other minor products are formed are uncertain. Decomposition of chloroketene (or its cycloadditions), produced in the ring fission process (paths "a" and "b") which also yields ethylene, or its attack of the starting material cannot be ruled out. Since the peak emerging at an 18-min retention time during the vpc analysis (see Table II) increases when the mixture of chloro-CB and CB is pyrolyzed, it would seem to indicate that either ethylene or ketene is somehow involved in its production.

Photolytic (Direct) and Triplet Benzene Sensitized Decomposition and Fluorescence Excitation Study of 2-Chlorocyclobutanone[1]

John Metcalfe and Edward K. C. Lee*

Contribution from the Department of Chemistry, University of California, Irvine, California 92664. Received December 6, 1972

Abstract: Direct photolysis of 2-chlorocyclobutanone (chloro-CB) has been extensively studied at 325.0 and 330 nm, and several photolyses were also conducted at 253.7, 276, 285, 298, and 309 nm. The primary photoproducts arise from ring cleavage and decarbonylation processes, and their quantum yields at low pressures add up to 0.83 ± 0.20, indicating that the decomposition yield is unity within experimental uncertainty. The vibrationally hot $c\text{-}C_3H_5Cl$ thus produced undergoes unimolecular isomerization and decomposition unless stabilized at high pressures. Chloro-CB(S_1*) has a "predissociative" lifetime less than 0.4 nsec at 340 nm, and it undergoes $S_1 \rightsquigarrow S_0^*$ internal conversion process to the extent of ~60% at λ_{ex} 325 nm and ~70% at 330 nm. The specific rate constants, $k(E)$, of the photoactivated vibrationally hot species (S_0^*) are 2.1×10^9 sec^{-1} for λ_{ex} 330 nm (86.6 kcal/mol) and 3.4×10^9 sec^{-1} for λ_{ex} 325 nm (89.0 kcal/mol). They are very similar to those observed for cyclobutanone(S_0^*). These experimental values of $k(E)$ are within 20% of the values calculated from an approximate formulation of the RRKM rate theory. Triplet benzene ($^3B_{1u}$, 84.4 kcal/mol) gives essentially the decarbonylation product with nearly unit quantum efficiency. A weak fluorescence emission was observed in the gas phase.

The photolysis of cyclobutanone (CB) and substituted cyclobutanones have been the subject of extensive research in recent years.[2,3] However, only one halogen substituted cyclobutanone (hexafluorocyclobutanone) has been investigated.[4] The present study was undertaken in an attempt to determine what effects, if any, a chlorine atom has on the primary and the secondary processes in the photolysis of cyclobutanone. The thermal decomposition of 2-chlorocyclobutanone (chloro-CB)[5] seems to indicate that a new pathway, not observed previously for an alkyl-substituted cyclobutanone, can occur, *e.g.*, elimination of HCl (followed by both ring fission and decarbonylation processes), in a manner analogous to the HCl elimination pathway in the thermal decomposition of chlorocyclobutane.[6]

Cyclobutanone has been shown to decompose photolytically, mainly, by a "singlet" pathway,[3f,i] whereas most other cyclic ketones decompose by a triplet pathway.[7] Substitution of a chlorine atom in the α-carbon position of cyclobutanone might cause an increase in the rate of $S_1 \rightsquigarrow T_1$ intersystem crossing (k_{ISC}) from the $^1(n,\pi^*)$ state of CB(S_1) to its triplet state (T_1) thus enhancing the triplet reaction by "heavy" atom effect of chlorine which could efficiently mix the two states.[8] It is known that the rate of $S_1 \rightsquigarrow S_0^*$ internal conversion (k_{IC}) of CB(S_1^*) with a few quanta of the out-of-plane C–O wagging vibrations is extremely fast.[3i] Hence, the $S_1 \rightsquigarrow T_1$ intersystem crossing may not effectively compete with the $S_1 \rightsquigarrow S_0$ internal conversion, even if k_{ISC} is increased. The present work is designed to shed some light on these important unknowns.

Experimental Section

Chemicals. 2-Chlorocyclobutanone was prepared as described elsewhere.[5] The following gases were used without further purification, and the purity quoted is that given by the commerical sources: Ar (99.995%, high purity grade, Matheson Co.); O_2 (99%, Air Products).

Direct Photolysis. Samples were handled on a glass-metal vacuum line free from grease and mercury. Photolyses were carried out in a quartz cell of 85.2-ml volume at 23° as previously described.[2b] All photolyses were carried out at 0.2 Torr of chloro-CB, except those at 254 and 276 nm which were at 1.0 Torr. This was necessary for analyzing the photoproduct, because the per-

---

[1] This research has been supported by National Science Foundation Grant No. GP 28010X.

[2] (a) S. W. Benson and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, **64**, 80 (1942); (b) N. E. Lee and E. K. C. Lee, *J. Chem. Phys.*, **50**, 2094 (1969); (c) see ref 2b for many of the earlier references cited therein.

[3] (a) R. F. Klemm, *Can. J. Chem.*, **21**, 3320 (1970); (b) D. C. Montague and F. S. Rowland, *J. Amer. Chem. Soc.*, **91**, 7230 (1969); (c) R. G. Shortridge, Jr., W. Yang, and E. K. C. Lee, *Mol. Photochem.*, **1**, 325 (1969); (d) P. Dowd, A. Gold, and K. Sachdev, *J. Amer. Chem. Soc.*, **92**, 5724, 5725 (1970); (e) N. J. Turro and D. R. Morton, *ibid.*, **93**, 2569 (1971), and reference cited therein; (f) J. C. Hemminger. C. F. Rusbult, and E. K. C. Lee, *ibid.*, **93**, 1867 (1971); (g) H. A. J. Carless and E. K. C. Lee, *ibid.*, **94**, 1 (1972); (h) J. Metcalfe and E. K. C. Lee, *ibid.*, **94**, 7 (1972); (i) J. C. Hemminger and E. K. C. Lee, *J. Chem. Phys.*, **56**, 5284 (1972); (j) H. A. J. Carless, J. Metcalfe, and E. K. C. Lee, *J. Amer. Chem. Soc.*, **94**, 7221 (1972).

[4] D. Phillips, *J. Phys. Chem.*, **70**, 1235 (1966).

[5] J. Metcalfe and E. K. C. Lee, **95**, 4316 (1973).

[6] A. T. Cocks and H. M. Frey, *J. Amer. Chem. Soc.*, **91**, 7583 (1969).

[7] R. G. Shortridge, Jr., C. F. Rusbult, and E. K. C. Lee, *ibid.*, **93**, 1863 (1971).

[8] S. P. McGlynn, T. Azumi, and M. Kinoshita, "The Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1970, p 246.

centage decomposition was very small at 254 and 276 nm. In general, photolyses were performed at a low pressure, in order to prevent adsorption of the parent ketone on the photolysis cell surface and because more reproducible results were obtained in this way. However, due to experimental limitations, the accuracy of pressure measurement was no better than ±15%. Also, all photolyses except one run were conducted in the presence of 1.3 Torr of O_2 in order to remove the long-lived free radical products. Ar was added to some photolytic mixtures in order to determine the effect of pressure on the product distribution, and it was used because it had been found to be a suitable inert gas for the photolytic system of dimethylcyclobutanones.[3h]

The quantum yield of decomposition of Chloro-CB was measured relative to cyclobutanone at 309 nm, since the quantum yield of decomposition of CB(S_1*) below 313 nm is known to be unity,[2b,i,9] The light intensity at 309 nm was calculated from the CB actinometry by measuring its total % decomposition yield. By knowing additionally the molar absorptivities of CB and chloro-CB and the % decomposition product yields of the photoexcited chloro-CB, then its decomposition quantum yield was calculated.

$C_6H_6(^3B_{1u})$ Sensitization at 253.7 nm. Triplet benzene sensitized decomposition of chloro-CB was carried out at 253.7 nm in the same quartz photolysis cell as used in direct photolysis. The benzene pressure was 2.5 Torr and chloro-CB pressure was 0.05 Torr, where it is expected that ~92% of the $C_6H_6(^3B_{1u})$ will be quenched by 2-chloro-CB, whereas only a minor amount (≤5%) of $C_6H_6(^1B_{2u})$ is expected to be quenched by chloro-CB.[10] To the C_6H_6/chloro-CB mixture, varying amounts of *cis*-2-butene were added as a competing triplet quencher. This caused a reduction of the triplet sensitized products, but had no effect on the singlet sensitization products or on the direct photolytic products. The C_6H_6/*cis*-2-butene mixture was also photolyzed under the identical experimental conditions so that this run would serve as an actinometer in counting the $C_6H_6(^3B_{1u})$ yield in the system. Through this procedure,[10a,11] the "quantum efficiency" of the decomposition of the chloro-CB*(T_1) was determined.

