tetraene complex III. Rearrangement of the tetraene complex during analysis at 100° broadened the tetraene peak, but did not contribute significantly to the area of the peak for the dihydroindene complex IV. No free ligand was detected by glpc during the course of the reaction. By standard analysis, the first-order rate constant was found to be $2.4 \pm 0.2 \times 10^{-4}$ sec^{-1} at 101°.

Low-Temperature Protonation of Complex III. The tetraene complex III (82 mg) in 0.2 ml of CD_2Cl_2 was protonated at −120° using a degassed solution of FSO_3H and SO_2ClF (1:2, v/v). The details of this protonation technique have been described previously.[6d] The pmr spectrum of the ion observed at −67° exhibits bands at δ 3.04 (4 H, broad singlet), 4.32 (2 H, mult.), 5.33 (2 H, broad singlet), 5.61 (2 H, quartet, J = 7.8, 9.8 Hz), and 7.17 (1 H, triplet, J = 7.8 Hz) and is assigned structure X.

Thermal Decomposition of 2-Chlorocyclobutanone[1]

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Abstract: The thermal decomposition of 2-chlorocyclobutanone has been studied at four different temperatures, and its rate of decomposition was found to be ~2.3 times as fast as that of cyclobutanone. The decomposition yields (1) ~94% of products from the ring fission modes, the ratio of C_2H_4 (plus chloroketene *via* mode a) to C_2H_3Cl (plus ketene *via* mode b) being ~6.5:1 with a slight temperature dependence; (2) ~3% of products from the decarbonylation process giving the C_3H_5Cl isomers and CO; (3) ~2% of products from the HCl elimination process, followed by fission or decarbonylation, giving acetylene, methylacetylene, and allene; and (4) ~1% of products which were not identified in gas chromatographic analysis. *Approximate* Arrhenius parameters are calculated for the ring fission, decarbonylation, and HCl elimination pathways.

The thermal decomposition of cyclobutanone (CB) has been shown to yield ethylene and ketene (>99%) and cyclopropane and CO (<1%).[2-4] The products arise from two consecutive, homogeneous thermal reactions which are first order above ~10 Torr pressure.[3,4] McGee and Schleifer inferred that both of the competing processes occur by "concerted" mechanisms on the basis of the energetics of decomposition reactions,[4] whereas Blades postulated biradical mechanisms.[3] The thermal decomposition of 2-*n*-propylcyclobutanone[5] and four of the six possible isomeric dimethylcyclobutanones (DMCB),[6] excluding optical isomers, also suggests that the decomposition processes are "concerted."

The present study was undertaken in order to observe any changes in the mechanism and rates of thermal decomposition of cyclobutanone caused by a chlorine atom substitution at the α position of cyclobutanone. This study is only a preliminary and limited step toward the complete study of the excited state chemistry of 2-chlorocyclobutanone (chloro-CB), and hence no attempt was made to obtain an *accurate* thermal rate of decomposition. The thermal decomposition of chloro-CB was found to differ from that of CB not only for the fission modes available (see Scheme I) but also for a new pathway available for HCl elimination.[7] This contrasts with the thermal decomposition of chlorocyclobutane which proceeds in a manner very similar to that of cyclobutene.[8]

Scheme I

Experimental Section

Preparation of 2-Chlorocyclobutanone. Chloro-CB was prepared by the method of Durig and Green.[9] Sulfuryl chloride (Eastman) (5.7 ml) in 20 ml of CCl_4 was slowly added to a stirred mixture of CB (5 g, Aldrich) and CCl_4 (35 ml) at 0°. The mixture was allowed to warm to room temperature and react for 30 hr. After removal of most of the volatile components by vacuum distillation at room temperature, chloro-CB was purified by preparative vpc on a Carbowax column (10 ft × 0.25 in.) at 90° and dried over 5A Linde molecular sieve. The ir spectrum was identical with the published spectrum.[9]

Chemicals. CB (Aldrich Chemical Co.) was used without further purification, as its impurities were found by vpc to be less than 0.005%. The following authentic chemical compounds were used for product identification by checking vpc retention times: C_2H_2, C_2H_4, cyclopropane, allene, methylacetylene, 1,3-butadiene, and C_2H_3Cl (all Matheson CP grade) *cis*- and *trans*-1-chloropropene (Chemical Samples and Columbia Organic Chemical Co.), 2-chloropropene (Chemical Procurement Lab., Inc.), and 3-chloropropene (Matheson Coleman and Bell). The trans isomer was the major component in the *cis*/*trans*-1-chloropropene mixture when the ir and nmr spectra were compared with the published spectra.[10,11] Chlorocyclopropane was made by the method of Dedio, *et al.*,[12] by the photochemical addition of chlorine gas to cyclopropane (both Matheson CP grade).

