Acknowledgments. Support from the S.R.C. of Great Britain and the C.N.R. of Italy is gratefully acknowledged by the authors.

E. M. Bradbury,* P. Cary, C. Crane-Robinson
Biophysics Laboratories, Physics Department
Portsmouth Polytechnic
Portsmouth P01 2DZ, England

L. Paolillo, T. Tancredi, P. A. Temussi
Istituto Chimico, University of Naples, Naples, Italy
Laboratorio per la Chimica e Fisica di
Molecole di Interesse Biologico del C.N.R.
Arco Felice, Naples, Italy

Received April 26, 1971

Photochemistry of Cyclopropanone

Sir:

The nature of primary photoprocesses important in the larger cyclic ketones has provoked considerable discussion in recent years, with the formation of biradical intermediates,[1] intersystem crossing to a triplet state,[2,3] internal conversion to the ground electronic state,[4] and predissociation[5] all having been invoked to explain diverse results of different workers. We are in the process of a thorough study of the photochemical and photophysical pathways in cyclopropanone which we hope will contribute toward the development of a systematic description of the fundamental factors determining the fates of electronically excited cyclic ketones in general. We wish to present here a preliminary report of our photochemical results for cyclopropanone—the first such report for this compound in the gaseous state.[6]

Upon irradiation of samples of gaseous cyclopropanone, at pressures from ~300 μ to 4 Torr and wavelengths from 2920 to 3650 Å, we find ethylene and carbon monoxide to be the only volatile photochemical products. Mass spectrometric analysis of a sample photolyzed to 93% of completion at 3130 Å confirmed that these two products are formed in equal amounts within experimental error (~3%). Other possible products such as acrolein, ketene, and cyclopropanone dimers have been searched for using gas chromatography, ir and uv spectrophotometry, and mass spectrometry without success. We estimate that these compounds could have been detected if they had amounted to as little as 2, 4, and 6%, respectively, of the total volatile products formed in a typical photolysis carried to 10% completion. The quantum yield for disappearance of cyclopropanone, determined by following the decay of absorption in its second uv band at 2057 Å (ϵ 763 M^{-1} cm^{-1}) and using gaseous azomethane as the actinometer,[7] was found to be 1.0 within experimental error at all pressures and wavelengths. In contrast, the quantum yield of ethylene formation is wavelength dependent, varying from 0.59 at 3650 Å to 0.98 at 2920 Å. Addition of up to 1270 Torr of CO_2, 420 Torr of O_2, and 650 Torr of 1,3-butadiene had no effect upon the quantum yields for ethylene or for cyclopropanone (except that ϕ_{cp} could not be measured in the presence of butadiene) at any wavelength of irradiation. In the case of added butadiene, the adduct between a cyclopropanone biradical and butadiene was looked for by means of gas chromatography but not found.

The averaged experimental conditions and results of ten photolyses carried out with no added gas are summarized in Table I. The 3650- and 3130-Å lines from a high-pressure mercury arc were isolated by interference filters and the 3341- and 2920-Å lines by a Bausch and Lomb high-intensity monochromator. The amount of ethylene formed was determined by gas chromatography with corrections for ~0.5% C_2H_4 impurity based on analysis of the photolysis blanks. The cyclopropanone used was prepared by a flow system modification of the method of Turro and Hammond,[8] purified by repeated trap-to-trap distillation on a high-vacuum line, and had ≤1% cyclobutanone impurity in the samples used for the data reported here.

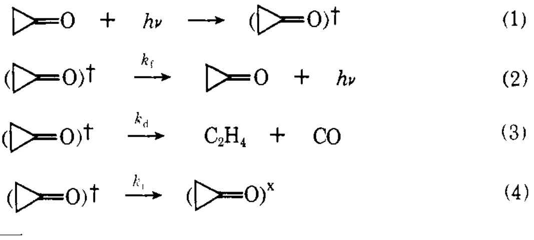
Table I. Cyclopropanone Photolysis Data[a]