Product analysis was carried out as described elsewhere,[5,12] using a 25-ft Carbowax 300 column and a flame ionization detector.

Light Sources. The photolyses were carried out at 253.7, 276, 285, 298, 309, 325.0, and 330 nm. The photolyses at 276, 285, 298, and 309 nm were carried out using a 200-W super-pressure mercury arc lamp (Osram HBO-200) operated by a stabilized dc power supply (PEK Model 701-A), the lamp emission being resolved by a high intensity grating monochromator (Bausch and Lomb, No. 33-86-01, uv grating, 3.2 nm/mm reciprocal dispersion). The band pass was ~3 nm for all of these wavelengths. The light intensity was ~8×10^{14} quanta/sec at 276 nm; ~1.4×10^{15} at 285; ~5×10^{15} at 298; ~5×10^{15} at 309.

The photolyses at 330 nm (~1.4×10^{15} quanta/sec, ~10 nm band pass) were carried out using a 450-W mercury arc lamp (Osram, HBO-450) operated by a stabilized dc power supply (Oriel Optics, Model 6128) together with the Bausch and Lomb high intensity monochromator. A 1-mm thick soft-glass plate and a 1.0-cm path length of 0.4 *M* KNO_3 (in H_2O) filter solution were used.

The photolyses at 325.0 nm were carried out using a He–Cd laser (Spectra-Physics, Model 185, rated at 15 mw) which had a light intensity of ~1.6×10^{16} quanta/sec. The intense primary beam was dispersed to a wider beam with a silica lens and a Corning CS-0-54 filter was placed in fromt of the photolysis cell.

The photolyses at 254 nm were carried out using a low-pressure mercury grid lamp (Ultra-violet Products, Mineralight R 51) together with a Corning CS 7-54 filter and a 1.0-cm thick D_3P filter solution.[13] The light intensity was ~5×10^{15} quanta/sec.

The lamp intensity fluctuation was relatively small for all of the light sources (≤10%), except that of the 450-Watt mercury lamp (for 330 nm) which was as much as 20%.

Absorption spectrum of chloro-CB for the $\pi^* \leftarrow n$ transition in the 240–355-nm region was recorded with a Cary 14R spectrophotometer, equipped with a 0–0.1 A range slidewire, using a gas cell with a 10-cm path length at 1.3 Torr pressure and 23°.

Fluorescence Excitation Spectrum (FES). The optical and photon counting electronic arrangement used for the high resolution fluorescence excitation spectrum was similar to that employed earlier.[3i] The FES was recorded at a spectral resolution of 0.1 nm. Due to the low quantum yield of fluorescence emission from chloro-CB compared to that from "cell glow," the FES was obtained by taking first the emission from the cell containing chloro-CB, second the emision fom the cell blank run (without chloro-CB), and third another emission from the cell containing chloro-CB. The net emission (attributable to chloro-CB) was calculated as the difference between the average of the two sample runs (the first and the third runs) and the second run.

Results

Effect of O_2. The hydrocarbon and monochlorohydrocarbon products observed in the direct photolysis are, in order of their elution time on the Carbowax 300 column, ethylene, allene, methylacetylene, vinyl chloride, *cis*-1-chloropropene, *trans*-1-chloropropene, chlorocyclopropane, and 3-chloropropene. All of these identified products result from unimolecular decomposition processes which do not involve any free-radical intermediates with long lifetimes, because a small amount of O_2 (1.3 Torr) has virtually no effect upon their product distribution as shown in Table I.

Table I. Effect of O_2 on the Product Distribution in Direct Photolysis of Chloro-CB (λ_{ex} 325 nm)

Run no.	170	171
Pressure of chloro-CB, Torr	0.21	0.20
Pressure of O_2, Torr	0	1.3
Product yields[a]		
C_2H_4	110	107
C_2H_3Cl	105	101
$CH_2{=}C{=}CH_2$	20.0	16.2
$CH_3C{\equiv}CH$	3.4	2.8
cis-$CH_3CH{=}CHCl$	2.1	1.9
trans-$CH_3CH{=}CHCl$	1.0	0.8
$CH_2ClCH{=}CH_2$	40.5	43.2
c-C_3H_5Cl	30.7	35.1
(18.3 min)[b]	2.3	
% decomposition[c]	0.90_0	0.92_1
Sum of C_3 product[c]	0.28_6	0.29_9

[a] Expressed as the sum of C_3 product in 100 units. [b] Unidentified peak (it is not 2-chloropropene). [c] Actual observed % decomposition (relative to the starting material = 100).

One unidentified peak (insignificant in amount) eluting at 18 min was scavenged by O_2, and we shall not be concerned with it.

Effect of Ar. The yields of C_2H_4 and C_2H_3Cl (C_2 products) were reduced in photolysis conducted at high pressures. The pressure to quench one-half of the C_2H_4 and C_2H_3Cl ($P_{1/2}$) was found to increase with decreasing photolysis wavelength (or increasing photoactivation energy) as expected. Tables II and III show the results of the photolyses at 330 and 325.0 nm, respectively. It has been found in the previous studies of cyclobutanone[2b] and alkyl-substituted cyclobutanone photolyses[3g,i] that the total yield of decarbonylation products is nearly constant with pressure. The total yield of the products containing three carbon atoms (C_3

---

[9] T. H. McGee, *J. Phys. Chem.*, 72, 1621 (1968).

[10] (a) See E. K. C. Lee in "Excited State Chemistry: A Symposium," J. N. Pitts, Jr., Ed., Gordon and Breach, New York, N. Y., 1970, p 59; (b) J. Metcalfe and E. K. C. Lee, *J. Amer. Chem. Soc.*, **95**, 1751 (1973).

[11] H. O. Denschlag and E. K. C. Lee, *J. Amer. Chem. Soc.*, **90**, 3628 (1968).

[12] No analysis of CO, ketene, chloroketene, and chloro-CB was undertaken. It is assumed that the quantity of ketene (or chloroketene) is equal to the amount of vinyl chloride (or ethylene) formed. The amount of chloro-CB remaining after photolysis, of course, is assumed to be equal to the number of moles present before photolysis less the number of moles of the observed products formed as hydrocarbons or chlorinated hydrocarbons.

[13] C. L. Braga and M. D. Lumb, *J. Sci. Instrum.*, 43, 341 (1966).

Table II. Effect of Ar Pressure on the Product Distribution[a] from the Photolysis of Chloro-CB (XCB) at 330 nm

Run no.	Pressure, Torr			Time, min	(C_2)		(C_3)							
	XCB	O_2	Ar		C_2H_4	C_2H_3Cl	Allene	Methylacetylene	*cis*-1-Chloropropene	*trans*-1-Chloropropene	3-Chloropropene	c-C_3H_5Cl	$(C_3)^b$	% dec
159	0.20	1.3		240	126	109	12.1	1.9	1.3	0.8	42.1	41.9	0.225	0.75
162	0.20	1.3		270	125	111	12.1	2.0	1.5	0.9	42.6	42.0	0.214	0.72
163	0.20	1.3	97	270	114	99	1.69	0.27	1.6	0.2	17.3	78.9	0.225	0.70
158	0.20	1.3	197	300	112	97	0.76		2.2		9.6	87.4	0.184	0.57
160	0.20	1.3	354	270	98	84	0.54		1.4		7.4	90.7	0.205	0.58
161	0.19	1.3	501	270	91	78	0.26		1.5		6.6	91.6	0.190	0.51
156	1.01	1.3		90	114	99	8.2	1.2	2.2	1.1	35.1	52.3	0.077	0.24
157	1.01	1.3	40	90	118	101	3.6	0.5	1.9		22.1	71.9	0.059	0.19

[a] Product yields are expressed as the sum of the C_3 products being 100 units. [b] The sum of the C_3 products is expressed as the % decomposition of the parent.