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

[2] M. N. Das, F. Kern, T. D, Coyle, and W. D. Walters, *J. Amer. Chem. Soc.*, **76**, 6271 (1954).

[3] A. T. Blades, *Can. J. Chem.*, 47, 615 (1969).

[4] T. H. McGee and A. Schleifer, *J. Phys. Chem.*, **76**, 963 (1972).

[5] H. A. J. Carless and E. K. C. Lee, *J. Amer. Chem. Soc.*, **94**, 1 (1972).

[6] (a) H. A. J. Carless and E. K. C. Lee, *J. Amer. Chem. Soc.*, **92**, 4482 (1970); (b) J. Metcalfe, H. A. J. Carless, and E. K. C. Lee, *ibid.*, **94**, 7235 (1972).

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

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

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

[10] J. W. Clump, *J. Org. Chem.*, **28**, 953 (1963).

[11] M. Y. Dewolf and J. D. Baldeschweiler, *J. Mol. Spectrosc.*, **13**, 344 (1964).

[12] E. L. Dedio, P. J. Kozak, S. N. Vinogradov, and H. E. Gunning, *Can. J. Chem.*, 40, 820 (1962).

Vacuum and Pyrolysis Equipment. Samples were handled on a glass-metal vacuum line free from grease and mercury as previously described.[13] Pyrolyses were carried out in a portable 21.0-ml Pyrex cell equipped with a Teflon needle valve (Fischer-Porter). The cell was inserted into a tubular electric furnace in which temperature fluctuations and gradients were substantial.

A series of three pyrolysis runs of chloro-CB was carried out at the same temperature but for different times to determine whether the reaction product composition varied with the percentage conversion. A second series of pyrolysis of chloro-CB was carried out at four temperatures using CB as an internal standard. Because C_2H_4 is a common product of pyrolysis of both CB and chloro-CB, a pyrolysis was performed in which pure chloro-CB was pyrolyzed at the same temperature, time, and pressure as the mixed pyrolysis runs, and from this test run the ratio of C_2H_4/C_2H_3Cl originating from chloro-CB was obtained. Using this ratio, the amounts of C_2H_4 originating from CB as well as from chloro-CB were determined. Typical conversion for these pyrolyses was to ~2% decomposition.

Pyrolyses were carried out at less than 1 Torr pressure of Chloro-CB to reduce the problem of condensation on "cold" areas of the pyrolysis vessel, because the vapor pressure of chloro-CB was ~1.5 Torr at 23°.

Product Analysis. Analysis of the pyrolysis products was carried out using a Carbowax 300 column (25 ft × 0.25 in. o.d., 20% by weight on 40-50 mesh Chromosorb P) at room temperature and a hydrogen flame ionization detector (Perkin-Elmer F-11) as described elsewhere.[6b] Typical retention times were C_2H_4 (2.8 min), CH_2CCH_2 (5.4), CH_3CCH (8.5), CH_2CHCl (9.5), *cis*-$CH_3CHCHCl$ (22.1), *trans*-$CH_3CHCHCl$ (26.0), c-C_3H_5Cl (41.3), and $CH_2ClCHCH_2$ (49.0). Parent chloro-CB and ketenes were not analyzed.

Results

Table I contains a series of three pyrolysis runs at one temperature and varying reaction times. It can be seen that the product distribution does not vary markedly between 2 and 56% decomposition, except that the fractional yields of C_2H_3Cl and c-C_3H_5Cl increase slightly while those of minor products (acetylene, allene, methylacetylene, etc.) decrease appreciably. The appearance of the C_3 olefinic chloride at high conversion could be due to the secondary decomposition of c-C_3H_5Cl, and the decrease of the acetylenic products may be due to their removal by another product such as ketene or chloroketene.

