JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 98, NUMBER 8 APRIL 14, 1976

Thermal, Photochemical, and Photophysical Processes in Cyclopropanone Vapor[1]

Hector J. Rodriguez,[2] Jung-Ching Chang,[2] and Timothy F. Thomas*

Contribution from the Department of Chemistry, University of Missouri-Kansas City, Kansas City, Missouri 64110. *Received June 26, 1975*

Abstract: The photochemical quantum yields of cyclopropanone vapor have been measured from 365 to 291 nm. For decomposition of the parent molecule $\phi \sim 1.0$ at all wavelengths, while $\phi_{C_2H_4}$ rises from 0.60 to ~ 1.0 as the irradiation wavelength is decreased. The fluorescence quantum yield was measurable only at λ_{ex} 365 nm, where $\phi_f = 6.8 \times 10^{-5}$ and $\tau_f(\text{calcd}) \sim 2 \times 10^{-10}$ s. A detailed mechanism is proposed involving predissociation of the $^1(n,\pi^*)$ state leading to two biradical intermediates. The thermal reaction of cyclopropanone, yielding polymer, was found to be surface catalyzed, with an activation energy of $\sim$2 kcal mol^{-1} in a Pyrex ir cell between 20 and 50 °C. An experimental value of +3.8 kcal mol^{-1} was obtained for the heat of formation of cyclopropanone and used to predict an activation energy of $\sim$30.5 kcal mol^{-1} for its homogenous decomposition via the oxyallyl biradical.

Cyclopropanone and its derivatives were proposed as intermediates in organic reactions several decades[3-7] before the first spectroscopic evidence[8,9] for the existence of the molecule was obtained. Following the first reports of a synthetic method yielding workable quantities of the unsubstituted compound,[10,11] there have been several studies of its reactions with a wide variety of acids, bases, and other adducts in solution, generally at subzero temperatures because of cyclopropanone's high reactivity.[7,12-14] Numerous theoretical calculations to various levels of approximation have been made regarding the structure,[15] heat of formation,[16] and potential energy surfaces[17-19] of cyclopropanone. But experimental measurements on the isolated molecule have been limited to determinations of its structure by microwave spectroscopy[20] and electron diffraction,[21] plus our preliminary report on its photochemistry in the gas phase.[22] We present here a detailed report of the experimental properties of gaseous cyclopropanone, including its photochemical and fluorescence quantum yields as a function of irradiation wavelength, its thermal decomposition rate constants (experimental vs. "theoretical"), and a detailed mechanism for its reactions via the $^1(n,\pi^*)$ state.

Experimental Section

Materials. Ketene was synthesized by passing acetic anhydride, carried in a stream of dry nitrogen, over a heated tungsten filament, removing by-products by traps at −22 and −63 °C, then collecting the desired product at −132 °C. Subsequent trap-to-trap distillation on a high vacuum line yielded material with $\sim$0.80 Torr vapor pressure at −132 °C, which was shown to be 99+% pure ketene by GC and ir analysis. Cyclopropanone was synthesized by the reaction between ketene and diazomethane,[10,11] with the modification that diazomethane was generated in a flow system (dry argon carrier) and bubbled through pure liquid ketene at −132 °C. The diazomethane was produced by the reaction between sodium hydroxide and *N*-nitrosomethylurea in ethylene glycol, taking pains to thoroughly dry the resulting diazomethane-argon stream. Product cyclopropanone was purified by: (i) removing the ketene solvent at −78 °C; (ii) distilling the residue at −45 °C; (iii) distilling the distillate from (ii) at −63 °C and keeping the middle fraction. The resulting material was shown to have a purity of $\sim$98%, the main impurities being cyclobutanone, $\sim$1.5%, and ethylene, $\sim$0.5%. Its vapor pressure at −45 °C was $\sim$0.8 Torr and its melting point lay between −78 and −63 °C. Yields of cyclopropanone were low (<1%, based on *N*-nitrosomethylurea), a consequence of the stringent methods employed to reduce the level of impurities and of partial polymerization of the cyclopropanone which occurred during its distillation in the vacuum line.

The mass spectrum of cyclopropanone showed the following major peaks: 56 (19.5%), 42 (7.2%), 28 (100%), 27 (30.5%), 26 (30.5%), in reasonable agreement with other determinations.[11,21] Except for a small 70 peak due to cyclobutanone, no peaks at *m/e* >56 were detected. Absorption maxima in the uv spectra of the vapor were found at 312 (±1) nm, ϵ 17 M^{-1} cm^{-1}; and at 201 nm, ϵ 1.0×10^3 M^{-1} cm^{-1} (see ref 22 for complete spectrum). Ir peaks (gas phase) include: 3086 (vw), 3020 (w), 3005 (w), 2990 (w), 1980 (m), 1905 (s), 1868 (m), 1818 (vs), 1050 (w), 1028 (w), 980 (m), 949 (m), 920 (m), 911 (m) cm^{-1}. Interference by peaks due to polycyclopropanone formed on the KBr windows occurred in the 1500-900-cm^{-1} region, making identification of the weaker monomer peaks in that region somewhat tentative. Preliminary results with cyclopropanone-d_2 and -d_4 indicate the multiplicity of peaks in the carbonyl region is probably due to Fermi resonance with overtones or combination bands of vibrations whose fundamentals lie in the 900-1050-cm^{-1} region, rather than the co-existence of several isomeric forms of cyclopropanone.[23]

The added gases used in the photochemical studies were all research grade: CO_2, from Air Products; O_2, from Matheson Gas Products; 1,3-butadiene and cyclopentane from Phillips Petroleum

Co. Compounds used in the cyclopropanone synthesis had the following sources and purity: acetic anhydride, MC/B reagent grade; ethylene glycol, MC/B chromatographic quality; *N*-nitrosomethylurea, K & K Laboratories, containing 3% acetic acid. Cyclobutanone was obtained from Aldrich Chemical and showed >99% purity by GC, after trap-to-trap distillation. Azomethane was synthesized from *sym*-dimethylhydrazine dihydrochloride by the method of Renaud and Leitch,[24] then purified by trap-to-trap distillation. Quinine sulfate, used as the emission standard in the fluorescence yield determination, was from K & K Laboratories and was used without further purification.

Procedures. Rates of the thermal reaction of cyclopropanone as a function of temperature were measured using a water-jacketed 10-cm Pyrex ir gas cell and recording the transmittance at 1905 cm^{-1} as a function of time on a Perkin-Elmer 621 ir spectrophotometer operating with ×5 scale expansion. The 1980- and 1818-cm^{-1} peaks were occasionally monitored and showed the same decay rate as the 1905-cm^{-1} peak, which was preferred because it is free from interference by traces of cyclobutanone which absorbs strongly at 1816 cm^{-1}. Temperatures were read using a calibrated thermister placed in a well just above the ir beam passing through the cell. For the surface-effect studies a stainless steel beam-conforming ir cell and a quartz photolysis cell (see below), in one case containing 0.88 g of thoroughly cleaned 200 mesh Pyrex powder, were also used. For these latter two cells the Cary 1501 spectrophotometer was used to follow the cyclopropanone disappearance.