Table III. Effect of Ar Pressure on the Product Distribution[a] from the Photolysis of Chloro-CB (XCB) at 325.0 nm

Run no.	Pressure, Torr			Time, min	(C_2)		(C_3)							
	XCB	O_2	Ar		C_2H_4	C_2H_3Cl	Allene	Methylacetylene	*cis*-1-Chloropropene	*trans*-1-Chloropropene	3-Chloropropene	c-C_3H_5Cl	$(C_3)^b$	% dec
127	0.2	1.3		7	105	100	18.7	2.8	2.0	1.7	41.9	32.8	0.267	0.81
131	0.2	1.3		7	103	101	15.9	2.6	2.1	1.1	43.3	35.1	0.330	1.00
132	0.2	1.3	96	7	102	96	3.1	0.4	2.7	0.4	21.5	71.8	0.376	1.12
128	0.2	1.3	200	7	98	94	2.2	0.4	2.1	0.3	13.7	81.4	0.274	0.80
126	0.2	1.3	290	7	93	91	1.1		2.0	0.6	12.2	84.1	0.300	0.85
114	0.2	1.3	380	7	88	89	0.8		3.2		10.5	85.4	0.296	0.82
125	0.2	1.3	410	7	84	88	0.8		1.8		9.4	88.1	0.285	0.77
129	0.2	1.3	596	7	83	82	0.8		1.9		8.3	89.0	0.258	0.68
130	0.2	1.3	900	7	72	76	0.6		1.6		5.3	92.4	0.227	0.56

[a] Product yields are expressed as the sum of the C_3 products being 100 units. [b] The sum of the C_3 products is expressed as the % decomposition of the parent.

Table IV. Effect of Exciting Wavelengths on the Product Distribution[a] from the Photolysis of Chloro-CB

Run no.	XCB	O_2	λ_{ex}, nm	(C_2)		(C_3)							
				C_2H_4	C_2H_3Cl	Allene	Methylacetylene	*cis*-1-Chloropropene	*trans*-1-Chloropropene	3-Chloropropene	c-C_3H_5Cl	(C_3)	% dec
159–162	0.20	1.3	330	37.4	32.9	3.6	0.6	0.4	0.2	12.6	12.3	0.297	0.74
127–131	0.20	1.3	325	34.2	33.0	5.7	0.9	0.7	0.5	14.0	10.8	0.328	0.90
134	0.20	1.3	309	29.8	35.0	9.0	1.9	0.9	0.6	14.5	8.4	0.352	1.15
121	0.20	1.3	298	28.1	35.2	10.6	2.8	1.0	0.8	14.3	7.3	0.367	1.07
123	0.20	1.3	285	26.5	35.7	12.7	4.6	1.2	0.9	12.0	6.3	0.378	0.45
133	1.11	1.3	276	24.6	35.6	12.3	4.7	1.3	0.8	13.3	7.3	0.398	0.07

[a] Product yields are expressed as the sum of the C_2 and C_3 products being 100 units.

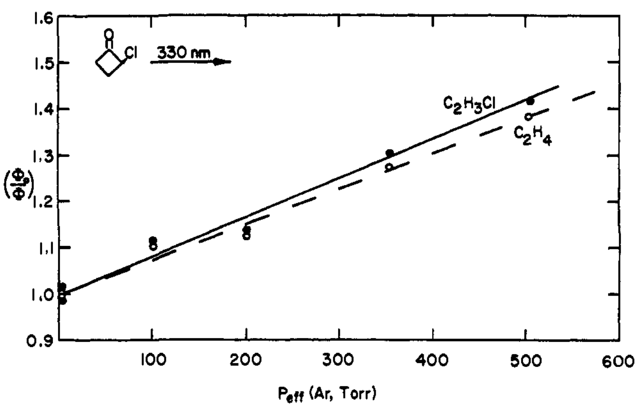


Figure 1. Stern–Volmer plot of the C_2H_4 (○) and C_2H_3Cl (●) yields at λ_{ex} 330 nm *vs.* Ar pressure.

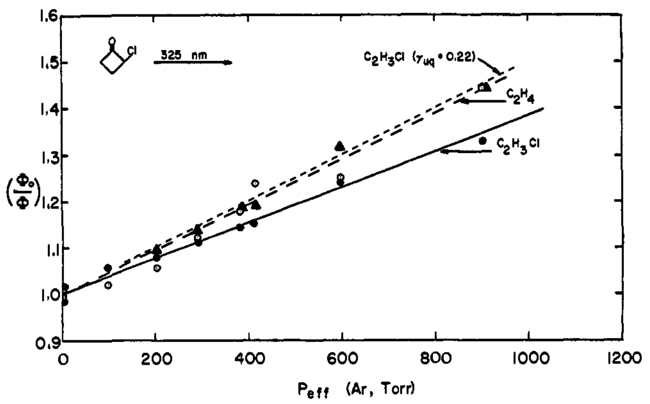


Figure 2. Stern–Volmer plot of the C_2H_4(○) and C_2H_3Cl (●) yield at λ_{ex} 325.0 nm *vs.* Ar pressure. The corrected S–V plot for C_2H_3Cl containing only 78% quencheable portion (▲) is shown in a broken line.

product) in the photolyses of chloro-CB also seems to be constant with pressure as shown in Tables II and III (see the column labeled (C_3)). The fluctuations in the C_3 yields are mainly due to the inaccuracies in measuring the chloro-CB pressure or the changes in light intensity. Since the total C_3 product yield is expected to be pressure independent,[2b,3j] it was used as the relative quantum yield reference.

Stern–Volmer plots for the quenching of C_2H_4 and C_2H_3Cl by Ar were drawn from the data in Tables II and III, where the yield of chloro-CB from photolysis without added Ar was used as the reference point. The total effective pressure (Ar = 1.00), P_{eff}(Ar), was estimated as the sum: $P_{Ar} + P_{O_2} + 5P_{chloro\text{-}CB}$, since the parent chloro-CB should be much better in vibrationally relaxing the chloro (S_0*) than Ar, as has been found for the cyclobutanone–Ar system[2b] and the dimethylcyclobutanone–Ar system.[3j]

Figure 1 shows the Stern–Volmer plot of C_2H_4 and C_2H_3Cl produced at 330 nm, and the linearity of the plot indicates that the precursor of C_2H_4 and C_2H_3Cl obeys the Stern–Volmer kinetics and presumably it has monoenergetic unimolecular decomposition characteristics. Furthermore, the fact that the $P_{1/2}$ values for C_2H_4 and C_2H_3Cl are the same within the experimental error, 1320 and 1200 Torr, respectively, is indicative of the one precursor (for both products) mechanism, as has been proposed previously.[2b,3g,j]

Figure 2 shows the Stern–Volmer plot of C_2H_4 and C_2H_3Cl at 325.0 nm, but unlike Figure 1 the apparent $P_{1/2}$ value for C_2H_3Cl (2750 Torr) is much greater than that of C_2H_4 ($P_{1/2}$ = 1980 Torr). By analogy to the 2-*n*-propylcyclobutanone case where similar problems arose,[3g] we have allocated the C_2H_3Cl yield into two parts; a "quenchable" and an "unquenchable" portion. We have assumed the quenchable portion of C_2H_3Cl is 22 ± 5% in order to fit the Stern–Volmer slope of $P_{1/2}$ = 1980 Torr for C_2H_3Cl as in C_2H_4 (100% quenchable). It is obvious that curvature of the Stern–Volmer plot for C_2H_3Cl was not observed because the "quenchable fraction (γ_Q)" was large compared to the "unquenchable fraction (γ_{uQ})" and because of the small pressure range covered in this experiment. The introduction of the second pathway for the formation of C_2H_3Cl (the "unquenchable" C_2H_3Cl) at high photoexcitation energies is consistent with earlier observations made with the 2-*n*-propylcyclobutanone and dimethylcyclobutanone photolyses.[3g,j]

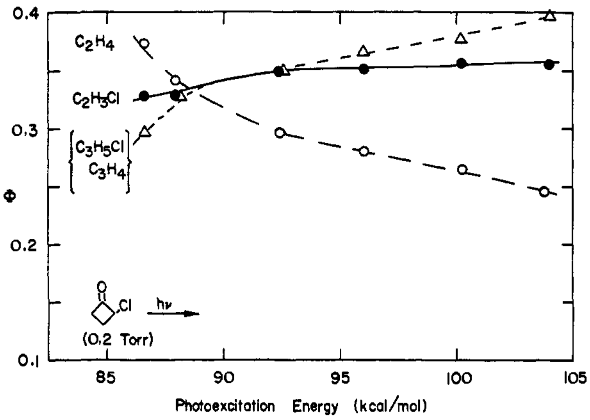


Figure 3. Quantum yields (Φ) of C_2H_4 (○), C_2H_3Cl (●), and the total C_3 products (△) are plotted as a function of photoexcitation energy.

Quantum Yield of Photodecomposition at 309 nm. The total quantum yield of photodecomposition of chloro-CB at λ_{ex} 309 nm using CB actinometry gave a value of 0.83 ± 0.20, when the two runs, one with 0.99 Torr of CB and the other one with 0.18 Torr of chlorocyclobutanone, were irradiated under the identical experimental conditions.

