310. *Catalysis by Hydrogen Halides in the Gas Phase. Part VII.* Cyclopropane and Hydrogen Bromide.*

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Whereas the uncatalysed isomerisation of cyclopropane to propene occurs at temperatures above 470° with an activation energy of 65 kcal./mole, this reaction takes place in the presence of hydrogen bromide at 369—452°. The rate is basically of the first-order in cyclopropane and hydrogen bromide and $E = 38{\cdot}8$ kcal./mole. However, significant deviations from simple kinetics occur.

CYCLOPROPANE isomerises to propene at temperatures above 469° and the reaction is unimolecular.[1] It also undergoes a slow iodine-catalysed, gas-phase isomerisation [2] at 245—280°. In the presence of hydrogen bromide, propene is produced at 369—452° and this reaction is now described.

Considerations of the electronic structure of cyclopropane [3] show that there is a concentration of electron density within the ring and that, from the point of view of reactivity, a high degree of delocalisation of the C–C bonding electrons gives to cyclopropane ethylenic properties, in particular the ability to combine with "cationoid reagents." For instance, cyclopropane forms complexes with platinum(IV) [4] and in these the ring is opened; it is adsorbed on the surface of metallic hydrogenation catalysts and combines with Friedel–Crafts catalysts; [5] it reacts with acidic reagents; organic acids and boron trifluoride,[6] and inorganic acids,[7] convert it into n-propyl esters, and, in particular, with hydrobromic acid it yields n-propyl bromide. However, the kinetics of these reactions are not simple.

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* Part VI, *J.*, 1962, 653.

[1] Chambers and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 399; Corner and Pease, *ibid.*, 1945, **67**, 2067; Pritchard, Sowden, and Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, *A*, **217**, 563; Flowers and Frey, *J.*, 1960, 2758; Falconer, Hunter, and Trotman-Dickenson, *J.*, 1961, 609.

[2] Ogg and Priest, *J. Chem. Phys.*, 1939, **7**, 736.

[3] Coulson and Moffitt, *Phil. Mag.*, 1949, **40**, 1; Sugden, *Nature*, 1947, **159**, 400; Walsh, *Trans. Faraday Soc.*, 1949, **45**, 179; Dewar, *Discuss. Faraday Soc.*, 1947, **2**, 75; Dewar, "The Electronic Theory of Organic Chemistry," Oxford, 1949, p. 156.

[4] Tipper, *J.*, 1955, 2045; Adams, Chatt, Guy, and Sheppard, *J.*, 1961, 738.

[5] Bond and Newham, *Trans. Faraday Soc.*, 1960, **56**, 1501; Schmerling, *Ind. Eng. Chem.*, 1948, **40**, 2072; Tipper and Walker, *J.*, 1957, 1199.

[6] Dorris and Sowa, *J. Amer. Chem. Soc.*, 1938, **60**, 358.

[7] Gustavon, *J. prakt. Chem.*, 1900, **62**, 290; Kharasch, Fineman, and Mayo, *J. Amer. Chem. Soc.*, 1939, **61**, 2139; Lawrence and Tipper, *J.*, 1955, 713.

Isomerisation is fast at low temperatures on the surface of acidic catalysts,[8] but in the gas phase only slight reaction was previously observed[9] for mixtures of cyclopropane and hydrogen chloride, bromide, or iodide in glass bulbs during several hours at 300°

EXPERIMENTAL

Materials.—Cyclopropane, of anæsthetic grade, was pumped through a trap at −80° and then gave only one peak when chromatographed. The hydrogen bromide, propene, and isobutene used have been described in previous Parts of this series.

Apparatus and Procedure.—The apparatus and general procedures have been described previously. A suitable coating for the reaction vessel was obtained by leaving propene or cyclopropane in the vessel for several days at 490°, a lustrous black surface being produced; this was finally " cured " during 12 hr. with a mixture of cyclopropane and hydrogen bromide. Reliable rates were obtained after a few runs. For a short while at the beginning of the investigation the coating produced by decomposing allyl bromide was used, as in previous investigations. The rates were only slightly higher. The former coating was preferred. The " blow-in " technique was generally used, cyclopropane being introduced first. The reverse procedure and the " distil-in " technique gave similar results.