Table I. Pyrolysis Time Dependence of Product Distribution from Chloro-CB (≈365°)

Run	164	165	166
Pressure of chloro-CB, Torr	0.65	0.55	0.56
Time, min	31.5	120	360
Product yields[a]			
$CH_2{=}CH_2$	82.0	81.6	83.1
$CH_2{=}CHCl$	11.8	13.5	13.0
$CH{\equiv}CH$	2.3_8	1.0_5	0.3_2
$CH_2{=}C{=}CH_2$	0.3_8	0.3_1	0.2_1
$CH_3C{\equiv}CH$	0.5_3	0.2_5	0.1_3
$CH_2{=}CHCH{=}CH_2$		0.0_6	0.0_4
$CH_2ClCH{=}CH_2$		0.0_3	0.0_3
cis-$CH_3CH{=}CHCl$		0.1_6	0.0_8
trans-$CH_3CH{=}CHCl$		0.1_3	0.0_3
c-C_3H_5Cl	2.1_8	2.6_7	2.6_3
A (11.8 min)[b]			0.2_7
B (15.2 min)[b]		0.1_2	0.0_7
C (18.3 min)[b]	0.4_2	0.0_7	0.0_3
% decomposition	1.94	14.5	56.1

[a] Product yields were expressed as the total of 100. [b] Unidentified product retention times on the 25-ft Carbowax 300 column at 23°.

The pyrolysis is expected to be unimolecular like the pyrolysis of cyclobutanone,[2-4] but the present data seem to indicate that the reaction rate increases slightly with the pyrolysis time. This is probably due to the pyrolysis apparatus in which a large decrease in temperature occurred at the start of the reaction when the portable pyrolysis cell was inserted into the tubular furnace. The reaction temperature had slowly increased until the furnace was again in equilibrium with its surroundings. The furnace temperature was thus affected by the temperature and conditions of its surroundings.

Table II contains the results of a series of eight pyrolysis runs in which a pair of runs were performed at 560, 571, 589, and 600°K. The first run was carried out with pure chloro-CB and the second run was carried out with a mixture of chloro-CB and CB. The "effective" pyrolysis temperature was determined by finding the rate coefficient for pyrolysis of CB, correcting it to the infinite pressure,[3] and then using the corrected unimolecular rate coefficient to calculate the temperature from the known Arrhenius parameters for CB pyrolysis.[2-4] The pressure corrections to the rate of pyrolysis of CB were necessary because the experiments were carried out at total pressure of ~3 Torr (at the pyrolysis temperature), and at that pressure the rate of pyrolysis of CB proceeds at a rate which is ~0.88 of the rate at infinite pressure.[3]

Although no attempt was made to study the "pressure fall-off" behavior of chloro-CB, it can safely be assumed that chloro-CB will behave similar to CB by comparison of the "pressure fall-off" behaviors found in cyclobutene,[14] 1-chlorocyclobutene,[8] and 1-bromocyclobutene.[8]

CB decomposes thermally to give mainly ring fission product (>99%),[3,4] and the present study shows ~94% of the products from chloro-CB are ring fission products (see Scheme I). The remaining product (<1%) in pyrolysis of CB is cyclopropane from decarbonylation,[3,4] whereas the decarbonylation product is observed to the extent of ~2.5% as chlorocyclopropane in pyrolysis of chloro-CB. The remaining products are allene, methylacetylene, and C_2H_2 (~2.5%) and the miscellaneous products, 1,3-butadiene, *trans*-1-chloropropene, etc. (~1%).

The decomposition of chloro-CB proceeds at ~2.3 times the rate of that of CB. Due to the inaccuracy in determining the amount of C_2H_4 produced by the decomposition of CB (as internal standard), and the amount of C_2H_4 produced from chloro-CB, it is impossible to determine accurately the difference in the temperature dependences of the decomposition rates of CB and chloro-CB. It would appear, however, that there is some temperature dependence. The ratio of C_2H_3Cl/C_2H_4 is certainly temperature dependent, becoming smaller at higher temperatures as observed in the "pure" chloro-CB runs. An Arrhenius plot of the relative rates of production of C_2H_3Cl and C_2H_4 is shown in Figure 1.

Discussion

Ring Fission Modes (Paths "a" and "b"). Previous discussion of the ring fission modes of alkyl substituted cyclobutanones have indicated that the

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

(14) (a) W. P. Hauser and W. D. Walters, *J. Phys. Chem.*, 67, 1328 (1963); (b) R. W. Carr, Jr., and W. D, Walters, *ibid.*, 69, 1073 (1965).