Samples for photolysis were prepared on a mercury-free high-vacuum line (routinely maintained at $<10^{-4}$ Torr) and contained in 10-cm long, 1.9 cm o.d., fused quartz optical cells with Martin-Kontes Kel-F high-vacuum stopcocks. A Bausch and Lomb SP-200 mercury arc was used as the radiation source; 313- and 365-nm mercury lines were selected by interference filters having a half-band width of 12 nm, while 334 and ~291 nm were obtained using a Bausch and Lomb High Intensity Monochromator ($\Delta\lambda_{1/2}$ 5 nm) preceded by water and bromine filters. Gaseous azomethane at 2–3 Torr was used as an actinometer to calibrate the RCA No. 935 vacuum photodiode used to monitor light intensities. Actinometry was done about once for every two cyclopropanone photolyses, and was based on the assumption that $\Phi_{C_2H_6} = 1.0$. Extinction coefficients used in the quantum yield calculations were obtained on both Cary 14 and 1501 spectrophotometers for azomethane and cyclopropanone; in the case of cyclopropanone, ϵ was found to be constant to $\pm\leq 6\%$ between 0.7 and 33 Torr. The effective extinction coefficient of cyclobutanone was determined directly from transmittance of a 45-Torr gas sample in the photolysis system, because of its sharply structured absorption spectrum.

Product analyses were carried out by means of gas chromatography (Varian 1200, hydrogen flame detector), mass spectrometry (Varian MAT CH4B), and ir (Perkin Elmer 621) and uv (Cary 1501) spectrophotometry. The GC was used to measure the amount of C_2H_4 produced in photolysis of cyclopropanone and C_2H_6 from azomethane, with cyclopentane as the internal standard in all samples. Columns used included 20% SF-96 on Chromosorb 102 at 100 °C (for C_2H_4 and cyclopentane) and 10% OV-17 on Chromosorb G at 120 °C (searching for other products). The following photoproducts were looked for but not found by GC (detection limits): acrolein ($<2\ \mu$), acetone ($<2\ \mu$), cyclohexane-1,4-dione, a possible dimer of cyclopropanone ($<3\ \mu$), cyclobutanone ($<3\ \mu$), and cyclopropanone–butadiene adducts such as 3-vinylcyclopentanone[25] ($<3\ \mu$; 2-octanone was used to set an upper limit to t_R and detection limit for the adduct). The mass spectrometer was used to confirm that the ratio of ethylene and carbon monoxide formed by photolysis of cyclopropanone was unity, within experimental error of $\pm<3\%$. In addition, a mass spectrum of cyclopropanone photolyzed to 93% completion showed no peaks greater than 1% of the base peak (28) for $m/e > 70$.

Attempts to monitor cyclopropanone itself by GC were unsuccessful, even using an all glass inlet system and a glass column packedwith Kel-F beads. Instead the absorbance at 48 600 cm^{-1}, where ϵ is 763 $M^{-1}\ cm^{-1}$ for cyclopropanone but the absorption by cyclobutanone impurity and C_2H_4 product was negligible, was used to measure the rates of both photo- and thermal decomposition of cyclopropanone. The uv absorption was also used to search for another possible photoproduct, ketene. This compound has ϵ_{max} $4.17 \times 10^3\ M^{-1}\ cm^{-1}$ at 47 080 cm^{-1} which permitted $\geq\sim 5\ \mu$ to be detected. Several experiments were done in which a sample of cyclopropanone was photolyzed while in the sample beam of the ir spectrophotometer, using a gas cell with two quartz and two KBr windows, in hopes of detecting any transient photoproducts. Scans of the ir spectrum during and immediately after photolysis of a 16-Torr cyclopropanone sample by λ_{irr} 313 nm revealed only C_2H_4, CO, and polymer. The polymer formed in both thermal and photochemical reactions was characterized by its NMR spectrum, obtained on a Varian T-60 NMR spectrometer, as well as by uv and ir absorption spectra (see Results section).

The procedures used to measure fluorescence quantum yields have been described in detail in a recent publication.[26] They were improved over ones used to obtain an earlier value[22] for ϕ_f of cyclopropanone vapor in several significant respects: a Wood's horn light trap was added opposite the viewing window of the fluorescence cell; the photomultiplier tube was cooled to −25 °C; emitted light intensity was measured on an SSR No. 1110 photon counter instead of a lock-in amplifier; and a quinine sulfate solution was used as the fluorescence standard at all wavelengths rather than biacetyl at λ_{ex} 365 nm and hexafluoroacetone at shorter λ_{ex}'s. The first three changes reduced the scattered light contribution and the random scatter of the data; the last improved the absolute accuracy of the resultant ϕ_f's. Because the continuous formation of polymer on the windows increased the scattered light contribution during the course of a measurement, the scattered light correction was determined initially on the evacuated fluorescence cell, then again, after measuring emission of the sample, with the sample frozen down by liquid nitrogen. An attempt was also made to measure the fluorescence lifetime of a 1.8-Torr sample of cyclopropanone, using the 337.1-nm line of a nitrogen laser,[26] but no difference in the intensity or time profile of oscilloscope traces could be discerned between the filled and the evacuated fluorescence cell. The fluorescence spectrum was scanned using a Perkin-Elmer "linear energy" spectrofluorimeter with the excitation monochromator system replaced by a mercury arc–interference filter combination. Because of the very weak emission and the relatively large contribution of scattered light (the spectrum of which suggested emission from cell windows and/or polymer deposit on same), the resulting spectrum had $S/N \leq 2{:}1$, permitting only the conclusion that the emission extends roughly from 410 to 610 nm, with a maximum in the vicinity of 480 nm.

The appearance potential of the $C_2H_4^+$ ion formed from cyclopropanone by electron impact was determined using a Fox-type RPD appearance potential accessory mounted on a Nuclide 12-90-G mass spectrometer.[27] The retarding voltage was modulated at 26 Hz with an amplitude of 100 mV permitting "lock-in" amplification of only those ions produced by a 100-mV slice out of the energy distribution of the ionizing electrons. High-frequency pulsing of the ion repeller electrode caused ionization to occur in a field-free region; the ionizing voltage was scanned digitally in steps of 10 mV. Further details will be given in a subsequent paper reporting appearance potential data for a series of cyclic and bicyclic ketones.