Effect of Photoactivation Wavelength (λ_{ex}). The relative quantum yields of the products at different photoexcitation energies are shown in Table IV and the quantum yields of C_2H_4, C_2H_3Cl, and the total C_3 products ($C_3H_4 + C_3H_5Cl$) are plotted in Figure 3. It has been shown that hot c-C_3H_5Cl can decompose to give other C_3 products (olefinic C_3H_5Cl as well as C_3H_4); these decomposition products increase at low pressures (see Tables II and III) and at higher photoexcitation energies (see Table IV), as expected.

The photolysis results at 254 nm were not included in the quantum yield *vs.* photoexcitation energy plot (Figure 3), because it was found that there was significant amount of secondary decomposition which prevented evaluation of the quantum yields with reasonable certainty. Table V shows the product distribution obtained at λ_{ex} 254 nm; the significant degree of time dependence indicating secondary decomposition reactions and the total recovery of the decomposition products for analysis is seriously questionable even at 0.2%

Table V. Effects of Photolysis Time on the Product Distribution[a] from the Photolysis of Chloro-CB at 253.7nm

Run no.	Pressure, Torr		Time, min	(C_2)		(C_3)							% dec
	XCB	O_2		C_2H_4	C_2H_3Cl	Allene	Methylacetylene	*cis*-1-Chloropropene	*trans*-1-Chloropropene	3-Chloropropene	c-C_3H_5Cl	(C_3)	
137	1.07	1.3	10	16.2	51.2	10.7	7.7	~0.3	0.3	4.5	9.0	32.5	0.14
138	1.09	1.3	5	17.4	50.1	10.9	7.4	~0.5	0.4	3.9	9.4	32.5	0.08
105	0.99	1.3	5	17.3	49.2	11.3	7.5	0.6	0.2	5.2	8.7	33.4	0.08
106	1.10	1.3	2	20.6	44.9	11.5	6.8	0.9	0.2	3.8	11.2	34.5	0.04

[a] Product yields are expressed as the sum of the C_2 and C_3 products being 100 units.

Table VI. Product Distribution[a] in Benzene Photosensitized Decomposition of Chloro-CB (λ_{ex} 253.7 nm)

Run no.	Pressure, Torr			Time, min	(C_2)		(C_3)						18.3 min
	C_6H_6	XCB	*cis*-2-C_4H_8		C_2H_4	C_2H_3Cl	Allene	Methylacetylene	*cis*-1-Chloropropene	*trans*-1-Chloropropene	3-Chloropropene	c-C_3H_5Cl	
62	2.5	0.05		1.3	0.72	1.02	0.20	0.05	0.22	0.07	5.3	29.2	0.15
60	2.5	0.05	0.09	1.3	0.74	~0.9[b]	~0.17[b]	~0.06[b]	0.20	0.06	4.5	24.3	0.13
61	2.5	0.05	0.70	1.3	0.78	~1.0[b]	~0.08[b]	~0.03[b]	0.09	0.06	2.0	11.0	0.06

[a] Product yields are in units of 10^{-9} mol as observed. [b] Inaccurate due to these products eluting in the tail of *cis*-2-C_4H_8.

conversion. Also at λ_{ex} 254 nm, the C_3 product quantum yield may not be constant, since chloropropenes are known to undergo photodecomposition at this wavelength.[14] This may account in part for the observed secondary photodecomposition.

Triplet Benzene ($^3B_{1u}$) Sensitization. Triplet benzene sensitized decomposition results are shown in Table VI. It shows that (1) c-C_3H_5Cl and $CH_2ClCH{=}CH_2$ are the major products ($\geq$93%); (2) C_2H_4 and C_2H_3Cl (within the uncertainty of its yield) are unaffected by the addition of *cis*-2-C_4H_8, because these are not the "characteristic" triplet products; and (3) all of the C_3 products are reduced by the addition of *cis*-2-C_4H_8, because these are the "characteristic" triplet products.[15] The yield of *trans*-2-C_4H_8 from the *cis*-2-$C_4H_8/C_6H_6(^3B_{1u})$ system, under similar experimental conditions to the chloro-CB/$C_6H_6(^3B_{1u})$ system, was used as a quantum yield reference, and it was found that the quantum efficiency of the "triplet" chloro-CB (triplet benzene sensitized) decomposing to give the C_3 products was >0.9.

Absorption Spectrum. The gas phase uv absorption spectrum of chloro-CB is shown in Figure 4. The value of ϵ_{max} 61 M^{-1} cm^{-1} at 300 nm agrees well with the published value of ϵ_{max} 68 M^{-1} cm^{-1} at 304 nm obtained in cyclohexane solution.[16] The lack of observable vibrational structure in the spectrum, unlike the spectrum of cyclobutanone ($\pi^* \leftarrow n$), may be due to the instrumental limit of resolution rather than an actual absence of the structure. The hatched area between 330 and 350 nm is the spectral region over which the fluorescence excitation spectrum can be observed.

Fluorescence Excitation Spectrum (FES). The gas-phase FES of chloro-CB run at ~0.1-nm resolution is shown in Figure 5. The error bar for two standard deviations (2σ) or 95% confidence limit is also shown. Each experimental point (at 0.1-nm intervals) was calculated by the difference between the sample run and the blank cell run. The peaks at 339.1, 340.5, and 342.0 nm are real, while the peaks at 337.3, 337.8, 338.6, and 347.6 nm may not be real because the signal/noise ratio was too small for their positive assignment. The peak at 340.5 nm gave a fluorescence quantum yield Φ_F value of $\sim 5 \times 10^{-4}$ as compared to the $\Phi_F = 19 \times 10^{-4}$ for cyclobutanone at 319.4 nm.[3i]

Discussion

Absorption Spectrum. The first electronic absorption band of chloro-CB ($\pi^* \leftarrow n$) shown in Figure 4 is *ca.* twice as intense as that of 2-*n*-propylcyclobutanone and red shifted by 15–20 nm.[3g] This may be due to a more significant electronic effect of α-chlorine atom substitution than α-alkyl group substitution. From the first absorption (electronically forbidden) band of chloro-CB the intrinsic fluorescence emission rate (k_F) can be calculated using the Strickler–Berg expression[17]

$$k_F = 2.880 \times 10^{-9} n^2 \langle \bar{\nu}_F^{-3} \rangle_{AV}^{-1} \frac{g_l}{g_u} \int \epsilon\, d(\ln \bar{\nu}) \quad (1)$$

where n (index of refraction) is 1.00 in the gas phase at low pressure, g_l and g_u (electronic degeneracy in the

---

(14) D. H. Volman, *Intra-Sci. Chem. Rep.*, 3, 263 (1969).

(15) A more comprehensive study on the competitive quenching of $C_6H_6(^3B_{1u})$ by chloro-CB and *cis*-2-C_4H_8 will be reported elsewhere.

(16) J. M. Conia and J. L. Ripoll, *Bull. Soc. Chim. Fr.*, 768 (1963).

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

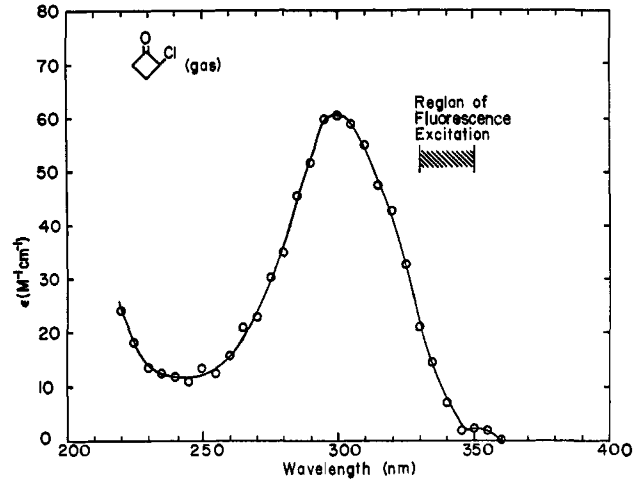


Figure 4. Uv absorption spectrum of gaseous chlorocylobutanone.

lower and upper states) are unity, $\epsilon(\bar{\nu})$ is the molar absorptivity (in M^{-1} cm^{-1}) and $\bar{\nu}_F$ is the frequency of the fluorescence emission (in cm^{-1}). We used a value of $\langle\bar{\nu}_F^{-3}\rangle_{AV}^{-1} = 1.15 \times 10^{13}$ cm^{-1}, as compared with a value of 1.3×10^{13} cm^{-1} found in CB and the dimethylcyclobutanone isomers.[18] The calculated value of k_F (S-B) was 3.7×10^5 sec^{-1}, and this value was further corrected by a normalization factor[18] of approximately 3.4× in order to generate the realistic value of $k_F \approx 1.3 \times 10^6$ sec^{-1} which may be reliable within a factor of 2.

