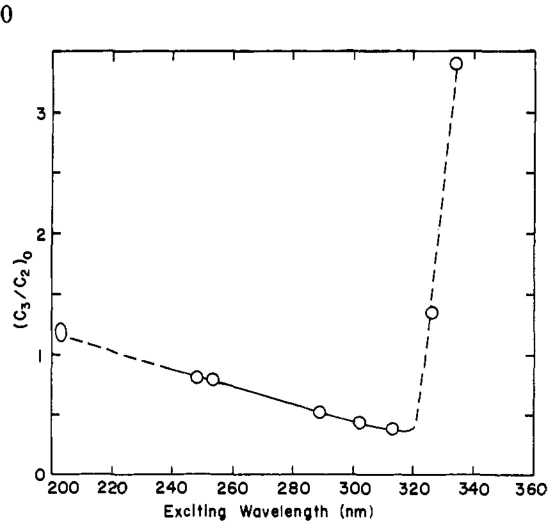
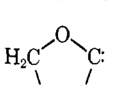


Figure 4. The ratio of the (C_3/C_2) product ratio at low total pressure *vs.* exciting wavelength.

acetone, cyclopentanone, and cyclohexanone for λ_{ex} 270–330 nm. (2) The fluorescence lifetime of $CB(S_1)$ in the *normal* region is 10^{-9}–10^{-8} sec, as determined chiefly by the $S_1 \rightsquigarrow T_1$ intersystem crossing rate. (3) The drastic decrease of the fluorescence lifetime in the liquid phase indicates the short-lived character of the vibrationally hot $CB(S_1^*)$.

The equilibrium configuration of the first excited singlet state of $CB(S_1)$ is pyramidal (about the carbonyl carbon atom) as in formaldehyde, and the out-of-plane O-atom wagging vibration has an interval of ~355 cm^{-1}.[15] It is conceivable that there is a considerable degree of ring strain for $CB(S_1)$ and the "predissociative behavior" may be resulting from the rupture of the C_1–C_2 bond. Furthermore, the drastic weakening of the fluorescence emission in the c-C_6H_{12} solution should be attributed to the enhancement of the "predissociative behavior" due to neighbor interaction of the vibrationally excited $CB(S_1^*)$ with the solvent molecules. This interpretation is consistent with the observation that cyclobutanone and its derivatives undergo photochemical ring-cleavage transformations in solution,[3,16] and one of the transient intermediates has been proposed as a cyclic oxycarbene having the five-membered ring structure shown below.[3]



Collisional Activation and Deactivation. The greatest ratio of C_3/C_2 thus far achieved is a value of 3.4 obtained at λ_{ex} 334.3 nm, where a hot-band excitation to the vibrationless state of $CB(S_1)$ is achieved; a much lower value of C_3/C_2 = 1.35 is obtained at λ_{ex} 326.1 nm, where an excitation to the vibrationally excited levels is achieved. The most probable one is the first level of the out-of-plane wagging vibration of the carbonyl oxygen (355 cm^{-1}).[15b,17] The fact that the C_3/C_3 ratios at the two different excitation wavelengths converge to the intermediate value upon the addition of a large excess of foreign gases indicates the following. (1) In the case of λ_{ex} 334.3 nm, the vibrationless $CB(S_1)$ is activated collisionally to a vibrationally excited level and thus a lower value of the C_3/C_2 ratio results at high pressures. (2) in the case of λ_{ex} 326.1 nm, the $CB(S_1)$ with some vibrational excitation energy is mostly deexcited by collision at high pressures, and thus a slightly higher value of the C_3/C_2 ratio results. Redistribution of the internal energy into the lower energy ring puckering vibrational mode (~0.1-kcal/mol interval)[15] is certainly expected.

At high pressures some of the internally converted $CB(S_0^*)$ is collisionally quenched to give a low yield of C_2H_4,[2] but it is difficult to estimate the extent of this quenching process from the present set of data. Particularly, when the 326.1-nm cadmium line is used, we cannot be sure that Beer's law is obeyed throughout the pressure ranges covered,[18] and thus we have no firm measurement of relative quantum yield as a function of pressure in Table II. The 334.3-nm line from the 500-W super-pressure mercury lamp is sufficiently broadened that Beer's law is presumably obeyed in the absorption by CB.