Results

The Thermal Reaction. Because the thermal reaction of the gaseous cyclopropanone proceeded at a significant rate at room temperature, actually at a slightly faster rate than the photolyses at 291 nm and about the same rate as the photolysis at 334 nm, it was necessary to investigate the thermal reaction before obtaining quantitative photochemical data. The analytical techniques described in the Experimental Section were used to search for products of the thermal reaction, but no volatile products were ever found. Infrared spectra run repetitively on gaseous cyclopropanone samples showed that the decay of peaks in the 1800 to 2000 cm^{-1} region was accompanied by a corresponding rise in peaks at 1450, 1310, 1125, 1005, 975, and 945 cm^{-1}, plus several weaker peaks in the same region. These peaks remained after evacuation of the ir cell and they correspond satisfactorily to the absorption spectrum previously reported for polycyclopropanone.[11] An NMR spectrum of the polymer formed in the thermal reaction, dissolved in $CDCl_3$ with 1% TMS, showed a single peak at δ 1.0 ppm, in good

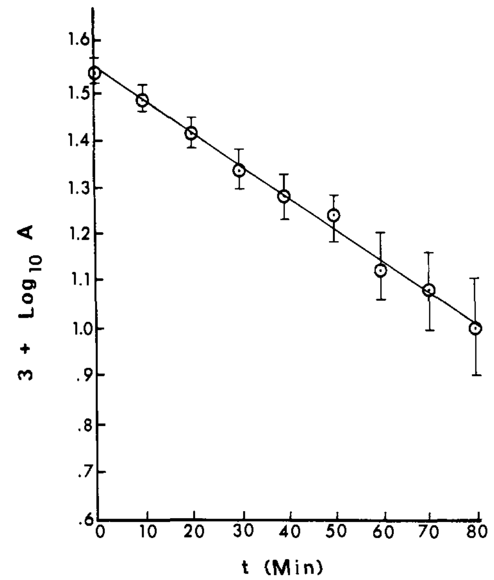
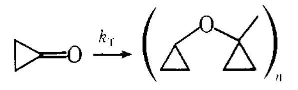


Figure 1. Thermal reaction rate of cyclopropanone: A = absorbance at 1905 cm^{-1} in a 10-cm Pyrex ir cell; P_{CP} = 810 μ; T = 49.5 °C.

agreement with Schaafsma, et al.'s value of 1.0 for polycyclopropanone.[11]

The kinetic order of the thermal reaction was estimated by continuously recording the transmittance at one of the "carbonyl" peaks in the water-jacketed gas ir cell described earlier. As shown in Figure 1 the decay of the absorbance due to cyclopropanone fits a first-order plot well for nearly 2 half-lives. Thus, the thermal reaction of cyclopropanone seems well summarized by



(1)

$$\text{rate} = k_T[\text{CP}]$$

The indicated structure of the polymer is due to Schaafsma, et al., whose conclusion was based on identification of characteristic cyclopropane ring frequencies in the near-ir spectrum of the polymer, as well as on its NMR spectrum.

The first-order rate constant, k_T, was measured in the water-jacketed gas ir cell at temperatures ranging from 21.8 to 49.5 °C. The results, shown in Figure 2, lead to an Arrhenius activation energy of 11.8 ± 1.7 kcal mol^{-1}. The large uncertainty in E_a as well as the apparent curvature in the plot may be partally a consequence of temperature gradients of the order of 2-3 °C along the length of the cell and 8-9 °C on the surface of the windows, but could conceivably indicate a change in reaction mechanism at higher temperatures.

The thermal reaction rate was also measured in a stainless steel ir cell and in a pair of quartz uv cells, a "seasoned" one and a clean one with added Pyrex powder. The results given in Table I show a strong dependence of k_T on both the surface-to-volume ratio and the nature of the surface in the container used. Our conclusion is that the thermal reaction of cyclopropanone, forming polycyclopropanone, is partly, if not entirely, a surface-catalyzed process. Thus, the value of the activation energy obtained from Figure 2 is only a lower limit to the activation energy for any homogeneous thermal reaction that may occur.

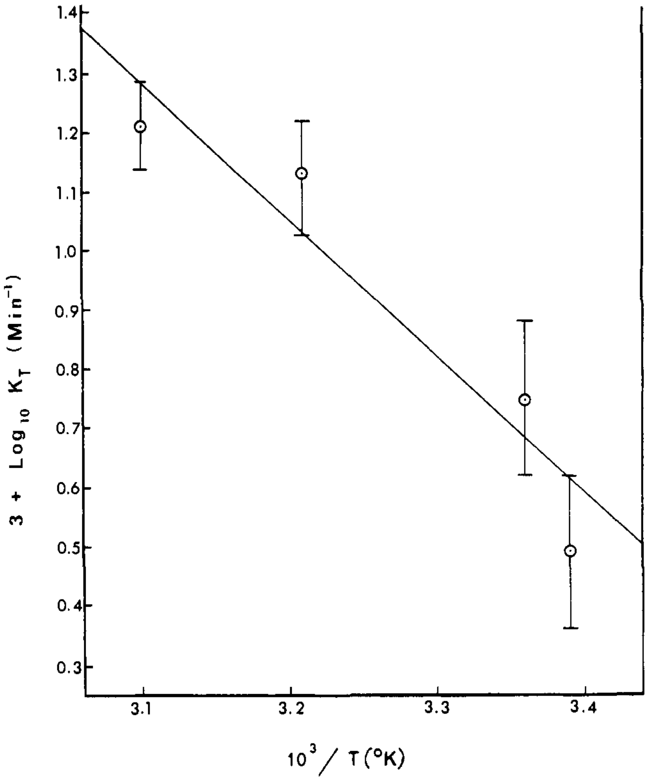


Figure 2. Temperature dependence of the thermal rate constant: P_{CP} ≃ 820 μ.

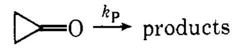
Table I. Effect of Surface on Thermal Rate Constant[a]

Vessel	S/V, cm^{-1}	P_{CP}, Torr	k_T, min^{-1}
Quartz photolysis cell (seasoned)	2.20	0.75	8×10^{-4}
Pyrex ir cell (KBr windows)	1.58	0.80	4×10^{-3}
Stainless steel ir cell (KBr windows)	3.13	0.70	2×10^{-2}
Quartz photolysis cell (+ pyrex powder)	13.03	0.75	7×10^{-2}

[a] T = 23 °C.