Fluorescence Quantum Yield and Singlet Lifetime at 340.5 nm. Fluorescence quantum yield (Φ_F) of chloro-CB can be estimated from the known fluorescence yield of CB ($\Phi_F = 1.9 \times 10^{-3}$ at $\lambda_{ex} > 319$ nm)[19] by comparing the FES of chloro-CB with the FES of CB run under the comparable experimental conditions. The average of two separate sets of measurements gives Φ_F at 340.5 nm for chloro-CB as $(5 \pm 2) \times 10^{-4}$.

From the relationship between the singlet lifetime of chloro-CB (τ_S), Φ_F and k_F, we estimate the value of τ_S

$$\tau_S = \Phi_F/k_F = [(5 \pm 2) \times 10^{-4}/(1.3 \pm 0.6) \times 10^6 \text{ sec}^{-1}] \approx 4 \times 10^{-10} \text{ sec} \quad (2)$$

Triplet Benzene Sensitization ($^3B_{1u}$, 84.4 kcal/mol). The product distribution for $C_6H_6(^3B_{1u})$ sensitized decomposition of chloro-CB shown in Table VI indicates that the main products ($\Phi > 0.9$) are c-C_3H_5Cl and 3-chloropropene (isomerization product of the "hot" c-C_3H_5Cl) and *cis*- and *trans*-1-chloropropene. Furthermore, the yields of these products are lowered by the addition of the "triplet competitor" *cis*-2-butene confirming that they are from the "triplet" chloro-CB (T_1).[20,21] The yields of C_2H_4 and C_2H_3Cl are formed mainly by either "singlet" ($^1B_{2u}$) sensitization or direct photolysis (253.7 nm) of chloro-CB, since they are unaffected by the addition of *cis*-2-butene.[20,21] Therefore, it would appear that, like CB(T_1),[20] chloro-CB(T_1) gives only decarbonylation product

$$\text{chloro-CB}(T_1) \longrightarrow \text{c-}C_3H_5Cl^{\dagger} + CO \quad (3)$$

An attempt to perform Hg($6^3P_{1,0}$) sensitization of chloro-CB was unsuccessful because no sensitized decomposition product was observed in a normal gas chromatographic analysis. This was thought to be due to removal of Hg ($6^3P_{1,0}$) as HgCl. No further attempts to clarify the mercury photosensitization process were made.

Direct Photolysis. Chloro-CB(S_0*) can react or be deactivated according to Scheme I in a manner similar to other cyclobutanones.[3g,i]

Scheme I

$$\text{chloro-CB}(S_0) \xrightarrow{h\nu} \text{chloro-CB}(S_1^*) \quad \text{excitation} \quad (4)$$

$$\text{chloro-CB}(S_1^*) \xrightarrow{\omega(M)} \text{chloro-CB}(S_1) \quad \text{collisional deactivation} \quad (5)$$

$$\longrightarrow \text{chloro-CB}(S_0) + h\nu_F \quad \text{fluorescence} \quad (6)$$

$$\longrightarrow \text{chloro-CB}(S_0^*) \quad \text{internal conversion} \quad (7)$$

$$\longrightarrow \text{chloro-CB}(T_1^*) \quad \text{intersystem crossing} \quad (8)$$

$$\xrightarrow{(a)} C_2H_3Cl + CH_2CO \quad (9a)$$

ring cleavage

$$\xrightarrow{(b)} C_2H_4 + CHClCO \quad (9b)$$

$$\longrightarrow C_3H_5Cl + CO \quad \text{decarbonylation} \quad (10)$$

As indicated earlier, the fluorescence quantum yield is extremely low, $\sim 5 \times 10^{-4}$, and the fluorescence decay time is extremely short, $\sim$0.4 nsec at λ_{ex} 340 nm. Hence, processes 5 and 6 are relatively insignificant below λ_{ex} 340 nm where all of the photolyses have been carried out, and at the low pressures used. Again, as indicated earlier, the photodecomposition yields at all wavelengths studied are expected to be unity, so the processes 7–10 should comprise nearly 100% of the photo processes. In the photolysis study of cyclobutanone it was found that the $S_1 \rightsquigarrow T_1$ intersystem crossing was an important process only at the long wavelength end of its uv absorption where "predissociation" is not so important,[3b,i] and a sharp increase in the triplet product yield (c-C_3H_6 and CO) was observed. No such large

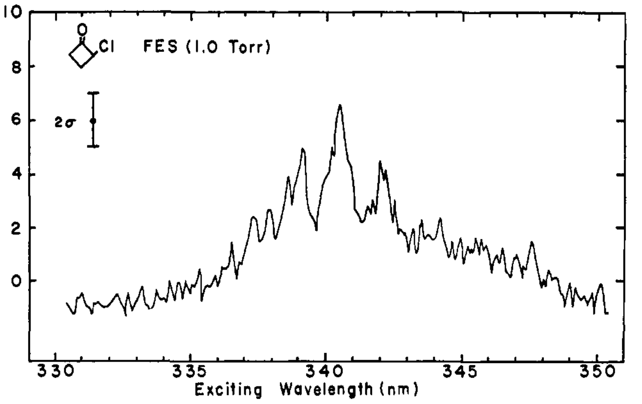


Figure 5. Fluorescence excitation spectrum of chlorocyclobutanone (0.1-nm resolution). The size of two standard deviation (95% confidence limit) in photon counting statistics is shown as 2 σ bar.

---

[18] J. C. Hemminger, H. A. J. Carless, and E. K. C. Lee, *J. Amer. Chem. Soc.*, **95**, 682 (1973).

[19] Quantum yield of fluorescence, $\Phi_F(\lambda)$, at a given excitation wavelength (λ) was calculated as follows

$$\Phi_F(\lambda) \approx \Phi_F'(\lambda)(I_F/I_F')(A'(\lambda)/A(\lambda))$$

where I_F is the fluorescence intensity and A is the absorbance of the gas sample. The "primes" refer to the calibration compound, CB in this case.

[20] H. O. Denschlag and E. K. C. Lee, *J. Amer. Chem. Soc.*, **90**, 3628 (1968).

[21] E. K. C. Lee in "Excited State Chemistry: A Symposium," J. N. Pitts, Jr., Ed., Gordon and Breach, New York, N. Y., 1970, pp 51–90.

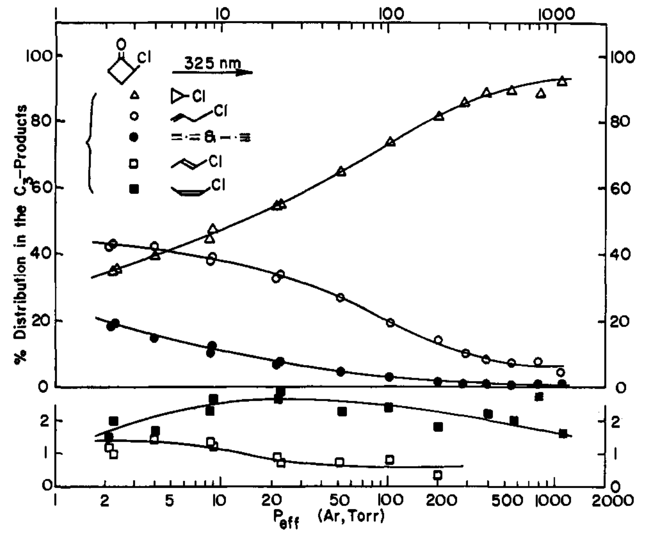


Figure 6. The percentage distribution of the various C_3 products *vs.* Ar pressure at 325.0 nm: (△) c-C_3H_5Cl; (○) 3-chloropropene; (●) the sum of allene and methylacetylene (~6:1 ratio); (□) *trans*-1-chloropropene; (■) *cis*-1-chloropropene.