Table II. Pyrolysis of Chloro-CB in the Absence and in the Presence of CB (Internal Standard)

Run no.	145	146	149	150	153	154	167	168
Pressure (Torr)[e]								
chloro-CB	0.54	0.56	0.50	0.55	0.51	0.56	0.58	0.68
CB		0.99		0.99		0.99		0.98
Time, min	6.0	6.0	8.0	8.0	30.0	30.0	60.0	60.0
Temp, °K	600	600	589	589	571	571	560	560
Products from Chloro-CB[a]								
$CH_2{=}CH_2$	81.4	(81.1)	81.6	(80.8)	82.5	(82.0)	82.0	(83.8)
$CH_2{=}CHCl$	13.3	13.3	12.6	12.4	11.0	10.9	10.2	10.4
$CH{\equiv}CH$	0.93	(0.90)	1.15	(1.15)	1.93	(1.74)	3.73	(2.19)
$CH_2{=}C{=}CH_2$	0.5	0.3	0.5	0.5	0.5	0.4	0.3	0.2
$CH_3C{\equiv}CH$	0.5	0.6	0.4	0.8	0.5	0.7	0.3	0.4
cis-$CH_3CH{=}CHCl$							0.5	0.2
trans-$CH_3CH{=}CHCl$			0.5	0.4	0.8	0.4	0.3	0.3
c-C_3H_5Cl	2.7	2.8	2.6	2.7	2.2	2.3	2.2	2.1
C (18.3 min)	0.6	1.0	0.7	1.3	0.6	1.2	0.2	0.4
% decomposition		3.03		1.66		1.86		2.12
(C_2H_4/C_2H_3Cl)	6.1		6.5		7.5		8.1	
k (10^{-5} sec^{-1})[b]		8.6		3.5		1.04		0.58
Products from CB[a]								
$CH_2{=}CH_2$		44.6		48.2		38.5		28.0
c-C_3H_6		0.40		0.39		0.35		0.14
% decomposition		1.36		0.81		0.72		0.60
k (10^{-5} sec^{-1})[c]		4.3		1.90		0.46		0.18
k(chloro-CB)/k(CB)		1.98 (2.24)[d]		1.83 (2.07)[d]		2.29 (2.59)[d]		3.17 (3.59)[d]

[a] Product yields from chloro-CB were expressed as the total of 100. [b] Rate coefficient shown is the observed value, and it is probably smaller than the true unimolecular rate observable at the high pressure limits, because of "pressure fall off" behavior. [c] Rate coefficient shown is the unimolecular rate value corrected to the high pressure limits, because the "fall-off" behavior of CB is known.[3] [d] The values in parentheses were calculated assuming that the fall-off behavior of chloro-CB is the same as that of CB. [e] Pressure measured at room temperature.

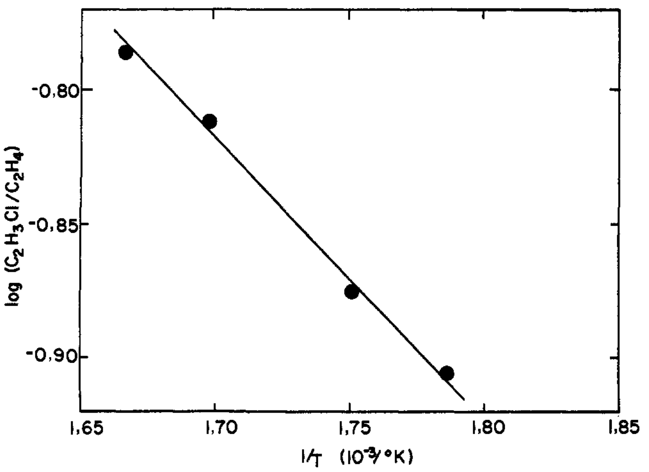

Figure 1. Relative Arrhenius plot of the yield ratios of C_2H_3Cl/C_2H_4 = ("b"/"a") in the chloro-CB pyrolysis (see Scheme I).

reaction proceeds in a concerted ($_\sigma2_s + {}_\sigma2_a$) manner.[4-6,15] An extensive discussion of the geometries (stereochemistry) of the possible transition states for the favorable decomposition of substituted cyclobutanones has already been presented.[5,6] It has also been shown that, for the cycloaddition of haloalkylketenes to some olefins, the relative size of the substituent alkyl group, rather than its electronic nature, on the ketene plays an important role in determining the stereochemical course of the reaction.[16] As this reaction follows a concerted ($_\pi2_s + {}_\pi2_a$) pathway[15] it follows that the halogen substituent in 2-chloro-CB will play a similar role in determining the stereochemical course of the retro-cycloaddition reaction.