λ, Å	$P_{0,cp}$, μ	I_0, photons sec^{-1}	Photolysis time, min	$\Delta P_{C_2H_4}$, μ	$\phi_{C_2H_4}$	ϕ_{cp}
3650[b]	790	7.32×10^{15}	62	41.7	0.59 ± 0.02	0.90 ± 0.07
3341	762	1.41×10^{15}	60	35.2	0.64	0.97
3130[c]	723	1.30×10^{16}	14	92.7	0.72 ± 0.01	1.02 ± 0.05
2920[d]	719	7.08×10^{14}	90	28.4	0.98 ± 0.06	0.99 ± 0.07

[a] Temperature 23°, photolysis cell volume 29.7 μ. Error ranges stated are mean deviations. Estimated limits of error for individual values are somewhat larger (*e.g.*, ±0.04 for $\phi_{C_2H_4}$ and ±0.17 for ϕ_{cp} at 3650 Å). [b] Average of three photolyses. [c] Average of four photolyses, including ones at 348 and 4340 μ (excluded from P_0 average). [d] Average of two photolyses.

Figure 1 shows the near-uv absorption spectrum of gaseous cyclopropanone, with arrows indicating the wavelengths of irradiation used. Some diffuse vibrational structure is indicated, ending near the shortest λ_{irr} of 2920 Å. Using the recent analysis of the spectrum of cyclobutanone[9] as a guide, we estimate the 0–0 band in this transition to lie near 3950 Å. Thus the vibrational energy of the electronically excited cyclopropanone produced by the different wavelengths of irradiation would range from ~6.0 kcal mol^{-1} at 3650 Å to ~25.5 kcal mol^{-1} at 2920 Å.

A simple mechanism which accounts for the observed products and quantum yields in the photolysis of gaseous cyclopropanone is



---

[1] R. L. Alumbaugh, G. O. Pritchard, and B. Rickborn, *J. Phys. Chem.*, **69**, 3225 (1965).

[2] E. K. C. Lee, *ibid.*, **71**, 2804 (1967).

[3] J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, **21**, 499 (1970).

[4] N. E. Lee and E. K. C. Lee, *J. Chem. Phys.*, **50**, 2094 (1969).

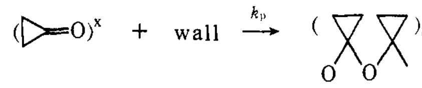
[5] J. C. Hemminger and E. K. C. Lee, *ibid.*, **54**, 1405 (1971).

[6] Unpublished work by N. J. Turro and W. B. Hammond showed C_2H_4 and CO to be produced upon irradiation of a solution of cyclopropanone in CH_2Cl_2 at −78°; see W. B. Hammond, Ph.D. Thesis, Columbia University, 1967, p 111.

[7] C. V. Cannon and O. K. Rice, *J. Amer. Chem. Soc.*, **63**, 2900 (1941); S. Toby and B. H. Weiss, *J. Phys. Chem.*, **68**, 2492 (1964).

[8] N. J. Turro and W. B. Hammond, *J. Amer. Chem. Soc.*, **88**, 3672 (1966).

[9] D. C. Moule, *Can. J. Phys.*, **47**, 1236 (1969).


(5)

The nature of the X state of cyclopropanone cannot be determined on the basis of our results alone, but there is extensive evidence by other workers for the significant involvement of triplet states in the photochemistry of cyclic ketones.[3] Therefore, we propose either that X is the triplet state of cyclopropanone or—more likely in view of the failure of added O_2 to effect the value of ϕ_{cp}—that X designates a relaxed form of cyclopropanone, such as oxyallyl, in its triplet state. Calculations by Hoffmann have predicted that oxyallyl's ground electronic state is the triplet,[10] which should therefore be relatively unaffected by the usual triplet quenchers and might be slow to revert to the more stable[11] closed ring form of cyclopropanone. Because of its zwitterion nature, oxyallyl might nevertheless be sufficiently reactive to form polycyclopropanone, possibly *via* a reaction on the surface. Failure to observe a chemical reaction between oxyallyl and butadiene has precedent in recent thermal rate studies in solution using furan in the trapping attempts.[12] The possibility that ethylene is also produced from the triplet state of cyclopropanone, in a process competitive with oxyallyl formation, cannot be ruled out by our present data. That such a process may be important is suggested by the proposed primary mechanism for cyclobutanone[13] as well as the report that the rate constant for α cleavage of cyclic ketones in solution is two orders of magnitude greater in the triplet than in the singlet (n,π^*) state.[14]