Mechanism. In the gas phase, the $S_1 \rightsquigarrow T_1$ intersystem crossing predominates over other processes *below the predissociation threshold*, and c-C_3H_6 is efficiently produced as the triplet product with Φ = 0.7–0.8. Furthermore, C_2H_4 is produced as the internally converted product with Φ = 0.2–0.3. It is obvious that the earlier proposed mechanism for the CB photodecomposition[2,5] is satisfactory above λ_{ex} 315 nm.

Below λ_{ex} 315 nm, a new mechanism becomes operative through the intermediacy of a $CB(S_1^*)$ or a *diradical* precursor which gives pressure-unquenchable products, c-C_3H_6 (and CO) with $\Phi \approx 0.3$, C_2H_4 (and CH_2CO- with $\Phi \leq 0.1$, and through the intermediacy of an internally converted $CB(S_0^*)$ with $0.6 \leq \Phi \leq 0.7$, which in turn gives the pressure-quenchable products C_2H_4 and CH_2CO.[19] This new mechanism can now permit a qualitative explanation of the photolysis results obtained in the liquid phase.

In the liquid phase, the vibrationally hot $CB(S_0^*)$ will be effectively quenched, and therefore all of the observed products are likely to arise from a $CB(S_1^*)$, a *diradical* intermediate $[\dot{C}H_2CH_2CH_2\dot{C}O]$, a triplet $CB(T_1^*)$, and the cyclic *oxycarbene* intermediate.[3] One can rule out the $CB(T_1^*)$ as an important intermediate, since no appreciable quenching of the products are observed in neat *cis*-1,3-pentadiene solution or in air-saturated n-C_7H_{16} solution, unless its lifetime is so short that the scavenging is improbable. The fact that Φ for the (C_2 + C_3) products is reduced to half when methanol is used as solvent rather than n-C_7H_{16} indi-

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[16] (a) See P. Yates, *Pure Appl. Chem.*, **16**, 93 (1968); (b) H. A. J. Carless and E. K. C. Lee, *J. Amer. Chem. Soc.*, **92**, 6683 (1970).

[17] The electronic origin of the $CB(S_1)$ corresponding to the ${}^1A_1 \rightarrow {}^1A_2$ transition is 30,291.2 cm^{-1}.[15a] The 334.3-nm transition corresponds to an excitation to the vibrationless level of S_1 from the ground state (S_0) with 1 quantum of the C=O out-of-plane wagging vibration (394 cm^{-1}). It is not possible to rule out that the 334.3-nm excitation could induce a nonnegligible amount of a $S_0 \rightarrow T_1$ transition.

[18] The line width of the 326.1-nm line is less than 0.06 Å as measured by us, and it is known that CB has a rotationally sharp absorption line.

[19] The value of $\Phi \leq 0.1$ for the pressure-unquenchable yield of C_2H_4 is only an upper-limit estimate based on the photolysis study of 2,3-dimethylcyclobutanone in the gas phase [H. A. J. Carless and E. K C. Lee, *J. Amer. Chem. Soc.*, **92**, 4482 (1970)]. If less than one-seventh of the C_2H_4 yield in the cyclobutanone photolysis[2] were pressure unquenchable at ~1000 Torr of C_3H_6, within the precision of the experiment, it would not have been possible to observe the nonlinearity of the Stern–Volmer plot in the pressure range covered.