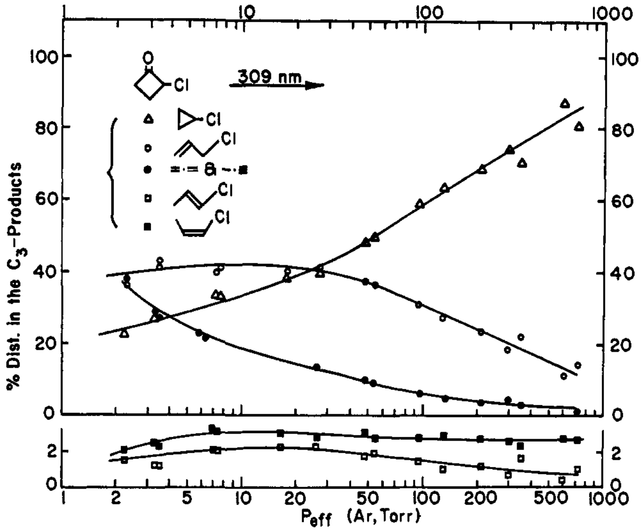
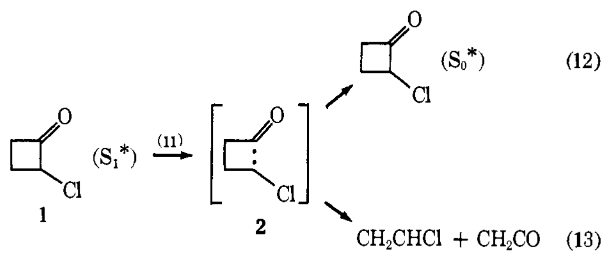


Figure 7. The percentage of the various C_3 products *vs.* Ar (effective) pressure at 309 nm; see legend for Figure 6.

Scheme II



increase in the c-C_3H_5Cl yield is observed in the photolyses of chloro-CB at the long wavelengths (below 330 nm), and thus it seems that the $S_1 \rightsquigarrow T_1$ process (8) is also unimportant at all of the wavelengths studied. It was unfortunate that we were unable to photolyze chloro-CB above 330 nm where $\tau_S \geq 0.4$ nsec, and the $S_1 \rightsquigarrow T_1$ process (8) may begin to play an important mechanistic role. We are now left with three major processes to consider, $S_1 \rightsquigarrow S_0$ internal conversion (7), ring cleavage (9), and decarbonylation (10).

The *"pressure unquenchable"* products must then arise from chloro-CB*$(S_1{}^*)$ or an intermediate which is neither chloro-CB$(T_1{}^*)$ nor chloro-CB$(S_0{}^*)$. Products from chloro-CB$(S_0{}^*)$ are *"pressure quenchable"* as it is longer lived than CB$(S_1{}^*)$ and the observed unimolecular decomposition rate will be shown later to be in agreement with the calculated rate of the $S_0{}^*$ state decomposition.

"Pressure Unquenchable" Ring Cleavage Products. It has been found that 22 ± 5% of the C_2H_3Cl at λ_{ex} 325 nm is probably produced from an unquenchable precursor (under pressure variation conditions employed), while probably no C_2H_4 is produced from this precursor (see Figure 2). Earlier explanations of the facile internal conversion which occurs in cyclobutanones have used the mechanism of the α C_1–C_2 bond cleavage of the ring followed by a rapid (in competition with other cleavage and decarbonylation process) ring formation to give finally a vibrationally excited ground-state molecule.[3g,i] It was consistently found that the α C—C=O bond having the alkyl group substitution cleaved preferentially, indicating that this α C—C=O tends to be the weaker bond of the two. The observed C_2H_3Cl production from an "unquenchable" chloro-CB precursor can thus be explained in a similar fashion as shown in Scheme II.

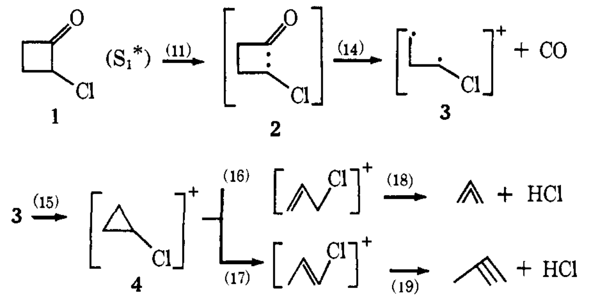
The production of "pressure unquenchable" C_2H_4 and CHCl=CO would have been expected, if the other (α') C—C=O had ruptured.

Decarbonylation Products. The pecursor of the decarbonylation product is also thought to be the same precursor (**2**) as that for the production of the "pressure unquenchable" C_2H_3Cl, although a "concerted" decarbonylation directly from the chloro-CB $(S_1{}^*)$ (**1**) is also conceivable. An extensive discussion of the decarbonylation mechanism has been given elsewhere.[3i]

Allene and methylacetylene are also produced by a process of decarbonylation of chloro-CB$(S_1{}^*)$, *this being either preceded or followed by the HCl elimination process.* It seems likely that, in the pyrolysis of chloro-CB $(S_0{}^*)$, allene and methylacetylene are produced by the mechanism involving first HCl elimination and then decarbonylation with 1,2-H atom migration. However, in the photolysis of chloro-CB, it would appear unlikely that a similar sequential process is occurring, because CB$(S_1{}^*)$ does not have excess vibrational energy to eliminate HCl first. Instead, the other mechanism of first decarbonylation, second rapid 1,2-H atom migration, and third HCl elimination is probably operative (see Scheme III).

The observed variation in the C_3 products with pres-

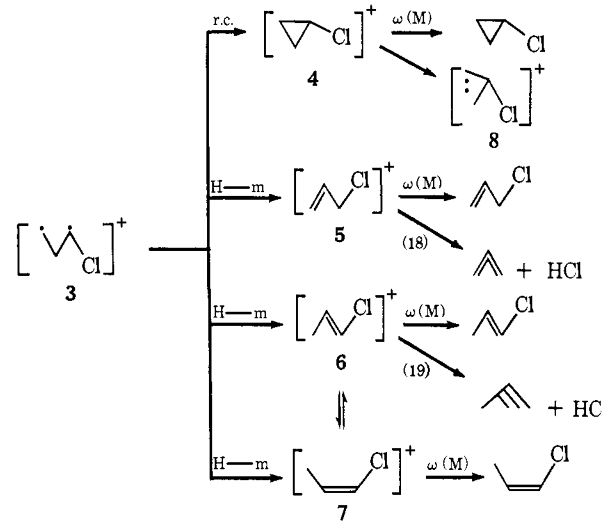
Scheme III



sure in the 325.0 and 309 nm photolyses are shown in Figures 6 and 7, respectively. From these plots, it can be seen that: (1) more decomposition and isomerization occur at 309 nm than at 325.0 nm; (2) allene and methylacetylene are produced at the expense of c-C_3H_5Cl at low pressures of quenching gas. This and the pressure dependence of the other C_3 products can be explained by Scheme III.

Intermediate **3** and consequently the other vibrationally excited intermediates are produced with a wide energy distribution[22] and hence Stern–Volmer-type plots are curved. However, "pressure quenchable" allene and methylacetylene and "pressure enhanced" production of c-C_3H_5Cl at their expense is expected with mechanisms such as Schemes III or IV. It should be noted that concerted decarbonylation of **1** to c-C_3H_5Cl plus CO is kinetically the same as the mechanism presented in Scheme III provided that ring closure is fast compared with hydrogen migration. It is probable that the HCl elimination step is following the decarbonylation process, because chloro-CB(S_1*) produced here has no sufficient vibrational excitation energy to redistribute rapidly and to overcome the minimum energy necessary for an HCl elimination on the S_1 surface, since the activation energy of HCl elimination in cyclobutyl chloride (S_0*) is 55 kcal/mol.[6] Clearly the HCl elimination process has much greater energy barrier to overcome compared to the "predissociative" α C–CO bond cleavage process.[3i] All of the products except c-C_3H_5Cl decrease with pressure. Curved Stern–Volmer type plots are not shown here since it is obvious that the c-C_3H_5Cl is formed vibrationally hot with a wide energy distribution (as in the cyclobutanone case).[22] There is more decomposition and isomerization at 309 nm than at 325.0 nm. Scheme IV, however, qualitatively describes the observed pressure dependence. How much of the vibrationally hot 2-chloropropenes (**5** and **6**) and 3-chloropropene (**7**) is produced by Scheme III or Scheme IV cannot be resolved here.[23] It should, however, be noted that the ratio of allene/methylacetylene is ~5–6 in most cases and that the ratio of 3-chloropropene/1-chloropropene is 10–15, implying that the HCl elimination from *trans*-1-propene may be twice as rapid as the HCl elimination from 3-chloropropene.

Scheme IV



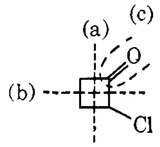
Pressure Quenchable Ring Fission Products. The rate of decomposition of the vibrationally hot ground state chloro-CB(S_0*) can be determined from the half-quenching pressure ($P_{1/2}$), the collision rate (ω), and the collision efficiency (β). It has been shown that Ar is less than 100% efficient as a vibrational energy quencher of cyclobutanones.[3f,24] An accurate value of the collisional quenching efficiency of Ar for the chloro-CB (S_0*) was not determined experimentally, but a value of 0.16 is expected to be good within a factor of 2. In the Ar–dimethylcyclobutanone system,[24] Ar was 0.16 times as efficient (pressure–pressure) as the parent dimethylcyclobutanone. The value of the collisional quenching efficiency measured for Ar in CB was not used, because it was felt that the reference molecule, propylene, could not be 100% as efficient as the parent CB.