Method of Analysis.—After various reaction times the mixtures were expanded directly into an evacuated 5-l. bulb containing fresh calcium hydroxide and magnesium perchlorate, where hydrogen bromide was absorbed. After *ca.* 10 min. the contents were transferred to a cylindrical tap-vessel of *ca.* 50 c.c. capacity and thoroughly mixed by heating with a pin-point flame for *ca.* 10 min. Control experiments showed that these procedures did not cause cyclopropane to react. The mixtures were analysed by gas–liquid chromatography in a 5 mm. × 10 ft. column of 30% w/w acetonylacetone on Celite 545 with nitrogen as the flow gas at room temperature. Retention times were: propene 130 sec., cyclopropane 160 sec.; and the peaks were completely separated. Column conditions were kept steady. The proportions were calculated from the relative areas of the peaks. Repeated analyses were consistent within *ca.* 0·5%, and at least two analyses of each mixture were made. The method was calibrated by using 15 mixtures of various proportions of cyclopropane and propene, accurately determined by pressures. The calibrations lay on a smooth curve within *ca.* ±1% and this curve was used in the estimation of unknown mixtures. The overall accuracy is probably better than 2% in the proportions.

At temperatures other than 402° variations of the procedure were not made; 10—12 cm. of cyclopropane were used and the pressures of hydrogen bromide and reaction times adjusted to give 33 ± 2% reaction. Times and pressures of hydrogen bromide used were: 452°, 5 min., 9 cm.; 440°, 10 min., 9 cm.; 421°, 13 min., 11 cm.; 386°, 42 min., 16 cm.; 369°, 60 min., 21 cm. The consistency of the rates measured under identical conditions can be seen in Table 1.

TABLE 1.

Rates at 385·7° (p_{Cp} = pressure of cyclopropane).

p_{Cp} (mm.)	p_{HBr} (mm.)	Time (min.)	Reaction (%)	10^5k_1 (sec.$^{-1}$)	$10^7k_1/p_{HBr}$ (sec.$^{-1}$ mm.$^{-1}$)
113	161	42	33·3	16·0	9·9
116	165	42	33·3	16·0	9·7
106	166	42	33·3	16·0	9·6
108	169	42	33·7	16·3	9·6

Products.—In three experiments cyclopropane (169, 343, 199 mm.) and hydrogen bromide reacted at 402·6° to 95%, 80%, and 52%, respectively. After being treated as described above the products were weighed (Found: 33, 66, and 36 mg. Calc. as cyclopropane and propen: 31, 63, and 36 mg.). These results show that no material was lost during the reaction. No liquid or gas uncondensed at liquid-air temperature was found. Gas-chromatography showed that propene was the only product. No induction periods were observed.

The Uncatalysed Reaction.—Throughout the investigation the rate of the uncatalysed

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[8] Egloff, " Reactions of Pure Hydrocarbons," Reinhold, Publ., Inc., New York, 1937, p. 698; Roberts, *J. Phys. Chem.*, 1959, **63**, 1400; Bassett and Habgood, *ibid.*, 1960, **64**, 769.

[9] Ogg and Priest, *J. Amer. Chem. Soc.*, 1938, **60**, 217.

isomerisation was used as a control in order to check the suitability of the experimental conditions. The agreement between the results obtained in this way and those of Chambers and Kistiakowsky[1] was very satisfactory, *viz.*, 10^4k_1 (sec.$^{-1}$) being 0·154 at 440·0°, 0·35 at 452·4°, 0·86 at 466·1°, and 1·82, 1·86, 1·80, 1·75, 1·88 with 265 mm. of propene, and 1·89 with 282 mm. of isobutene at 479·2° (calc. 0·15 at 440·0°, 0·31 at 452·4°, 0·87 at 466·1°, and 1·91 at 479·2°); with the packed vessel at 481·2° the value found was 2·3 (calc. 2·2). A correction (never $>2\%$) for the uncatalysed reaction was made to the rates at 440° and 452°.