cates the importance of the cyclic *oxycarbene* intermediate. It is certainly conceivable that the *oxycarbene* intermediate could be in equilibrium with the *diradical* intermediate. The quantum yield of these intermediates in the liquid phase can be much higher than 0.20 in *n*-C_7H_{16}, since we cannot be certain that the *oxycarbene* intermediate did not insert into the C–H bonds in *n*-C_7H_{16} before the intermediates decomposed to the C_2 and C_3 products. If one expects the quantum yield for the internal conversion process in the liquid phase to be about the same as in the gas phase, 0.6–*ca.* 0.7, then the total quantum yields of the observed products should be 0.3–0.4. Since the overall observed product quantum yields are less than 0.22, the unaccounted quantum yields are 0.1–0.2. It should be noted that the short-lived nature of the photoexcited cyclobutanone in the liquid phase is analogous to that of the photoexcited oxetanones previously studied.[20]

We hope to obtain further mechanistic insight into the roles played by the above proposed transient intermediates through the study of the thermal decomposition and the photochemical decomposition of *cis*- and *trans*-2,3-dimethylcyclobutanone as well as *cis*- and *trans*-2,4-dimethylcyclobutanone.[16b,19] One feature of cyclobutanone photochemistry worthy of attention is the rapid electronic relaxation process probably *via* a chemical isomerization route[12] which is responsible for the "predissociative" behavior.

Acknowledgment. Authors are grateful to Dr. D. C. Moule of Brock University for his kindness in giving us the spectral assignments from the high-resolution absorption spectra of cyclobutanone. Discussions with Drs. R. J. Campbell and R. F. Klemm have been helpful.

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(20) P. J. Wagner, C. A. Stout, S. Searles, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1242 (1966).

Electrochemical Reduction of Pyrimidine in Acetonitrile. Behavior of the Anion Free Radical

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Abstract: The electrochemical reduction of pyrimidine, which is the model compound for the reduction of the biologically important purine–pyrimidine series, has been investigated in acetonitrile media. Pyrimidine is initially reduced in a one-electron, reversible, diffusion-controlled process at fairly negative potential to produce an unstable radial anion, which is quickly deactivated *via* two competitive pathways: (1) fast dimerization to form a pyrimidine anionic dimer (probably the 4,4′ species) with a rate constant of $8 \pm 5 \times 10^5$ l./(mol sec) and (2) proton abstraction from residual water [rate constant of *ca.* 7 l./(mol sec)], which is rapidly followed by a further one-electron reduction to produce ultimately 3,4-dihydropyrimidine. Addition of acid to pyrimidine solutions results in the appearance of a new wave at less negative potential, which is attributed to the one-electron reduction of an N-protonated pyrimidine species to produce a free radical which dimerizes very quickly, probably to the 4,4′ compound; this wave is very similar to the first one-electron wave of pyrimidine in aqueous media. Pyrimidine is the only aromatic system thus far systematically examined which shows initial one-electron reductions in both aqueous (proton rich) and nonaqueous (proton poor) media.

In recent years, much interest has developed in the electrochemical behavior of biologically important compounds.[1–3] As a result of our concern with purines, pyrimidines, and their nucleosides and nucleotides, considerable work has been done on pyrimidine (1,3-diazine) itself in aqueous solution[4–6] since it is the prototype compound for the purine–pyrimidine series; *e.g.*, the electrochemical reduction of purines occurs in the pyrimidine ring. Recent work has concentrated on the nature of the initial, rate-controlling, one-electron (1-e) reduction of pyrimidine, more definitive information on which should provide additional insight into the redox behavior of the biologically important purines and pyrimidines. Consequently, the electrochemical reduction of pyrimidine has been investigated in acetonitrile on the basis that the information obtained in an inert solvent would reflect, more directly, the properties of pyrimidine itself and not its solvent–solute interaction, as well as the properties and behavior of the anion free radical expected in proton-poor medium.

Another and more fundamental reason for investigating the pyrimidine reduction mechanism in a nonaqueous solvent is that it affords the unique opportunity of studying a 1-e reduction process in an aromatic system, which also undergoes 1-e reduction in aqueous media. Many organic compounds, *e.g.*, aromatic hydrocarbons, which exhibit a 1-e or two separate 1-e reduction steps in nonaqueous media, show only a 2-e reduction in aqueous media due to a fast ECE mechanism involving protonation of the electrogenerated radical anion. The development of information regarding the reduction of the C–N aromatic double bond

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