The Photochemical Reaction. Using the analytical methods described in the Experimental Section the only photoproducts detected were ethylene and carbon monoxide (in a 1 to 1 ratio) and polymer. As detailed in our previous report,[22] the identification of polymer as a photoproduct was based on the nearly twice as rapid increase of absorbance in the ~190-220-nm region for the evacuated photolysis cell as for the matched dark reaction cell. After completion of all the photochemical experiments reported here, the photolysis cell was washed out with $CDCl_3$ containing 1% TMS. The resulting solution gave an NMR spectrum with a single peak at δ 1.0 ppm and an ir spectrum with showing peaks at 1450, 1310, 1125, 1010, 975, and 945 cm^{-1}, both essentially identical with spectra for the polycyclopropanone formed in the thermal reaction alone.

In calculating the photochemical quantum yields for loss of cyclopropanone and formation of ethylene (the amount of polymer formed per run being too small to be measured accurately) the simultaneous loss of cyclopropanone via the thermal reaction was accounted for as shown in the following equations. Since in no case case did the absorbance of a sample at the wavelength of irradiation exceed 0.04, the photolysis followed first-order kinetics:



(2)

$$\text{rate} = k_P[\text{CP}]$$

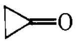
where $k_P = 2.303\phi_{CP}\epsilon l I_0$. Here ϕ_{CP} is the quantum yield of cyclopropanone disappearance; l, the cell path length; ϵ, the molar extinction coefficient; and I_0, the incident light intensity. Since simultaneous steps 1 and 2 are both first order, the change in cyclopropanone concentration during photolysis time t is given by

$$\ln [\mathrm{CP}]_t/[\mathrm{CP}]_0 = -(k_\mathrm{P} + k_\mathrm{T})t \quad (3)$$

The ratio of concentrations is now replaced by the ratio of absorbances at 48 600 cm^{-1} and the equation solved for k_P, giving finally:

$$\phi_\mathrm{CP} = \frac{1}{\epsilon l I_0}\left[\frac{1}{t} \log \left(\frac{A_0}{A_t}\right) - \frac{k_\mathrm{T}}{2.303}\right] \quad (4)$$

Similarly,



$$\xrightarrow{k_\mathrm{E}} \mathrm{C_2H_4} + \mathrm{CO} \quad (5)$$

$$\text{rate} = k_\mathrm{E}[\mathrm{CP}]_t$$

where $k_\mathrm{E} = 2.303\phi_{\mathrm{C_2H_4}}\epsilon l I_0$ and $[\mathrm{CP}]_t$ can be obtained from eq 3. The integrated rate equation from (5) is

$$\Delta[\mathrm{C_2H_4}] = \left(\frac{k_\mathrm{E}}{k_\mathrm{P} + k_\mathrm{T}}\right)[\mathrm{CP}]_0(1 - e^{-(k_\mathrm{P}+k_\mathrm{T})t}) \quad (6)$$

which yields, on using eq 3 and solving for k_E:

$$\phi_{\mathrm{C_2H_4}} = \frac{\Delta[\mathrm{C_2H_4}] \log (A_0/A_t)}{\epsilon l I_0[\mathrm{CP}]_0 t[1 - (A_t/A_0)]} \quad (7)$$

where $\phi_{\mathrm{C_2H_4}}$ is the quantum yield of $\mathrm{C_2H_4}$ formation.

Because of the heterogeneous nature of the concurrent thermal reaction, it seemed advisable to determine the k_T used in eq 4 for each photolysis. This was routinely done by measuring the decrease of the far-uv absorption band for a 1-h time period after the photolysis but before GC analysis of products. Values of k_T so determined varied erratically between the extremes of 5.3×10^{-4} and 2.3×10^{-3} min^{-1}; the k_T appearing in the first line of Table I represents a mean value. The value of $\Delta[\mathrm{C_2H_4}]$ appearing in eq 7 was determined by the GC analysis, with correction for a small amount of $\mathrm{C_2H_4}$ present in the blank photolysis cell The initial concentration of cyclopropanone, $[\mathrm{CP}]_0$, was obtained from the absorbance at 48 600 cm^{-1} before starting the photolysis. I_0 was based on the average current of the vacuum photodiode, calibrated as described in the Experimental Section. The experimental values of the extinction coefficients used are given in Table II.

The experimental values obtained for ϕ_CP and $\phi_{\mathrm{C_2H_4}}$, from eq 4 and 7, respectively, are shown in Table III. The indicated uncertainties in the average ϕ's shown for each wavelength are standard deviations. The estimated experimental errors in individual quantum yields ranged from ±0.02 at 313 nm to ±0.05 at 291 nm, for $\phi_{\mathrm{C_2H_4}}$, and from ±0.07 at 313 nm to ±0.15 at 291 nm, for ϕ_CP. Examination of the results shows that, even at pressures above one atmosphere, none of the added gases had an effect on the two quantum yields in excess of the estimated experimental error. In addition, no new products were found when the potentially reactive gases $\mathrm{O_2}$ and 1,3-butadiene were added to the samples to be photolyzed. In particular, no cyclopropanone-butadiene adduct could be detected.[25] There is, however, a clear effect of the wavelength of irradiation on $\phi_{\mathrm{C_2H_4}}$, the quantum yield increasing with decreasing λ_irr until the limiting value of 1.0 is attained by 291 nm. In contrast, ϕ_CP appears to be essentially unity at all irradiation wavelengths. Values for ϕ_CP could not be obtained in the runs in which cyclopentane or butadiene were added gases, because of strong absorption by these compounds at 48 600 cm^{-1}. In these cases $[\mathrm{CP}]_0$ was determined from the measured initial pressure of cyclopropanone, corrected for the presence of small amounts of $\mathrm{C_2H_4}$ and cyclobutanone impurities.

Table II. Extinction Coefficients (M^{-1} cm^{-1})

Compd	ϵ_{365}	ϵ_{334}	ϵ_{313}	ϵ_{291}
Cyclopropanone	2.7	11.8	16.8	8.9
Azomethane	3.55	4.78	2.89	0.77
Cyclobutanone	n.d.	n.d.	5.67	n.d.

As a check on the experimental procedures used for cyclopropanone, a 902-μ sample of cyclobutanone was photolyzed, using the same methods of sample preparation, photolysis, analysis, and actinometry. For λ_irr 313 nm the quantum yields obtained were: propylene, 0.05; cyclopropane, 0.23; ethylene, 0.65. At 4.5 Torr, 40 °C, and 313 nm McGee[28] reports the ϕ's: propylene, 0.02; cyclopropane, 0.28; ethylene, 0.70, Allowing for th known pressure effect on the propylene:cyclopropane ratio,[29] the agreement seems satisfactory.