Possible Loss of Hydrogen Bromide by its Combination with Olefin.—Agius and Maccoll[10] and Maccoll and Thomas[11] took account of the equilibrium Pr^nBr or $Pr^iBr \rightleftharpoons$ Propene + HBr in their studies of the decompositions of n-propyl bromide at 300—380° and isopropyl bromide at 310—350°. In each case it lay well to the right. On consideration of their results and with allowance for dead-space corrections it is likely that, for pressures of *ca.* 100 mm. each of propene and hydrogen bromide, less than 1% of combination occurs at temperatures above 400°; this figure could be several % at 370°. The equilibrium Isobutene + HBr $\rightleftharpoons Bu^tBr$ is well known. Kistiakowsky and Stauffer[12] measured it at 102—258° and Howlett[13] at 99—210°. It is clear that for temperatures above 370° the amount of combination is negligible.

Rates in a Packed Reaction Vessel.—In a vessel of *ca.* 250 c.c. capacity, packed with concentric glass tubes at *ca.* 3 mm. spacings and having surface : volume ratio *ca.* 8 times that of the unpacked vessel, the rate constant for the catalysed reaction at 402·4° was $10^7k/p_{HBr} = 21 \pm 2$ sec.$^{-1}$ mm.$^{-1}$ (8 values with variations of initial pressures of cyclopropane 104—200 mm., hydrogen bromide 92—150 mm., and reaction 20—47%). Additions of isobutene (78—218 mm.) to reaction mixtures of cyclopropane (105—123 mm.) and hydrogen bromide (186—238 mm.) affected the rate in the same way as they did in the unpacked vessel.

RESULTS AND DISCUSSION

Hydrogen bromide catalyses the conversion of cyclopropane into propene at measurable rates at temperatures 369—452°. The reaction is accompanied by a large decrease in free energy and goes to completion. Propene is the only product. First-order rate constants have been calculated from the relative proportions of cyclopropane and propene at various times. Rate constants at *ca.* 30% reaction are roughly proportional to the pressure of hydrogen bromide, and with the small deviations discussed below the reaction follows the rate equation (where Cp = cyclopropane): $-\mathrm{d}p_{Cp}/\mathrm{d}t = k_2p_{Cp}p_{HBr}$. At 402° variations of the pressures of hydrogen bromide and cyclopropane by a factor of ten give "k_2" consistent within *ca.* 20%. The reaction takes place in the gas phase since substantial increase of surface : volume ratio of the reaction vessel does not alter the rate. The variation of rate with temperature, shown in Table 2, follows the Arrhenius equation

TABLE 2.

Variation of rate with temperature.

Temp.	452·4°	440·0°	421·1°	402·6°	385·7°	369·6°
No. of runs	6	6	5	17	4	7
$10^7k_1/p_{HBr}$ (sec.$^{-1}$ mm.$^{-1}$)	138	78	42	19·3	9·7	4·7
k_1/p_{HBr} (sec.$^{-1}$ c.c. mole^{-1})	625	348	180	81	40·4	18·7

$k_2 = 3{\cdot}0 \times 10^{14} \exp(-38{,}800/RT)$ sec.$^{-1}$ c.c. mole^{-1} (calculated by the method of least squares). Catalysis by hydrogen bromide has reduced the activation energy by *ca.* 26 kcal./mole. Calculation by means of collision numbers shows that the steric factor for the catalysis is close to unity.

Deviations from Simple Kinetics at 402°.—Although the reaction eventually reaches completion the rate falls as it proceeds (cf. Fig. 1). k_1 is very nearly proportional to p_{HBr}, especially at high p_{HBr}, but the graph of k_1 against p_{HBr} does not pass through the

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[10] Agius and Maccoll, *J.*, 1955, 973; Semenov, Sergeev, and Kaprilova, *Doklady Akad. Nauk S.S.S.R.*, 1955, **105**, 301; Blades and Murphy, *J. Amer. Chem. Soc.*, 1952, **74**, 6219.

[11] Maccoll and Thomas, *J.*, 1955, 979.

[12] Kistiakowsky and Stauffer, *J. Amer. Chem. Soc.*, 1937, **59**, 165.

[13] Howlett, *J.*, 1957, 2834.

origin (cf. broken line of Fig. 2), and, further, k_1/p_{HBr} is not completely independent of the initial pressure of cyclopropane, p_{Cp} (Fig. 3).

