The Thermal Unimolecular Decomposition of Chlorocyclobutane

A. T. Cocks and H. M. Frey

Contribution from the Department of Chemistry, Reading University, Reading, England. *Received June 2, 1969*

Abstract: The gas-phase thermal decomposition of chlorocyclobutane has been investigated from 394 to 503° In an "aged" reaction vessel, the decomposition is homogeneous and first order, and the rate constant is independent of pressure in the range 28–90 Torr. The primary decomposition proceeds by two paths, one to yield ethylene and vinyl chloride and the other to yield 1,3-butadiene and hydrogen chloride. The Arrhenius equations for the two primary processes were found to be: $k_{\text{ethylene}} = 10^{14.76}\exp(-60{,}070 \text{ cal mol}^{-1}/RT) \text{ sec}^{-1}$ and $k_{\text{butadiene}} = 10^{13.61}\exp(-55{,}240 \text{ cal mol}^{-1}/RT) \text{ sec}^{-1}$. At times greater than the half-life for decomposition, these products react further.

Cyclopentyl[1] and cyclohexyl[2] chlorides eliminate hydrogen chloride on pyrolysis in a similar manner to open-chain analogs. Chlorocyclopropane[3] and *gem*-dichlorocyclopropanes,[4,5] however, pyrolyze to give isomerization products, though by a different mechanism to that of cyclopropane and alkylcyclopropane isomerizations. A study of chlorocyclobutane is, therefore, of interest as it provides the intermediate case between the two classes above.

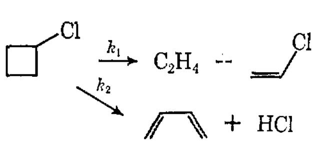
Experimental Section

Cyclobutane was prepared from 1,4-dibromobutane by refluxing with lithium amalgam in dioxane[6] under argon. The effluent cyclobutane was trapped in a receiver cooled to −78°. The cyclobutane was photochlorinated[7] using a Pyrex reactor and medium-pressure mercury lamp. The products were distilled to yield 95% pure chlorocyclobutane (bp 82–83°). Final purification was by preparative gas chromatography using a 15 ft by 0.25 in. column packed with 20% w/w squalane on Chromosorb P, and operated at 50°. Analysis on several chromatographic columns showed the material to be 99.3% pure. The nmr spectrum was compatible with the chlorocyclobutane structure, and the ir spectrum was in agreement with the literature spectrum.[7] The impurities were shown to be thermally stable. Magnesium sulfate and molecular sieve were found to catalyze the formation of a second product, probably a rearrangement isomer, and the chlorocyclobutane was, therefore, dried under vacuum over anhydrous sodium sulfate for 48 hr. Ethylene, vinyl chloride, and butadiene were Matheson CP grade.

Apparatus. The kinetic apparatus and pressure measurement system were essentially the same as described elsewhere.[8] The variable-speed potentiometric recorder, on which the pressure transducer output was displayed, produced a change in recorder reading of about 2 mm for a 1-Torr pressure change. Analyses of reaction mixtures were performed using a Perkin-Elmer Model 452 gas chromatograph fitted with a gas-sampling valve. A 12 ft by 1/8 in. column containing 20% w/w bis(2-methoxyethyl) adipate on Chromosorb P operated at 50° was employed. Signals from the flame ionization detector were fed to a potentiometric recorder and were integrated using a Perkin-Elmer D2 electronic integrator.

Results

In the temperature range 394–503°, chlorocyclobutane decomposed by two paths (eq 1 and 2), one giving ethylene and vinyl chloride, and the other giving 1,3-butadiene and hydrogen chloride as major products.



(1)

(2)

Identification was by comparison of the retention times of the organic products with those of authentic samples on four different chromatographic columns (12 ft by 1/8 in. 20% bis(2-methoxyethyl) adipate on Chromosorb P, 10 ft by 1/8 in. bis(cyanoethoxypropane) on Chromosorb P, 100-m poly(propylene glycol) capillary, and 50-m squalane capillary). The mass spectrum of the reaction mixture showed peaks compatible with the products above.

Before any kinetic studies were performed, the reaction vessel was "aged" by pyrolyzing large samples of chlorocyclobutane, butadiene, vinyl chloride, and mixtures of these for 24 hr at 500°. Several such pyrolyses were needed before reproducible results for chlorocyclobutane were obtained. The reaction vessel had a volume of 22.40 ml and after temperature corrections the dead space was about 2%. Corrections for this were made by two methods, Allen's correction[9] and the method of Robinson.[10] Using Allen's correction, the reactant pressure, P_r, is given by

$$P_r = P[2(P_0/P)^a - 1]$$

where a is the ratio of the total volume of the system, after applying temperature corrections, to the volume of the reaction zone. The rate constant, k, is obtained from the slope, S, of a plot of log P_r against time by the relationship

$$k = 2.303S[2 - (1/a)]$$

In Robinson's method, log $(P_\infty - P)$ is plotted against time. In this case P_∞ was calculated from $P_\infty = P_0 \cdot 2^{1/a}$. The rate constant is found from the slope of the plot by the relationship

$$k = 2.303[2^{1/a} - 1]Sa$$

After correcting for the impurities, plots of log P_r against time and log $(P_\infty - P)$ against time were linear to about 50% decomposition in most cases. The Allen method, however, gave rate constants about 3% higher than the Robinson method in all cases. P (final) never attained the value of P_∞ (calculated). For example, at 452.3°, P/P_0 after eight half-lives was 1.87, whereas the