Table VII contains the experimental half-quenching pressures of Ar for chloro-CB(S_0*) and the expected $P_{1/2}$ value of chloro-CB(S_0*) if it could have been used as the efficient quencher. From these data, the unimolecular rate constant k(E)[25] was calculated and shown in Table VII. Also the values of k(E) calculated from the approximate RRKM rate formulation, as described previously,[3b,g,j] are shown in Table VII; (a) production of C_2H_4 + CHClCO; (b) C_2H_3Cl + CH_2CO; (c) c-C_3H_5Cl + CO; (d) HCl elimination plus decarbonylation to give C_3H_4. The parameters used in this calculation are given in the Appendix.

Table VII. Rates of Chloro-CB(S_0*)

λ_{ex}, nm	330	325.0
$E_{h\nu}$, kcal/mol	86.6	88.0
$P_{1/2}$ (Ar, Torr)	1.26×10^3	2.0×10^3
$P_{1/2}$ (chloro-CB, Torr)[a]	$\sim 2.0 \times 10^2$	3.2×10^2
Obsd k(E), 10^9 sec^{-1}	2.1	3.4
k_a for C_2H_4, 10^9 sec^{-1} [c]	0.80	0.93
k_b for C_2H_3Cl, 10^9 sec^{-1} [c]	1.52	1.82
k_c for c-C_3H_5Cl, 10^9 sec^{-1} [c]	0.22	0.26
k_d for C_3H_4, 10^9 sec^{-1} [c]	0.04	0.05
Σk_i, 10^9 sec^{-1} [c]	2.58	3.06

[a] $P_{1/2}$ of parent, chloro-CB, is 0.16 times $P_{1/2}$ of Ar. [b] Observed k(E) value was calculated from the formula shown in ref 27, k(E) = $\omega_{1/2}$(M) where M = chloro-CB. [c] The values estimated from the approximate RRKM calculation.



Examination of Table VII reveals the estimated overall rate of disappearance of chloro-CB(S_0*), $k_{calcd} = k_a + k_b + k_c + k_d$, is the same as the experimentally obtained value within 20%. The predicted

---

(22) (a) R. J. Campbell, E. W. Schlag, and B. W. Ristow, *J. Amer. Chem. Soc.*, **89**, 5098 (1967); (b) R. J. Campbell and E. W. Schlag, *ibid.*, **89**, 5103 (1967); (c) F. H. Dorer, *J. Phys. Chem.*, 77, 954 (1973).

(23) R. C. S. Grant and E. S. Swinbourne, *Chem. Commun.*, 620 (1966).

(24) J. Metcalfe, H. A. J. Carless, and E. K. C. Lee, *J. Amer. Chem. Soc.*, **94**, 7235 (1972).

(25) k(E) of chloro-CB is equal to ω(M)(D/S) where ω(M) is the collision rate and D/S is the ratio of decomposition/stabilization of chloro-CB. From the pressure where (D/S) = 1.00 and the half-quenching pressure $P_{1/2}$ (in Torr) and from the formula, $\omega_{1/2}$(M) = $1.07 \times 10^7 P_{1/2}$ sec^{-1}, k(E) can be calculated. The gas kinetic collision diameter of 5.5 Å for chloro-CB was taken to be a reasonable estimate.

ratio of C_2H_4/C_2H_3Cl production at 330 nm is 0.53, whereas the observed ratio is 1.12 ± 0.05. While the agreement is only fair, it should be noted that the Arrhenius parameters used to calculate the reaction rates were obtained from the thermal decomposition data of limited accuracy.

Generation of cyclobutenone from chloro-CB(S_0*) *via* HCl elimination process (k_d) is probably a very minor process. This immediate source of acetylene (or allene and methylacetylene) would require a half-quenching pressure in excess of 10^3 Torr (Ar), much higher than that coming directly from the c-C_3H_5Cl or chloropropene intermediates (**4** and **5** in Scheme IV) as observed. About 8% of the chloro-CB(S_0*) is expected to give c-C_3H_5Cl according to the RRKM calculation, if the Arrhenius parameters used are valid for this calculation. It should be noted that the c-C_3H_5Cl produced can further decompose to chloropropenes, allene and methylacetylene; according to the values of k_a–k_d in Table VII, the quantum yield of C_3 products *via* chloro-CB(S_0*) can be 0.08, so that a test of this mechanistic possibility could be made. However, the present data in Tables II and IV do not warrant any definitive conclusion on this matter.

It is interesting to note that the unimolecular decay lifetime of chloro-CB(S_0*), 0.3 nsec at 325 nm, is approximately equal to that of CB(S_0*), ~0.4 nsec at 313 nm.[2b, 26] This is to be expected since it has been shown previously that substitution of a Cl atom or a Br atom for a H atom does not greatly affect the pressure at which fall-off of the rate of decomposition occurs in cyclobutenes.[27] This is probably because the halogen does not greatly alter its environment in the critical configuration. Clearly, the C_2H_4/C_2H_3Cl ratio from the photoactivated chloro-CB(S_0*) is much smaller (1.1 at 325 nm and 330 nm) than the ratio of $C_2H_4/C_2H_3Cl \cong 6.5$ observed in the thermal decomposition of chloro-CB(S_0*) at 560–600°K.[5] This energy dependence is consistent with what is expected on the basis of the experimental Arrhenius parameters measured.

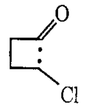
Wavelength Dependence of Product Yields. Table IV and Figure 3 contain the data on the change in the product distribution with photoexcitation energy. The two photolysis systems at 330 nm (86.6 kcal/mol) and 325 nm (88.0 kcal/mol) have been better studied than the other photolysis wavelengths, and the quantum yield data for these photolyses are shown in Table VIII.

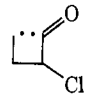
Table VIII. Quantum Yields of the Primary Photochemical Processes (Extrapolated to Zero Pressure) for Chloro-CB

λ_{ex}	330 nm	325 nm
$\Phi_1(S_0^*)$[a]	0.70	0.60
$\Phi_1(C_2H_4)$[b]	~0.00	~0.00
$\Phi_1(C_2H_3Cl)$[c]	~0.00	~0.07
$\Phi_1(C_3)$[d]	0.30	0.33
$\Phi_0(C_2H_4)$[e]	0.37	0.32
$\Phi_0(C_2H_3Cl)$[e]	0.33	0.28

[a] $\Phi_1(S_0^*) = k_7/(\Sigma^{10}{}_{i=6}k_i)$ in Scheme I. [b] $\Phi_1(C_2H_4) = k_{9b}/(\Sigma k_i)$ likewise. [c] $\Phi_1(C_2H_3Cl) = k_{9a}/(\Sigma k_i)$ likewise. [d] $\Phi_1(C_3) = k_{10}/(\Sigma k_i)$ likewise. [e] From the chloro-CB(S_0*) decomposition.

It can be seen that the quantum yield of $S_1^* \rightsquigarrow S_0^*$ internal conversion $\Phi_1(S_0^*)$ is becoming smaller at the higher photoexcitation energy, and the quantum yield of the C_3 product $\Phi_1(C_3)$ and the quantum yield of the ring cleavage product $\Phi_1(C_2H_3Cl)$ are becoming greater. These trends are also observable from Figure 3 definitely. The fact that the value of $\Phi_1(C_2H_3Cl) = 0.07$ and $\Phi_1(C_2H_4) = 0.00$ at 325 nm is indicative of the production of the biradical **2** rather than **8** or of the fact


2


8

that a faster ring closure occurs with **8** compared with **2**. A similar tendency to rupture preferentially the α C–CO bond with the alkyl substituent over the α' C–CO bond with no substituent has been found in the photodecomposition of 2-*n*-propylcyclobutanone[3g] and dimethylcyclobutanone.[3j] It is, however, expected the biradical **8** will become more important at higher excitation energies.