Preliminary investigation of the fluorescence of cyclopropanone shows $\phi_f \sim 5 \times 10^{-4}$ at 3650 Å, the yield decreasing with decreasing wavelengths. Both the increase of $\phi_{C_2H_4}$ with decreasing λ and the accompanying decrease of ϕ_f are explicable in terms of k_d increasing more rapidly with the vibrational energy of (cyclopropanone)† than k_i. This is consistent with the proposed identification of k_i with the intersystem crossing rate constant and in qualitative agreement with the report of predissociation in the vicinity of 3100 Å in the case of cyclobutanone.[5] The lack of effect of the high pressures of inert gases on the value of $\phi_{C_2H_4}$ may perhaps be explained in terms of the inefficiency of these gases in removing vibrational energy from a molecule in a state of low vibrational excitation. For example, at 3130 Å we estimate from our fluorescence yield measurements plus the calculated[15] natural radiative lifetime of 1.2×10^{-5} sec that the mean lifetime of the (cyclopropanone)† formed is $\simeq 1.1 \times 10^{-9}$ sec. Since removal of about 2 kcal mol^{-1} of vibrational energy from this species would be required to reduce $\phi_{C_2H_4}$ at 3130 Å by an amount outside of experimental error, the lack of any observable effect by 1270 Torr of CO_2 indicates that more than 15 collisions, on the average, are required to remove that amount of energy from (cyclopropanone)† containing a total $E_{vib} \simeq 19$ kcal mol^{-1}.[16]

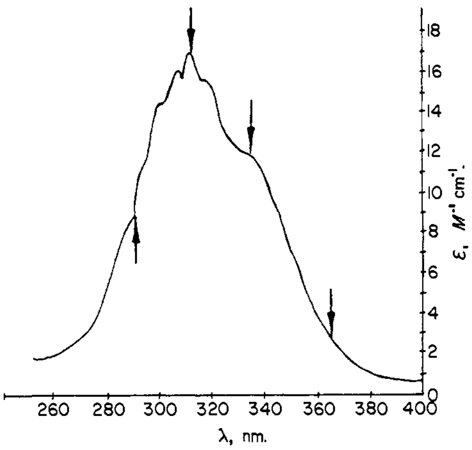


Figure 1. Near-uv absorption spectrum of cyclopropanone scanned on a Cary 14 spectrophotometer with resolution 1.1 Å, P_{cp} 16 Torr, temperature 20.1°. Arrows indicate wavelengths of irradiation used in photolyses.

All quantum yield calculations reported here include corrections for the competing thermal reaction of cyclopropanone, which yielded polycyclopropanone[17] as the only observable product. Our conclusion that polycyclopropanone is also produced *via* a photoinitiated reaction is based not only on the discrepancy between $\phi_{C_2H_4}$ and ϕ_{cp} at the three longer wavelengths combined with the absence of volatile products other than CO and C_2H_4, but also on an observed decrease in transmittance of the photolysis cell windows in the 2000–3000-Å region, compared with the identically treated blank cell. After some 30 photolyses without cleaning, the evacuated photolysis cell transmitted only 67% as much light at 2180 Å and 52% as much at 1890 Å as its companion blank cell, although the "absorption spectrum" of the coating on the windows had the same shape as that of the thermally produced coating in the blank cell.

Acknowledgments. We wish to express our appreciation to Professor K. R. Fountain, now of Wisconsin State University at La Crosse, for many stimulating discussions of the work reported here, and to Mr. George Vaughn of Midwest Research Institute for running the mass spectrometric analyses. Support of the National

---

(10) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(11) Cyclopropanone is ~78 kcal mol^{-1} more stable than oxyallyl in the singlet state according to MINDO/II calculations by N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).

(12) S. Edleson and N. J. Turro, *ibid.*, **92**, 2770 (1970).

(13) E. K. C. Lee in "Excited State Chemistry," J. N. Pitts, Jr., Ed., Gordon and Breach, New York, N. Y., 1970, p 79.