Consideration of the interactions in the critical configurations for chloro-CB leads to the conclusion that the transition state of C_2H_4 production is expected to involve less steric interactions than that for C_2H_3Cl.[17]

The appreciable variation in the ratio of C_2H_3Cl/C_2H_4 (0.11 $\sim$ 0.13) with temperature is not to be expected from consideration of the critical configuration analysis just mentioned above. The relative rate expression (obtained from Figure 1 by the method of least squares) for the ratio of C_2H_3Cl to C_2H_4 production from chloro-CB is

$$k(C_2H_3Cl)/k(C_2H_4) = 9\exp(-4800/RT) \qquad (1)$$

Assuming that the Arrhenius A factor for C_2H_4 production from chloro-CB is 1.8×10^{14}, the same as for C_2H_4 production from CB taking into account the reaction path degeneracy of 2 for CB, and the activation energy is 50.6 kcal/mol (calculated from the rate of C_2H_4 production from chloro-CB at 600°K), one obtains the Arrhenius parameters for production of C_2H_3Cl from chloro-CB of

$$k(C_2H_3Cl) = 1.6 \times 10^{15}\exp(-55{,}400/RT)\ \text{sec}^{-1} \qquad (2)$$

One would expect that the Arrhenius A factor for C_2H_3Cl and C_2H_4 production would be almost the same from the critical configuration analysis as the transition states are similar. Thus, the unexpectedly large ob-

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(15) R. B. Woodward and R. Hoffmann, "Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(16) W. T. Brady and R. Roe, Jr., *J. Amer. Chem. Soc.*, 93, 1662 (1971).

(17) See ref 15, p 5. If the *n*-propyl group is replaced by a Cl atom, it can be seen that critical configuration C will be most favored and this leads to formation of C_2H_4. Configuration D, leading to the C_2H_3Cl production, is expected to be more stable than configurations A or B, but it involves more steric interaction than configuration C.

served A factor for C_2H_3Cl production may indicate that a different pathway (or a second pathway) exists for its production. This pathway could be a "biradical" pathway as one would expect a higher A factor for this. Note that in the unimolecular decomposition of cyclobutanes, where a biradical mechanism predominates, the A factors are $10^{15.62}$ for cyclobutane and $10^{16.31}$ for 1,1,3,3-tetramethylcyclobutane.[18] But without more accurate data for chloro-CB, further speculation is of limited value. It should be noted that this increase in the ratio of C_2H_3Cl/C_2H_4 with increasing photoexcitation energy is also observed in the photolytic decomposition of chloro-CB(S_0*),[19] as expected from eq 1.

Decarbonylation Products (Path "c"). Pyrolysis of chloro-CB produces a larger amount of decarbonylation products than is produced in the pyrolysis of CB. The Arrhenius parameters for decarbonylation of CB have been reported,[3,4] but the agreement between the two determinations is poor. Hence, the A factor of 1.2×10^{14} was obtained as the logarithmic mean value, and then the average of the activation energy was obtained

$$k(\text{c-}C_3H_6) = 1.2 \times 10^{14} \exp(-57{,}100/RT) \text{ sec}^{-1} \quad (3)$$

Assuming the A factor is the same for production of c-C_3H_5Cl from chloro-CB as for production of c-C_3H_6 from CB, one can determine the Arrhenius parameters for production of c-C_3H_5Cl. These were calculated from the rate of production of c-C_3H_5Cl from chloro-CB at 600°K. The rate of production of c-C_3H_5Cl relative to that of C_2H_4 plotted against $1/T$ as shown in Figure 2 gives the relative Arrhenius equation by the method of least squares as

$$k(\text{c-}C_3H_5Cl)/k(C_2H_4) = 0.65 \exp(-2800/RT) \quad (4)$$

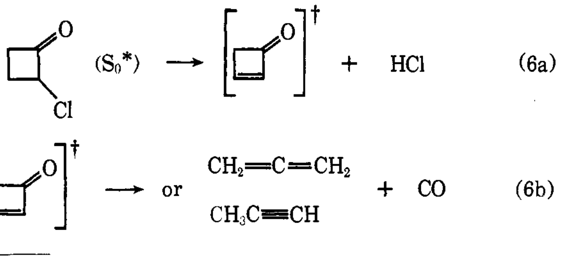
Taking the previous approximate Arrhenius parameters for C_2H_4 production[2-4] and using eq 4, one obtains

$$k(\text{c-}C_3H_5Cl) = 1.2 \times 10^{14} \exp(-53{,}400/RT) \text{ sec}^{-1} \quad (5)$$

Note that the A factor for c-C_3H_5Cl from chloro-CB is exactly the same as that for c-C_3H_6 from CB [or is comparable to the A factor for C_2H_4 from chloro-CB (1.8×10^{14} sec^{-1})] but the former is smaller by a factor of ~13 from the A factor for C_2H_3Cl from chloro-CB. This could imply that decarbonylation process may involve a "concerted" mechanism rather than a "biradical" mechanism.