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Table I

			Allen Method				
Temp, °C	394.5	405.8	417.4	428.8	440.4	446.5	
k(total) × 10^{-4}	0.4648	0.9663	1.857	3.660	7.183	10.07	
k_1 × 10^{-4}	0.1265	0.2771	0.5429	1.099	2.282	3.273	
k_2 × 10^{-4}	0.3383	0.6892	1.314	2.561	4.901	6.797	
Temp, °C	452.3	465.0	478.2	490.0	503.1		
k(total) × 10^{-4}	13.73	26.39	52.80	100.8	189.0		
k_1 × 10^{-4}	4.571	8.951	18.85	37.25	72.74		
k_2 × 10^{-4}	9.161	17.44	33.95	63.51	116.3		
			Robinson Method				
Temp, °C	394.5	405.8	417.4	428.8	440.4	446.5	452.3
k(total) × 10^{-4}	0.4508	0.9126	1.809	3.550	6.965	9.769	13.34
k_1 × 10^{-4}	0.1228	0.2617	0.5288	1.065	2.213	3.175	4.441
k_2 × 10^{-4}	0.3280	0.6509	1.280	2.485	4.752	6.594	8.889
Temp, °C	465.0	478.2	490.0	503.1			
k(total) × 10^{-4}	25.91	51.35	97.61	186.3			
k_1 × 10^{-4}	8.786	18.33	36.09	71.71			
k_2 × 10^{-4}	17.12	33.02	61.52	114.6			

calculated value is 1.97. In preliminary experiments, it was found that the rate constants were independent of initial reactant pressure in the range 28–90 Torr. Subsequent rate determinations were carried out with initial pressures in the range 50–62 Torr. Two complete runs were carried out at each of 11 temperatures, the pressure at various times being obtained from the recorder trace of the transducer output. Total rate constants for the two runs normally agreed within 2%. Excellent agreement with these values was obtained with a small sample of chlorocyclobutane of 98.6% purity supplied by Dr. W. G. Rothschild, after corrections were made for the impurities. Also at each temperature, analyses of several reaction mixtures, taken to low decomposition, were performed to obtain ethylene/butadiene ratios. (In all cases the amounts of ethylene and vinyl chloride were equal within ±1%.) From these ratios and the average total rates, the individual rate constants k_1 and k_2 were obtained. The results are shown in Table I. (The rate constants quoted are those obtained directly from a least-squares analysis; we do not claim four-figure significance.) Arrhenius plots of the above data gave good straight lines from which the Arrhenius parameters were evaluated by the method of least squares, whence

$$k_{1,\mathrm{Allen}} = 10^{14.76\pm0.09} \exp(-60{,}070 \pm 300 \text{ cal mol}^{-1}/RT) \text{ sec}^{-1}$$

$$k_{2,\mathrm{Allen}} = 10^{13.61\pm0.06} \exp(-55{,}240 \pm 190 \text{ cal mol}^{-1}/RT) \text{ sec}^{-1}$$

$$k_{1,\mathrm{Robinson}} = 10^{14.80\pm0.09} \exp(60{,}260 \pm 280 \text{ cal mol}^{-1}/RT) \text{ sec}^{-1}$$

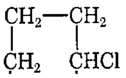
$$k_{2,\mathrm{Robinson}} = 10^{13.65\pm0.05} \exp(-55{,}430 \pm 180 \text{ cal mol}^{-1}/RT) \text{ sec}^{-1}$$

The error limits are the standard deviations, and it can be seen that the parameters from the Allen and Robinson methods are the same within these limits. We estimate that the maximum error in E for ethylene production is ±800 cal which gives an uncertainty of ±0.25 in the A factor. For the path leading to 1,3-butadiene, these errors are smaller.

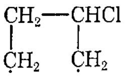
Runs carried out at 446.5° in an "aged" vessel packed with glass tubes having a surface/volume ratio ten times that of the unpacked vessel gave a rate constant within 4% of that obtained in the unpacked vessel. There is thus no appreciable heterogeneous component of the reaction. A complete run at 446.8° was followed analytically by gas chromatography and gave a rate constant almost identical with that obtained from the Arrhenius equation from the Robinson method. The uncertainty in the analytical results is high, however, due to the difficulty in obtaining reliable calibration factors for chlorocyclobutane. Above 50% decomposition, new products were observed on the chromatogram. These totaled about 3 at 60% decomposition, and about 7 at 70% decomposition. These products were not identified, but the major peaks were eluted after chlorocyclobutane, indicating that they were probably formed by condensation of the primary products. The ethylene/butadiene ratio was found to increase above 50% decomposition and slightly more ethylene than vinyl chloride was found, also indicating secondary condensation reactions. This would account for the premature leveling off of the pressure–time curve. Titrations of the hydrogen chloride gave considerable scatter and only agreed within about 10% with pressure measurements. Owing to the small amounts involved, however, this agreement can be considered reasonable.