Triplet Products. The results shown in Table VI can be analyzed as follows: if the yield of C_2H_4 and C_2H_3Cl is assumed to be mainly from the direct photolysis (at 253.7 nm) or from the singlet benzene sensitization ($^1B_{2u}$, 109 kcal/mol), then the expected "singlet" product distribution can be calculated from run 106 (Table V) to be approximately 0.30 (allene), 0.18 (methylacetylene), 0.02 (*cis*-1-propene), 0.004 (*trans*-1-propene), 0.10 (3-chloropropene), and 0.29 nmol (c-C_3H_5Cl). If these amounts due to "singlet" process are subtracted from the observed yields in run 62 (see Table VI), then we obtain the "triplet" yield of 0.20 (*cis*-1-chloropropene), 0.06 (*trans*-1-chloropropene), 5.2 (3-chloropropene), and 28.9 nmol (cyclopropyl chloride), or we obtain the % C_3 product yields of 0.7, 0.3, 15, and 84%, respectively. Hence, approximately $^6/_7$ of "hot" c-C_3H_5Cl survives while approximately $^1/_7$ isomerizes to chloropropenes. This means that the chloro-CB (T_1) produced by the energy transfer from the C_6H_6 ($^3B_{1u}$, 84.4 kcal/mol) is somewhat less internally excited than chloro-CB(S_1) produced at the longest wavelength of direct photolyses carried out, 330 nm (86.6 kcal/mol), so far (see Table II for comparison). The most probable energy distribution of chloro-CB(T_1) thus produced is estimated as ~80 kcal/mol. These interpretations are compatible with the earlier result obtained in the benzene–CB system.[20]

Photochemistry of Chloro-CB *vs.* CB. It appears that chloro-CB "predissociates" at lower photoexcitation energy than CB, but the *vibrational energy content necessary for predissociation appears comparable*, since the wavelength (or frequency) range over which FES is observable seems about the same for both, *e.g.*, 349–333 nm (see Figure 5) in chloro-CB *vs.* 329–313 nm in CB.[3i] The electronic origin of chloro-CB may lie close to 28,600 cm^{-1} (~1700 cm^{-1} red shift) as compared with that of CB[28] at 30,291.2 cm^{-1}.

The fact that the ratio of the C_3/C_2 products observed near the threshold of predissociation are similar, *e.g.*, 0.43 for chloro-CB (at λ_{ex} 330 nm) compared with that of 0.42 for CB[2b] (at λ_{ex} 313 nm), implies that the "singlet" biradicals of the type **2** have similar kinetic

---

(26) See footnote 13 of ref 3j for a new estimate of the CB(S_0*) lifetime based on the correction of collisional efficiency value.

(27) D. Dickens, H. M. Frey, and J. Metcalfe, *Trans. Faraday Soc.*, 67, 2328 (1971).

(28) D. C. Moule, *Can. J. Phys.*, 47, 1235 (1969).

properties. The ring closure process (k_{12} in Scheme II) to give the internally converted S_0* proceeds equally competitively with the decarbonylation process (k_{14} in Scheme III) in CB and chloro-CB. There appears to be no "heavy atom effect," implying that these processes are much more rapid than the possible spin forbidden intersystem crossing process which might enhance the C_3 product quantum yield. In other words, the "heavy atom enhancement" by Cl atom here is not sufficient to influence the overall "singlet pathway."

There is one difference of importance in the secondary processes the cyclopropanes undergo. Energetically, the hot c-C_3H_6 resulting from the CB(S_1*) decomposition should be similar to the c-C_3H_5Cl, but the Arrhenius parameters for their isomerization to an olefin by 1,2-H migration (for CB)[29] and 1,2-Cl migration or the subsequent HCl elimination (for chloro-CB)[23,30] are very different. The lower activation energy for isomerization to an olefin for c-C_3H_5Cl (52.6 kcal/mol)[30a] allows it to isomerize more readily than c-C_3H_6 (65.6 kcal/mol)[29b] at comparable pressure and photoactivation energy as witnessed in Figures 6 and 7 and Tables II and III. The many isomerization and HCl elimination channels render the energy partitioning study more cumbersome. One could easily estimate the value of $\langle\tau(E)\rangle$ for the hot c-C_3H_5Cl produced at λ_{ex} 325 and 309 nm to be ≥ 5 and ≥ 2 nsec, respectively, from Figures 6 and 7. An energy partition study in the future may be worthwhile on the basis of this study.

The fact that τ_S of chloro-CB $\approx$ 0.4 nsec compared with τ_S of CB $\approx$ 4.9 nsec[31] below their "predissociation" limit could mean that the rate of the $S_1 \rightsquigarrow T_1$ intersystem crossing may be 10 times faster for chloro-CB-(S_1*) than that of CB(S_1*).

Appendix

The parameters used to calculate the specific rate constant k(E) of the processes shown in Table VII, according to the approximate formulation of the RRKM rate theory[31]

$$k(\mathrm{E}) = A'\left[\frac{E - E_0 + a^+E_z^+}{E + aE_z}\right]^{s-1}$$

are $s = 27$; $E_z = E_z^+ = 50.2$ kcal/mol estimated from the fundamental vibrational frequencies,[32] $E_{th} = 2.2$ kcal/mol; $a = a^+ = 0.90$. The Arrhenius parameters for the processes "a"–"d" (see Table VII) are as determined previously.[5]

$$k_a = 1.8 \times 10^{14} \exp[-50{,}600/RT]$$

$$k_b = 1.6 \times 10^{15} \exp[-55{,}400/RT]$$

$$k_e = 1.2 \times 10^{14} \exp[-53{,}400/RT]$$

$$k_d = 4.1 \times 10^{13} \exp[-55{,}000/RT]$$

---

(29) (a) T. C. Chambers and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, **56**, 399 (1934); (b) W. E. Falconer, T. F. Hunter, and A. F. Trotman-Dickinson, *J. Chem. Soc.*, 609 (1961); $k_{(\mathrm{isomerization})} = 10^{15.45}$ exp($-$65,600/RT) sec^{-1} for cyclopropane.

(30) (a) R. C. S. Grant and E. S. Swinbourne, *Chem. Commun.*, 620 (1966); see ref 23 k (isomerization to 3-chloropropene) = $10^{14.8}$ exp($-$56,200/RT) sec^{-1}; (b) B. C. Young and E. S. Swinbourne, *J. Chem. Soc. B*, 1181 (1967): k ($-$HCl) = $10^{14.49}$ exp($-$50,200/RT) sec^{-1} for 2,2-dichlorobutane.

(31) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962).

(32) J. R. Durig and W. H. Green, *J. Mol. Spectrosc.*, **27**, 95 (1968).

A Mechanistic Study of the Quenching of Naphthalene Fluorescence by *cis,trans*-1,3-Cyclooctadiene

Steven L. Murov,* Loh-sheng Yu, and Linda P. Giering

Contribution from the Department of Chemistry,
State University of New York at Stony Brook, Stony Brook, New York 11790.
Received November 8, 1972

Abstract: Quenching rates of naphthalene fluorescence have been measured for *cis,trans*-1,3-cyclooctadiene (**1**) and 1,2-dimethylcyclobutene (**2**) and are 5.0 × 10^8 and 1.7 × 10^7 l./(mol sec), respectively. For **1**, the quenching leads to isomerization to *cis,cis*-1,3-cyclooctadiene (**4**) and adduct formation with naphthalene with quantum yields of 0.07 and 0.12, respectively. The compound bicyclo[4.2.0]oct-7-ene (**3**) is not formed from **1** despite a low activation energy for this process. For compound **2**, the only result of quenching is a small amount of adduct formation. These observations lead to the conclusion that isomerization in nonclassical singlet quenching systems is a result of bonding changes that occur during the formation of the exciplex.

The observation that dienes and quadricyclene quench the fluorescence of aromatic hydrocarbons despite the fact that the conditions for classical energy transfer are not met has led to several investigations.[1–12] Most investigators agree that exciplex formation is

---

(1) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 3665 (1966).

(2) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968).

(3) L. M. Stephenson, D. G. Whitten, and G. S. Hammond, "The Chemistry of Ionization and Excitation," Taylor and Francis, Ltd., London, 1967, p 35.

(4) L. M. Stephenson and G. S. Hammond, *Angew. Chem., Int. Ed. Engl.*, **8**, 261 (1969).

(5) B. S. Solomon, C. Steel, and A. Weller, *Chem. Commun.*, 927 (1969).

(6) T. R. Evans, *J. Amer. Chem. Soc.*, **93**, 2081 (1971)

(7) G. N. Taylor, *Chem. Phys. Lett.*, **10**, 355 (1971).

(8) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3679 (1972).

(9) G N. Taylor and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3684 (1972).

(10) G. N. Taylor and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3687 (1972).

(11) S. L. Murov, R. S. Cole, and G. S. Hammond, *J. Amer. Chem. Soc.*, **90**, 2957 (1968).

(12) S. L. Murov and G. S. Hammond, *J. Phys. Chem.*, **72**, 3797 (1968).