The Thermal Isomerization of Chlorocyclopropane and of Bromocyclopropane

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A study of the thermal isomerization of fluorocyclopropane as reported by Casas, Kerr, and Trotman-Dickenson[1] has shown that four isomeric fluoropropenes are formed: the rate of isomerization and the kinetics being similar to those reported for alkyl-substituted cyclopropanes. Recent studies by us have shown that chlorocyclopropane and bromocyclopropane isomerize at considerably greater rates. The isomerizations were carried out in Pyrex vessels seasoned by prolonged contact with the decomposition products of the particular compound. Analysis of organic products was by gas chromatography, and of HBr by titration.

Chlorocyclopropane was found to isomerize at 340–420° entirely to 3-chloropropene by a first-order kinetic law which was obeyed to at least 70% reaction. Values for the rate coefficient at a given temperature were independent of initial pressure over the range 35—440 mm. There was slight subsequent decomposition of 3-chloropropene at temperatures above 400°. Runs in a clean Pyrex vessel were not noticeably different from those in coated vessels, and the rate of isomerization was unchanged by the addition of HCl of propene, or by increasing the surface-to-volume ratio of the vessel from 0·8 cm.$^{-1}$ to 4·6 cm.$^{-1}$

In the case of the bromocyclopropane study the major products obtained were: 3-bromopropene present in the greater proportion in the early stages of the reaction, and 1-bromopropene (*cis–trans*-mixture) which increased in proportion as the reaction proceeded. There was no detectable amount of 2-bromopropene. These results are consistent with an isomerization of bromocyclopropane to 3-bromopropene and subsequent isomerization of the latter to 1-bromopropene. A separate study on 3-bromopropene at 336° showed that it isomerized to 1-bromopropene at about one-half the rate of the bromocyclopropane isomerization. Both of these isomerizations were catalysed by HBr. The disappearance of bromocyclopropane followed a first-order kinetic law to at least 60% reaction over the temperature range 310—360°, and over the range of initial pressures 120—320 mm. values for the rate coefficient were substantially constant at a given temperature. The rate of disappearance of bromocyclopropane was unaffected by the presence of propene but was approximately doubled in the presence of an equimolar amount of HBr. The effect of increasing the surface-to-volume ratio of the vessel was not studied. Other reaction products detected in smaller amounts were HBr, propene, and benzene. Separate studies showed these to be the major pyrolysis products of 1-bromopropene and 3-bromopropene (see also ref. 5).

TABLE

Compound	Isomerization products		E (kcal.)	log A	Relative Rates[a] (336°)
Cyclopropane[2]	propene		65·1	15·3	1
Methylcyclopropane[3]	but-1-ene	48%	65·0	15·5	2
	but-2-ene[b]	44%	—	—	—
	isobutene	8%	—	—	—
Ethylcyclopropane[4]	pent-1-ene	44%	61·6	14·4	2
	pent-2-ene[b]	48%	—	—	—
	2-methylbut-1-ene	8%	—	—	—
Fluorocyclopropane[1]	1-fluoropropene[b]	79%	61·0	14·6	6
	2-fluoropropene	9%	—	—	—
	3-fluoropropene	11%	—	—	—
Chlorocyclopropane	3-chloropropene		56·2	14·8	500
Bromocyclopropane	1-bromopropene[b]		47·3	13·5	40,000
	3-bromopropene[c]		—	—	—

[a] Estimated from $k_1 = Ae^{-E/RT}$

[b] *cis–trans*-Mixture

[c] The proportion of 1-bromopropene to 3-bromopropene increased during the reaction; equal amounts were present when 30% of the bromocyclopropane had isomerized at 336°.

The range of products formed during the isomerization of fluorocyclopropane and of the alkylcyclopropanes may be accounted for by the ring rupture being associated with the migration of a hydrogen atom between any two adjacent carbon atoms on the cyclopropane ring. The close similarity of the rates to that for cyclopropane is also strongly suggestive of a common mechanism. For this mechanism to apply in the case of chlorocyclopropane which forms a single isomerization product, the hydrogen atom transfer would have to be only towards the carbon atom to which the halogen atom is attached. This is probably also true for bromocyclopropane. However, in view of the considerably greater rates of isomerization of these two compounds, a much more likely possibility is that the ring rupture is associated with the migration of the halogen atom to an adjacent carbon atom. Assuming this atom transfer process to be rate-determining, the regular decreases in activation energies in the series cyclopropane, chlorocyclopropane, bromocyclopropane are in line with the regular decreases in bond energies from C–H to C–Cl to C–Br. Subsequent studies on substituted chloro- and bromo-cyclopropanes should provide evidence for checking this suggested mechanism.

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