(14) J. C. Dalton, *et al.*, *J. Amer. Chem. Soc.*, **92**, 2564 (1970)

(15) Using the method of S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, **37**, 814 (1962), and the absorption coefficients of Figure 1.

(16) For comparison, vibrational deactivation—removal of 5–10 kcal mol^{-1} of energy—of bicyclopentane produced with $E_{vib} \simeq 76$ kcal mol^{-1} by photolysis of diazabicycloheptene requires ≥ 5 collisions with CO_2: T. F. Thomas, C. I. Sutin, and C. Steel, *J. Amer. Chem. Soc.*, **89**, 5107 (1967). At the other extreme, removal of a single vibrational quantum (E_{vib} = 2.1 kcal mol^{-1}) from cyclopropane by cyclopropane requires 1160 collisions, as determined by ultrasonic dispersion and absorption measurements: T. L. Cottrell and J. C. McCoubrey, "Molecular Energy Transfer in Gases," Butterworths, London, 1961, p 121. The case of (cyclopropanone)† by CO_2 lies intermediate between the two previous cases both in terms of degree of excitation and number of collisions required for removal of one or more vibrational quanta. In the β-naphthylamine system, CO_2 was reported to remove 1.6 kcal mol^{-1} per collision from the excited singlet state with E_{vib} = 24.2 kcal, demonstrating a higher deexcitation efficiency than indicated by our results (see T. L. Cottrell and J. C. McCoubrey, "Molecular Energy Transfer in Gases," Butterworths, London, 1961, p 176, and references therein). The greater complexity of β-naphthylamine, which possesses 54 vibrational modes in contrast to the 18 of cyclopropanone may, however, account for the difference between the two systems.

(17) Based on comparison of the infrared spectrum of the polymer with that reported by S. E. Schaafsma, H. Steinberg, and Th. J. De Boer, *Recl. Trav. Chim. Pays Bas*, **85**, 1170 (1966).

Science Foundation (by Grant No. GP-9578) for this research is gratefully acknowledged.

Timothy F. Thomas,* Hector J. Rodriguez
Department of Chemistry, University of Missouri—Kansas City
Kansas City, Missouri 64110

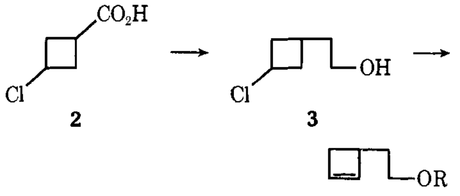
Received June 19, 1971

Strained Ring Systems, X.[1] Buffered Acetolysis of 2-(Δ^2-Cyclobutenyl)ethyl and *trans*-3,5-Hexadienyl Tosylates

Sir:

We wish to report the results of our attempt to form the delocalized carbonium ion reported from the acetolysis of *exo*-bicyclo[2.2.0]hex-2-yl tosylate[2] by the π route with 2-(Δ^2-cyclobutenyl)ethyl tosylate (**1**). While double bond participation of the type expected was not observed with **1**, this study developed solution rate data for the cyclobutene → butadiene rearrangement of **1**, and rate and product data from the acetolysis of *trans*-3,5-hexadienyl tosylate (**10**), the simplest system possible with which to observe homodienylic participation.[3]

Tosylate **1** was prepared by Arndt–Eistert chain extension of 3-chlorocyclobutanecarboxylic acid (**2**),[4] followed by hydride reduction to the ethanol **3**, dehydrochlorination to **4** (KO-*tert*-Bu–DMSO),[5] and tosylation.



2 **3**

1, R = Ts
4, R = H

5

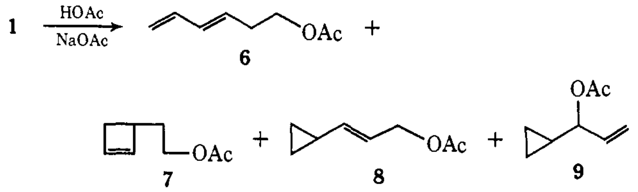
The kinetic results (Table I) for buffered acetolysis of **1** were at first encouraging with a small rate enhancement relative to the saturated derivative **5** (k_1/k_5 = 3.8 at 100°) and the $\Delta S^{\ddagger}$ of the correct magnitude expected for participation. However, analysis of the products derived from **1** made it clear that double bond participation of the type expected had not occurred.