Fluorescence Yields and Lifetimes. Table IV shows the fluorescence quantum yields measured for cyclopropanone vapor, with previously reported values for cyclobutanone[26] included for comparison. The ϕ_f listed for cyclopropanone at λ_ex 365 nm replaces an earlier, less accurate value of ~5 $\times 10^{-4}$ (see Experimental Section for improvements made in the method of measurement).[22] The earlier value was probably too high because of insufficiently accurate correction for the relatively large contribution by "scattered light" from polymer being continuously deposited on the cell windows. Estimated "probable errors" are: $\pm 9 \times 10^{-6}$ at λ_ex 365 nm for cyclopropanone; $\pm 3 \times 10^{-4}$ at λ_ex 334 nm, and $\pm 5 \times 10^{-6}$ at the other wavelengths for cyclobutanone.

As stated earlier, the attempt to measure the lifetime of the fluorescing state of cyclopropanone was not successful. However, the natural radiative lifetime, Υ_0, of the $^1(\mathrm{n},\pi^*)$ state was calculated by the method of Strickler and Berg[30] to be $1.2 \pm 0.2 \times 10^{-5}$ s, assuming $\langle \tilde{\nu}_\mathrm{f}^{-3} \rangle = 1.1 \times 10^{-13}$ cm^3 (corresponding approximately to a mean fluorescence wavelength of 480 nm). The Strickler-Berg formula has been found to be inaccurate for the n → π^* transition in ketones, however, giving values for Υ_0 that are too long by a factor of 4 in the case of cyclobutanone[31] and by a factor of 8 in acetone.[32] The smaller discrepancy in the cyclic compound may be a consequence of a more constrained geometry near the carbonyl chromophore;[33] therefore, a correction factor of 4 will be used in the case of cyclopropanone, yielding the estimate: $\Upsilon_0 = 3.0 \times 10^{-6}$ s. The fluorescence lifetimes, or their limits, shown in Table IV were calculated from this value and the experimental results for ϕ_f via the formula

$$\Upsilon_\mathrm{f} = \phi_\mathrm{f}\Upsilon_0 \quad (8)$$

The Υ_0 used for cyclobutanone was 2.46×10^{-6} s.[31]

Heat of Formation. A total of nine determinations of the appearance potential of the $\mathrm{C_2H_4^+}$ ion from cyclopropanone were made on three different samples, two containing xenon and one containing benzene to calibrate the energy scale. The two samples containing xenon yielded AP(28) = 9.67 ± 0.03 and 9.66 ± 0.03 eV; the sample containing benzene gave AP(28) = 9.73 ± 0.03 eV. Making a small (−0.2 kcal/mol) correction from the source temperature of 50 to 25 °C and using literature values for[34] $\Delta H_\mathrm{f}°$'s of CO and $\mathrm{C_2H_4^+}$ gives the following heats of formation for cyclopropanone: $\Delta H_\mathrm{f}°(298\ \mathrm{K}) = +4.2$, +4.5, and +2.8 kcal/mol. We have a slight preference for the latter value, since the shape of the ionization efficiency curve for $\mathrm{C_6H_6^+}$ near onset more closely resembles that of $\mathrm{C_2H_4^+}$ from cyclopropanone than does the $\mathrm{Xe^+}$ curve, possibly leading to some small cancellation of errors. But the differences are so close to the estimated experimental precision of ±0.7 kcal mol^{-1} that it only seems justified to take the mean value, +3.8

Table III. Photochemical Quantum Yields[a]

$P_{0,CP}$, μ	P_{add}, Torr	$10^{-15} \times I_0$, photons s^{-1}	t, min	$\Delta P_{C_2H_4}$, μ	(A_0/A_t)[b]	$\phi_{C_2H_4}$	ϕ_{CP}
			λ_{irr} 365 nm				
783	0	7.69	60	38.9	1.14	0.55	0.94
815	0	7.57	60	45.9	1.11	0.62	0.79
774	0	6.86	65	40.3	1.14	0.59	0.97
781	197 CO_2	7.03	65	44.5	1.13	0.63	0.89
783	398 CO_2	7.54	60	43.3	1.14	0.62	1.02
796	792 CO_2	7.69	60	43.1	1.15	0.63	0.87
745	1268 CO_2	6.86	65	41.0	1.14	0.63	0.88
772	327 $c\text{-}C_5H_{10}$	6.17	70	37.5	n.d.	0.58	n.d.
718	100 O_2	6.56	65	34.2	1.16	0.57	1.00
519	420 O_2	6.20	72	24.2	1.28	0.57	0.95
780	651 (1,3-C_4H_8)	14.00	45	65.0	n.d.	0.65	n.d.
						Av 0.60 ± 0.03	0.92 ± 0.07
			λ_{irr} 334 nm				
762	0	1.40	60	35.2	1.15	0.64	0.97
			λ_{irr} 313 nm				
687	0	14.0	7	59.6	1.14	0.72	0.97
759	0	13.1	15	126.0	1.30	0.74	1.00
4340	0	12.5	15	685.0	1.29	0.73	0.98
348	0	12.8	20	68.5	1.49	0.70	1.12
614	364 CO_2	13.4	15	89.0	1.32	0.64	1.01
754	1307 CO_2	13.7	15	126.0	1.38	0.72	1.12
694	113 O_2	13.4	7	56.1	1.14	0.72	1.01
763	651 (1,3-C_4H_8)	12.8	15	125.0	n.d.	0.72	n.d.
						Av 0.71 ± 0.03	1.03 ± 0.06
			λ_{irr} 291 nm				
669	0	0.72_4	90	28.2	1.30	1.05	0.92
769	0	0.70_3	90	28.5	1.21	0.93	1.05
731	1150 CO_2	0.73_9	90	28.4	1.33	0.97	0.92
610	389 O_2	0.74_8	90	24.4	1.39	1.01	11.00
						Av 0.99 ± 0.05	0.97 ± 0.06

[a] $T \approx 23$ °C, photolysis cell $V = 29.7$ cm^3. [b] A = absorbance at 205.7 nm.

kcal mol^{-1}, as the enthalpy of formation of cyclopropanone at 298 °K, and increase the range of uncertainty to ±1 kcal mol^{-1}.

Dewar et al.[16] have previously calculated the heat of formation of cyclopropanone to be −34.1 kcal/mol using the MINDO/2 method which admittedly underestimated the strain energies of cyclopropane rings. If the group additivity method of Benson[35] is used to calculate the heat of formation, using the specified 27.6 kcal mol^{-1} correction for strain energy in the cyclopropane ring, a value of −13.9 kcal mol^{-1} is obtained. For the group additivity method to reproduce our experimental value, the ring strain energy correction in cyclopropanone must be set equal to 45.3 kcal mol^{-1}.