Dehydrohalogenation Process (HCl Elimination). Allene and methylacetylene can be produced by two mechanisms: first, an HCl elimination to form "hot" cyclobutenone followed by a decarbonylation as in Scheme II; secondly a decarbonylation to form "hot" cyclopropyl chloride followed by an HCl elimination, possibly with the intermediacy of *trans*-1-chloropropene or 3-chloropropene as in Scheme III.

Scheme II



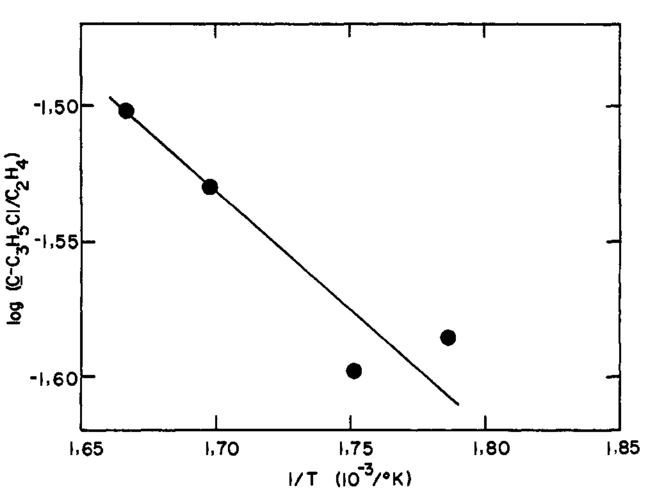
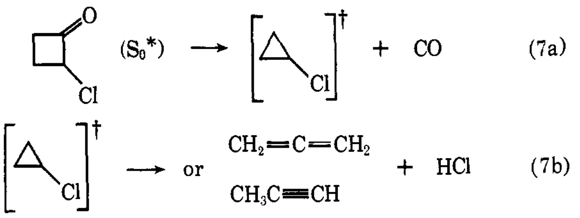


Figure 2. Relative Arrhenius plot of the yield ratios of c-C_3H_5Cl/C_2H_4 = ("c"/"a") in the chloro-CB pyrolysis (see Scheme I).

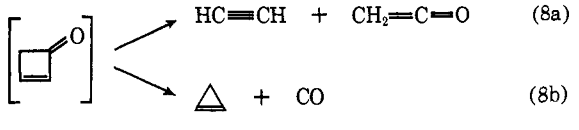
Scheme III



The Arrhenius parameters for the HCl elimination process (6a) are expected to be very similar to those for the HCl elimination process from chlorocyclobutane,[7] *e.g.*, $A = 10^{13.61}$ sec^{-1} and E_a = 55 kcal/mol. Calculation of the rate of HCl elimination at 600°K shows that 0.5% of the chloro-CB would be expected to decompose by this pathway. Since 1% of the reaction products are allene and methylacetylene, this pathway can account for their production if process 6b is fast compared to process 6a.

An argument against the alternative mechanism, processes 7a and 7b, for producing allene and methylacetylene is that cyclopropyl chloride decomposes to 3-chloropropene faster than to other isomeric products,[20] while virtually no 3-chloropropane is produced in the pyrolysis of chloro-CB. Otherwise, it would have been possible to observe 3-chloropropene as a trace product in the vpc analysis.

The production of acetylene also seems to urge that the process 6a occurs. The intermediate "hot" cyclobutenone formed is expected to undergo a ring fission process as well as a decarbonylation process (by analogy to CB) to give acetylene (plus ketene) or cyclopropene (plus CO), respectively.



Other Minor Products. The processes by which the

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[18] See A. T. Cocks and H. M. Frey, *J. Chem. Soc. A*, 2566 (1970).

[19] J. Metcalfe and E. K. C. Lee, *J. Amer. Chem. Soc.*, **95**, 4320 (1973).

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

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]

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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-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-

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[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.