Table I. Buffered Acetolysis Rate Data for 2-(Δ^2-Cyclobutenyl)ethyl OTs (**1**), 2-Cyclobutylethyl OTs (**5**), and *trans*-3,5-Hexadienyl OTs (**10**)

Compd	Temp, °C	$10^5 k_t$,[a] sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
1	85.0	(0.289)[b]		
	100.0	1.36 ± 0.02	27.4 ± 0.4	−7.9 ± 1.1
	120.0	9.70 ± 0.02		
5	85.0	(0.128)[b]		
	100.0	0.488 ± 0.002	23.4 ± 0.3	−20.5 ± 0.7
	120.0	2.57 ± 0.02		
10	85.0	2.85 ± 0.02		
	100.0	12.6 ± 0.1	25.6 ± 0.3	−8.3 ± 0.6

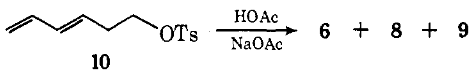
[a] Average k_t from duplicate runs. Errors are the maximum deviation from the average. [b] Extrapolated from rates at higher temperatures.

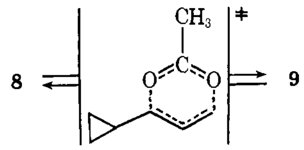
The products from **1** after one solvolytic half-life were a mixture of 49% *trans*-3,5-hexadienyl acetate (**6**), 18% 2-(Δ^2-cyclobutenyl)ethyl acetate (**7**), 29% *trans*-3-cyclopropylallyl acetate (**8**), 2% 1-cyclopropylallyl acetate (**9**), and 2% unidentified materials; no tosylate other than **1** was recovered. After ten solvolytic half-lives, this product composition was 92% **6**, 6% **7**, 1% **8**, and 1% **9**, with a trace of the unidentified materials remaining.



The combined information of (a) formation of these products from **1**, (b) the relative instability of alcohol **4** and acetate **7** to glpc conditions toward rearrangement to their *trans*-3,5-hexadienyl analogs, and (c) the small, negative $\Delta S^{\ddagger}$ suggested that the rate-determining step in the buffered acetolysis of **1** was *not* an ionization process, but rather involved the sum of a cyclobutene → butadiene retrocycloaddition of **3** to *trans*-3,5-hexadienyl OTs (**10**), k_r, and a solvent displacement leading to **7**, k_s.[6]

To examine the validity of this proposal, we have prepared and examined the buffered acetolysis of **10**. The kinetic data and activation parameters for **10** are given in Table I. The products of buffered acetolysis of **10** were varying amounts of acetates **6**, **8**, and **9** dependent on the extent of reaction. The acetate product composition has been determined from 0.25 to 10 solvolytic half-lives for **30** and is plotted in Figure 1. From this plot we can see that the first formed acetate is **9** whose concentration builds and decays rapidly in the early stages of the reaction. The allylic isomer of **9**, **8**, is formed somewhat more slowly and appears to be more stable than **9**. From this and data obtained with pure samples of **8** and **9** an equilibrium exists between these two acetates with K = 9–10 which probably involves **11** as a transition state.





11

Plotting the data in Figure 1 as a function of the total composition during the buffered acetolysis gives a "textbook" type of plot shown in Figure 2. Here we see what appears to be a brief induction period in the formation of acetate **6**. This would be expected if

---

(1) For paper IX in this series see R. N. McDonald and R. R. Reitz, *J. Org. Chem.*, **35**, 2666 (1970).

(2) R. N. McDonald and C. E. Reineke, *ibid.*, **32**, 1878 (1967).

(3) M. Simonetta and S. Winstein, *J. Amer. Chem. Soc.*, **76**, 18 (1954).

(4) W. A. Nevill, D. S. Frank, and R. D. Trepka, *J. Org. Chem.*, **27**, 422 (1962).

(5) M. Hanack and K. Riedlinger, *Chem. Ber.*, **100**, 2107 (1967).

(6) The lack of double bond participation in **1** is a common observation in such 4-pentenyl systems; see A. A. Youssef and S. M. Sharaf, *J. Org. Chem.*, **33**, 2581 (1968).