Discussion

The decomposition pathway leading to ethylene and vinyl chloride occurs at a slower rate than the decomposition of monoalkylcyclobutanes or of cyclobutane itself. At 450° it is 0.73 times that for cyclobutane and one-half of that of methylcyclobutane. Thus while the presence of the chlorine lowers the energy of activation for the decomposition, relative to cyclobutane, this is more than compensated by a decrease in the A factor. It is generally considered that the presence of a chlorine atom will stabilize a radical (as compared with a hydrogen atom), and while there appears to be no direct quantitative evidence for this for monosubstitution there is such evidence for polyhalogenated radicals. On the basis of such stabilization, the biradical I would be preferred over II.

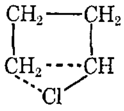


I

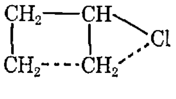


II

We think it is unlikely that the difference in stabilities between I and II is appreciably more than 2 kcal mole^{-1}, but even a figure as small as this would ensure that I was very much the more important species in determining the Arrhenius parameters for the decomposition. This would explain the reduction in the energy of activation for this reaction compared with cyclobutane. The lowered *A* factor must come from a tightening of the transition complex and is probably to be associated with the loss of entropy of internal rotations again as compared with the cyclobutane activated complex. This cannot be simply due to an increase in the barrier to internal rotation of the type as occurs in going from ethane to ethyl chloride, since such an effect would be far too small. We suggest it arises from a structure involving a chlorine bridge. Such a complex is shown in Ia. Alternatively, if in fact the stabilization by the chlorine substitution is appreciably less than 2 kcal mol^{-1}, then II must be seriously considered, and it then follows that IIa might be a reasonable representation of the transition complex. It should be noted that a chlorine bridge of the type shown in IIa has been proposed in the transition complex for the isomerization of chlorocyclopropane,[4] though in this case chlorine migration occurs.

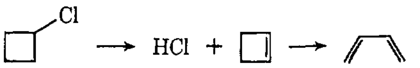


Ia



IIa

The reaction leading to the elimination of hydrogen chloride has a "normal" *A* factor which is typical of such eliminations from open-chain alkyl chlorides. The activation energy is, however, higher than for 2-butyl chloride (50.1 kcal mol^{-1}) and also for cyclohexyl and cyclopentyl chlorides (49.2 and 48.3 kcal mol^{-1}, respectively). This must be attributed to the greater strain involved in bringing the chlorine and hydrogen to the transition-state configuration. On the basis of the analytical data alone, it is not possible to distinguish between the direct formation of butadiene as depicted in eq 2 or a two-stage process involving the intermediate formation of cyclobutene as shown in eq 3. Since the



(3)

HCl elimination will be favored by a reduction in the carbon–carbon bond involved, it appears unlikely on energetic grounds that the reaction yields butadiene directly and we favor (3).

It is interesting to note that while the concerted *cis* elimination of HCl from alkyl chlorides and alicyclic chlorides is an orbital symmetry-forbidden process,[11] the one-step formation of butadiene and HCl would be a symmetry-allowed process. If such considerations were of importance in controlling the energetics of these eliminations, then it would have been anticipated that in the present study this reaction would have had an appreciably lower energy of activation than that observed in the case of cyclopentyl chloride. It is possible that the approximation of treating the σ C–Cl bond as equivalent to the σ C–H bond when constructing the appropriate MO which is inherent in the orbital symmetry arguments is at the bottom of this unexpected finding. An alternative statement of this suggestion is that the differences between these bonds is so marked that the molecular orbitals are not appreciably delocalized, and delocalized molecular orbitals are required (indeed are inherent) in the application of the orbital symmetry arguments.

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Vibrational Effects in the Xylenes[1]

W. Albert Noyes, Jr., and D. A. Harter

Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439. *Received May 29, 1969*

Abstract: An increase in pressure of inert gas enhances the fluorescences of the xylenes when exposed to radiation of shorter wavelengths than the 0,0 bands. At longer wavelengths the reverse effect is noted. An increase in temperature causes a decrease in fluorescence. Quantum yields of isomerization of xylenes to each other are wavelength dependent and are very small near the 0,0 band. These yields increase slightly with increase in temperature. 1,3-Pentadiene effectively quenches the singlet states of the xylenes. A mechanism can be advanced which correlates these various facts.

It is recognized that when light emission from an excited molecule is competitive with some other process whose rate increases with increase in vibrational level there may be enhancement of fluorescence with increase in total pressure.[2-4] The competing processes may be hard to elucidate but could include dissociation, isomerization, and intersystem cross-over to a state of different multiplicity.

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