Reasonably enough, this value for the strain energy lies between the 39.3 kcal mol^{-1} calculated for the methylene cyclopropane structure[36] and the 53.7 kcal mol^{-1} given for cyclopropene.[35]

Discussion

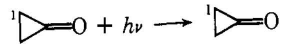
The photochemical results and calculated fluorescence lifetimes show that essentially all cyclopropanone molecules produced in the $^1(n,\pi^*)$ state by absorption at any of the wavelengths used undergo chemical reaction very rapidly, in ≤2 × 10^{-10} s. Considerable previous work on the photochemistry of cyclic ketones, in both gaseous and liquid phases, suggests that the initial chemical step is scission of the bond between the carbonyl and α-carbon atoms (C_1–C_2).[37-39] The intermediacy of the $^3(n,\pi^*)$ state in this process has been directly established in the case of acetone in the vapor phase[40] and cyclic ketones in various solvents,[41] but only indirectly indicated in the case of cyclic ketones in the vapor phase.[42] Rate constants for intersystem crossing from $^1(n,\pi^*)$ to $^3(n,\pi^*)$ in simple carbonyl compounds appear to be relatively independent of vibrational energy, phase, or even molecular structure: 4.2 × 10^8 [32a] (or 3.7 × 10^8)[32b] s^{-1} for acetone at 23 °C and 313 nm; ≤2.0 × 10^8 s^{-1} for cyclobutanone;[31] and ≤4.2 × 10^8 s^{-1} for cyclopentanone[32b] at 23 °C and 320 nm. To account for the estimated lifetimes of the $^1(n,\pi^*)$ state of cyclopropanone, however, radiationless rate constants from 5 × 10^9 s^{-1} to >3 × 10^{11} s^{-1} are required. It therefore seems likely that the dominant process occurring from the $^1(n,\pi^*)$ state of cyclopropanone is predissociation rather than intersystem crossing.

Table IV. Fluorescence Yields and Lifetimes[a]

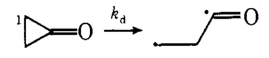
	ϕ_f		Υ_f, s	
λ_{ex}, nm	CP	CB[d]	CP	CB
365	6.8 × 10^{-5} [b]		2.0 × 10^{-10}	
334	<4 × 10^{-6} [b]	2.5 × 10^{-3}	<1.2 × 10^{-11}	6.2 × 10^{-9}
313	<1 × 10^{-6} [c]	1.86 × 10^{-4}	<3 × 10^{-12}	4.6 × 10^{-10}
302.5	<1 × 10^{-6} [c]	1.4 × 10^{-5}	<3 × 10^{-12}	3.4 × 10^{-11}
291		2 × 10^{-6}		5 × 10^{-12}

[a] T = 25 °C for CP, 23 °C for CB. [b] P_{CP} = 1.1 Torr. [c] P_{CP} = 1.6 Torr. [d] P_{CB} = 17 Torr.

Based on the above points, the following detailed mechanism is advanced.



(I)



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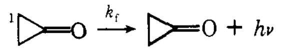

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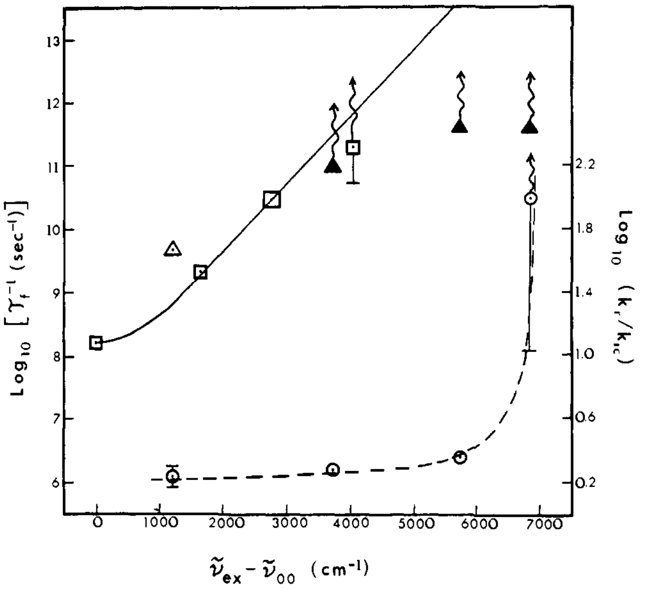
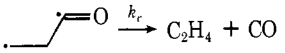
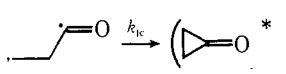


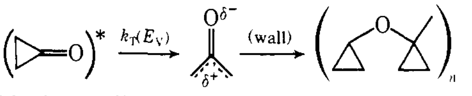
Figure 3. Primary rate constants vs. vibrational energy: Υ_f^{-1} for cyclobutanone (□); cyclopropanone (△); filled symbols indicate only lower limit determined; k_r/k_{ic} (○). Error bars are shown only when probable error exceeds size of the symbols. The solid curve is "best fit" to cyclobutanone data based on earlier analysis.[26]



(IV)



(V)



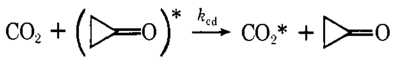
(VI)

Step II is the predissociation process, proposed previously to explain the effect of excitation wavelength on fluorescence efficiencies in the n → π^* transitions of several cyclic ketones,[31,43] 7-ketonorbornane,[26] acetone,[26] and 2,3-diazabicyclo[2.2.1]hept-2-ene,[44] in addition to many known diatomic cases.[45] The competing processes IV and V account for the wavelength dependence of $\phi_{C_2H_4}$, as shown by eq 9.

$$\phi_{C_2H_4} = (1 - \phi_f)/(1 + k_{ic}/k_r) \qquad (9)$$

Thus the rapid increase in k_r with increasing vibrational energy content of the biradical results in $\phi_{C_2H_4}$ ultimately approaching 1.0 as $\lambda_{irr} \rightarrow$ 291 nm. The "chemical" mechanism for internal conversion represented by step V has been previously proposed in the cases of several cyclic ketones,[26,46] as well as earlier for benzene;[47] the indications are that its rate is not a strong function of vibrational energy. The vibrationally excited molecule (designated by an asterisk) formed in this step in presumed to yield polycyclopropanone. A key intermediate in this process is the oxyallyl structure, originally proposed by Hoffmann[15] to be more stable than cyclopropanone itself and invoked by Greene et al.[14] to explain the thermal-only racemization of *trans*-2,3-di-*tert*-butylcyclopropanone. Once formed, the oxyallyl structure presumably has sufficient stability (recent theoretical calculations suggest a small potential barrier to its recyclization[17,18]) to reach the cell walls where it ultimately adds to the already present polymer. Collision with added gases while enroute to the walls may further stabilize the oxyallyl by inducing intersystem crossing to its ground triplet state.[15] It is noteworthy that previous attempts to "trap" oxyallyl with 1,3-butadiene and furan in solution have been unsuccessful[12b] just as were the experiments with added butadiene and oxygen in the present work.

Collisional deactivation of the vibrationally excited molecule formed by internal conversion was attempted by adding up to ~1300 Torr of CO$_2$. If deactivation, shown in step VII, occurs, the quantum yield for polymer formation will be reduced according to eq 10. As noted in the Results section, however, addition of CO$_2$ had no discernible effect on either ϕ_{CP} or $\phi_{C_2H_4}$. An RRKM estimate (see below) of $k_T(E_V)$ for λ_{irr} = 365 nm gives a value of ~3×10^{11} s^{-1}. A standard kinetic theory calculation, assuming a mean collision diameter of 3.5 Å and a deactivation efficiency of 0.2, yields $k_{cd} \sim 2.3 \times 10^{10}$ M^{-1} s^{-1}. Using these rate constants, the second factor in parentheses in eq 10 decreases from 1.0 to 0.9949 when the pressure of CO$_2$ is raised from 0 to 1268 Torr; this predicts a 0.0017 decrease in ϕ_{poly} at 365 nm, compared with a standard deviation of 0.08 in experimental values about the mean of 0.32. Thus the failure to observe an effect of added CO$_2$ is entirely compatible wih the proposed role of internal conversion, even allowing for reasonable uncertainties in the estimates of $k_T(E_V)$ and k_{cd}.



(VII)

$$\phi_{poly} = \phi_{CP} - \phi_{C_2H_4} = \left(\frac{1 - \phi_f}{1 + k_r/k_{ic}}\right) - \left(\frac{1}{1 + k_{cd}[CO_2]/k_T(E_V)}\right) \qquad (10)$$

Figure 3, together with eq 11, shows the predissociation rate constant, k_d, as a function of the vibrational energy content of cyclopropanone in the $^1(n,\pi^*)$ state. To obtain

$$k_d = \Upsilon_f^{-1} - k_f \simeq \Upsilon_f^{-1} \qquad (11)$$

the latter quantity it was necessary to estimate the 0′-0″ transition energy, $\tilde{\nu}_{00}$. Consideration of several kinds of experimental data (the shift of cyclopropanone's absorption maximum from those of acetone and cyclobutanone, plus the known $\tilde{\nu}_{00}$ values for these compounds;[48,49] the midpoint on the $\tilde{\nu}$ scale between absorption and fluorescence maxima in cyclopropanone; and the long wavelength "onset" ($\epsilon/\epsilon_{max} \sim 0.05$) of absorption) leads to a value of $\tilde{\nu}_{00} \simeq 26\,200 \pm 300$ cm^{-1}. A somewhat higher value, 27 300 cm^{-1}, is obtained using the CNDO/S method of Jaffe et al.[50] A discrepancy of this size may not be significant, however; for cyclobutanone the same program predicts $\tilde{\nu}_{00}$ = 28 757 cm^{-1}, compared with an experimental value of 30 291 cm^{-1}.[49]

In the case of the cyclobutanone data shown in Figure 3 Υ_f^{-1} is essentially equal to the sum of k_d and the rate constant for intersystem crossing. Comparison of the one accurately known value of k_d for cyclopropanone with the empirical curve drawn through the cyclobutanone points indicates that predissociation in the former occurs at a rate ~8 times the sum of $k_d + k_{isc}$ in the latter, for equal vibrational energy contents. Put another way, if $k_{isc} = 2 \times 10^8$ s^{-1} is assumed for cyclobutanone, ~2050 cm^{-1} (5.9 kcal mol^{-1}) of vibrational energy is required for the rate constant of predissociation in cyclobutanone to equal the k_d of cyclopropanone at E_{VIB} = 1200 cm^{-1}. In view of the greater stability of the cyclobutanone ring structure in the ground state (strain energy only 29 kcal mol^{-1} [51] vs. 45 kcal mol^{-1} for cyclopropanone), the lower energy requirement for predissociation of cyclopropanone via the $^1(n,\pi^*)$ state is not surprising. It has also been shown by CNDO/S calculations that the "n$_O$" electron involved in the 291-365-nm transitions contributes more to the C$_1$-C$_2$ bond strength in cyclopropanone than in cyclobutanone.[52] Thus the bond is more seriously weakened in the $^1(n,\pi^*)$ state of cyclopropanone, permitting a dissociative potential energy surface to cross the $^1(n,\pi^*)$ surface at a longer $r_{C_1-C_2}$ value and thus at a lower energy relative to $\tilde{\nu}_{00}$, than in the case of cyclobutanone.

The problem of scattered light from polycyclopropanone described earlier resulted in no upper limits being obtained for Υ_f^{-1} in cyclopropanone when $E_{\mathrm{VIB}} > 1200$ cm^{-1}. Thus it is not possible to say whether k_d varies in ca. an exponential manner with E_{VIB} in cyclopropanone as appeared to be the case with several other ketones studied previously.[26] The trend of the k_r/k_{ic} ratio with E_{VIB} shown in Figure 3 is similar to, but more dramatic than, the results obtained for the corresponding quantity in the 7-ketonorbornane system in vapor phase.[26] Although the functional relationship between this ratio and E_{VIB} cannot be determined from the present data, it seems reasonable to propose that the critical energy for decarbonylation of the biradical formed in step 11 exceeds the critical energy for internal conversion via recyclization (step V) by 6000-7000 cm^{-1} (17-20 kcal mol^{-1}). A similar trend, although again a less strong dependence on E_{VIB} than reported here for cyclopropanone, has been found for the C_3/C_2 ratio in cyclobutanone at wavelengths where predissociation predominates.[28,29,53] By analogy, the C_3/C_2 ratio may be identified with the ratio of rate constants for decarbonylation and internal conversion via recyclization of the biradical produced by scission of the C_1-C_2 bond in cyclobutanone.

RRKM Estimate of Thermal Rate Constant. The rate constant $k_T(E_V)$, appearing in step VI, is for the unimolecular reaction of a molecule with a specific amount of vibrational excitation, approximately equal to the energy of the photon absorbed (ignoring rotational energy and a small amount of initial thermal energy). This rate constant can in principle be calculated by the RRKM theory of unimolecular reactions.[54,55] If the rotational modes are assumed to be adiabatic during formation of the activated complex (denoted by $^+$), the reaction path is assumed to be nondegenerate, and the total number of possible vibrational states in the activated complex and the density of states in the excited molecule are estimated by the method of Whitten and Rabinovitch,[55,56] the equation for the rate constant becomes

$$k_T(E_V) = \frac{Q_R{}^+}{Q_R}\left(\frac{E_V{}^+ + (1 - \beta^+ w^+)E_Z{}^+}{E_V + (1 - \beta w)E_Z}\right)^{s-1}\left(\frac{1}{1 - \beta w'}\right) \times \prod_{i=1}^{s} \nu_i \Big/ \prod_{i=1}^{s^+} \nu_i{}^+ \quad (12)$$

The Q_R are rotational partition functions, E_V is the vibrational energy content of the excited molecule, $E_V{}^+ = E_V - E_0$. E_0 is the critical energy for the reaction, β is a modified vibrational frequency dispersion parameter, w is an empirical parameter depending on the ratio E_V/E_Z, $w' = E_Z$ (dw/dE_V), the ν_i are fundamental vibrational frequencies, s is their total number, and the E_Z's are total zeropoint vibrational energies.

Table V. RRKM Parameters for Cyclopropanone

	Molecule	Activated complex	Units
E_Z	46.46[a]	44.41	kcal mol^{-1}
E_V[b]	78.4	47.9	kcal mol^{-1}
β	1.190	1.190	None
w	0.0635	0.085	None
w'	−0.0259		None
s	18	17	None

[a] Obtained by multiplying total E_Z for the 12 "known" frequencies by 1.5. [b] For λ_{irr} 365 nm.

Although a complete vibrational analysis of cyclopropanone is not yet available it was judged sufficient for the present purposes to evaluate the necessary parameters from the ir frequencies given in the Experimental Section. Of the 14 frequencies listed there, two (at 1868 and 1980 cm^{-1}) were excluded as possibly due to Fermi resonance and the remainder were used to calculate the parameters for the excited molecule. In the activated complex it is assumed that a parallel ring deformation mode, possibly corresponding to the ir peak at 980 cm^{-1}, becomes the reaction coordinate, and that another possible ring mode at 911 cm^{-1} is reduced to one-half its value in the normal molecule. With these changes

$$\prod^{18} \nu_i \Big/ \prod^{17} \nu_i{}^+ = 7.84 \times 10^{13}\ \mathrm{s}^{-1} \quad (13)$$

is obtained. It is further assumed, for convenience, that $Q_R{}^+/Q_R \simeq 1.0$, although a ratio as large as 2-4 is possible.

Evaluation of the quantities $E_V{}^+$ and w^+ depends upon the number chosen for E_0, which is estimated as follows. The experimental activation energy for the surface-catalyzed polymerization of cyclopropanone, 11.8 kcal mol^{-1}, serves to set a lower limit to E_0 for the homogenous process. The reported activation energy for thermal decomposition of the much more stable cyclobutanone, 52 kcal mol^{-},[57] sets an upper limit, assuming an initial ring-opening step in this case also. To narrow the range of possible values, Benson's group additivity method[35] was used to estimate the heat of formation of the oxyallyl intermediate shown in (VI) as +27.5 kcal mol^{-1}, using a resonance energy correction of 12.6 kcal mol^{-1} by analogy with the corresponding allyl radical.[36] Combined with the experimental heat of formation of cyclopropanone = +3.8 kcal mol^{-1} reported above, this gives a minimum value for E_0 of 23.7 kcal mol^{-1}. Recent theoretical studies suggest that the energy maximum on the reaction path from cyclopropanone to oxyallyl occurs as the methylene groups are being rotated from a perpendicular orientation into the molecular plane.[17,18] It therefore seems reasonable to assume some steric inhibition of resonance in this maximum energy configuration, which is specified as the activated complex. Assuming that only ½ the eventual resonance stabilization is available in the activated complex, the estimated value of E_0 becomes 30 kcal mol^{-1}. A similar result, 31 kcal mol^{-1}, is estimated from the reported activation energy (40.3 kcal mol^{-1}) of the ethylidenecyclopropane → 2-methylmethylenecyclopropane isomerization[58] by subtracting the difference in strain energies of the former compound and cyclopropanone (35.6 vs. 45.3). The value of E_0 = 30.5 kcal mol^{-1} is used hereafter; it is felt to be good to ±5 kcal mol^{-1}.

The calculated RRKM parameters are shown in eq 13 and Table V. For λ_{irr} = 365 nm, the desired rate constant is predicted to be

$$k_T(E_V) = 3.1 \times 10^{11}\ \mathrm{s}^{-1}$$

The rate constant for thermally equilibrated molecules, at the high pressure limit and to the same level of approximation in the RRKM theory as used above (including $Q_R{}^+/Q_R \sim 1.0$), is:

$$k_{T,\infty} = 7.84 \times 10^{13} e^{-30,500/RT}\ \mathrm{s}^{-1} \quad (14)$$

At 23 °C, this predicts $k_{T,\infty} = 1.42 \times 10^{-9}$ s^{-1},[59] compared with $k_T = 1.3_3 \times 10^{-5}$ s^{-1} measured in a seasoned quartz cell (from Table I). The magnitude of this discrepancy is another demonstration that the thermal reaction studied in our system does not proceed homogeneously, but is aided by surface catalysis.

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(1) This research was supported in part by the National Science Foundation.

(2) Support by graduate fellowships from the University of Kansas City Trustees and the Kansas City Association of Trusts and Foundations is gratefully acknowledged.

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(32) Using measured Υ_l from (a) A. M. Halpern and W. R. Ware, *J. Chem. Phys.*, **54,** 1271 (1971), and (b) G. M. Breuer and E. K. C. Lee, *J. Phys. Chem.*, **75,** 989 (1971), with our ϕ_f(313 nm) = 2.08×10^{-3} (ref 26) yields $\Upsilon_0 = 1.15 \times 10^{-6}$, 1.30×10^{-6} s, respectively, for acetone.

(33) See recent analyses of this effect by (a) S. J. Strickler, J. P. Vikesland, and H. D. Bier, *J. Chem. Phys.*, **60,** 664 (1974); (b) D. A. Hansen and E. K. C. Lee, *ibid.*, **62,** 183 (1975).

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Selection Rules for the Charge Transfer Transitions in the Symmetrical Tetracyano-*p*-quinodimethane–Anthracene Molecular Complex

C. J. Eckhardt* and R. R. Pennelly[1]

Contribution from the Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588.

Received August 11, 1975

Abstract: The specular reflection spectra and their Kramers–Kronig transforms for the crystalline TCNQ–anthracene molecular complex have been obtained from 5 to 46 kK for light polarized along the *a*, *b*, and *c* crystallographic axes as well as one other principal direction. The assignment of the charge transfer transitions observed is made according to the group theoretical selection rules for the approximate C_{2v} symmetry of the complex as well as the exact C_s symmetry. The first two charge transfer transitions are taken to originate from the penultimately occupied molecular orbital of anthracene to the lowest two unoccupied orbitals of TCNQ. Comparison is also made to current exciton theories for crystals of molecular complexes.

There have been many studies of the charge transfer (CT) transitions of electron-donator-acceptor (EDA) complexes in all phases. Of special interest have been studies of crystalline complexes of organic molecules. In these systems it has been possible to observe multiple charge transfer transitions which cannot be observed in vapor phase or solu-