These deviations arise from the fact that propene retards the reaction. Propene and isobutene added initially caused a marked reduction in rate (cf. Fig.. 4). This retarding effect takes place in the gas phase since it occurs in a similar fashion for reactions carried out in a packed vessel (Fig. 5). For a constant pressure of isobutene the retarded rate increases with increasing pressure of hydrogen bromide (Fig. 6). The retardation cannot be due to withdrawal of hydrogen bromide from the reaction mixture by the equilibrium Olefin + HBr $\rightleftharpoons$ Alkyl bromide, as it lies well to the left at this temperature.

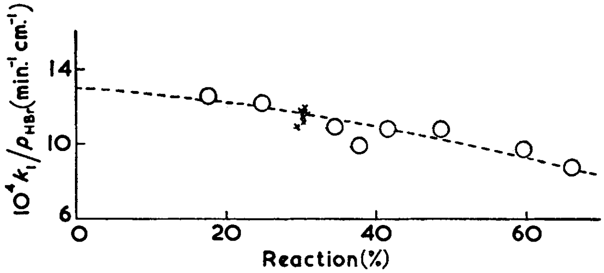


FIG. 1. . Variation of the first-order rate constant with percentage reaction.

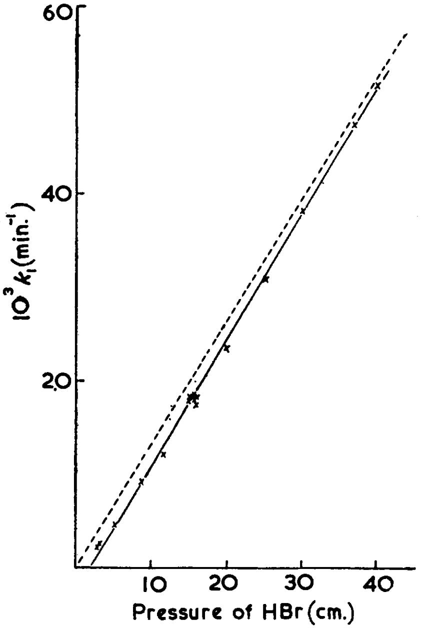


FIG. 2. Variation of first-order rate constant at 402·6° and 30% reaction with pressure of hydrogen bromide. The broken line corresponds to that in Fig. 3.

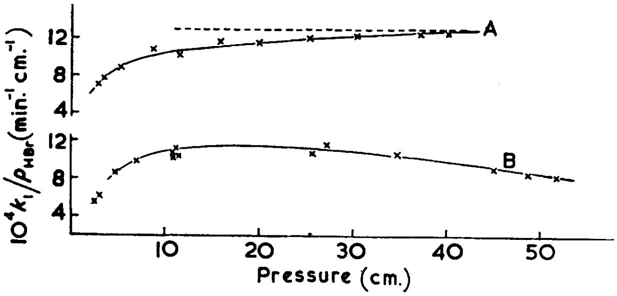
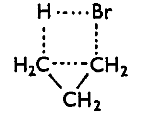


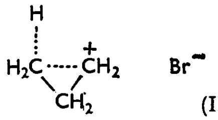
FIG. 3. Variation of rate at 402·6° and 30% reaction. (A) with pressure of hydrogen bromide, $p_{\mathrm{Cp}} \sim 11$ cm., and (B) with pressure of cyclopropane, $p_{\mathrm{HBr}} \sim 16$ cm.

On the approximately true assumption that the decrease of catalytic rate constant is proportional to the pressure of propene (p_{P}) (broken line of slope α in Fig. 4), *i.e.*, $-\mathrm{d}p_{\mathrm{Cp}}/\mathrm{d}t = (k_0 - \alpha p_{\mathrm{P}})p_{\mathrm{Cp}}$, the times ($t$) required for various amounts of reaction (x/a) have been calculated. The decrease in the apparent first-order rate constant {calc. from $k_1 = (1/t) \log [a/(a - x)]$} with x/a is compared with the experimental results in Fig. 1 (broken curve). Although the calculations are extremely sensitive to the value of α chosen, the agreement confirms the ascription of retardation to propene.

Possible Reaction by Way of n-Propyl Bromide.—n-Propyl bromide might be formed from cyclopropane and hydrogen bromide through a four-centre (I) or a heterolytic (II)

(I)





(II)

transition state. The former is like the four-centre transition state formerly accepted for the decompositions of alkyl bromides, and the latter resembles the heterolytic type recently suggested.[14]

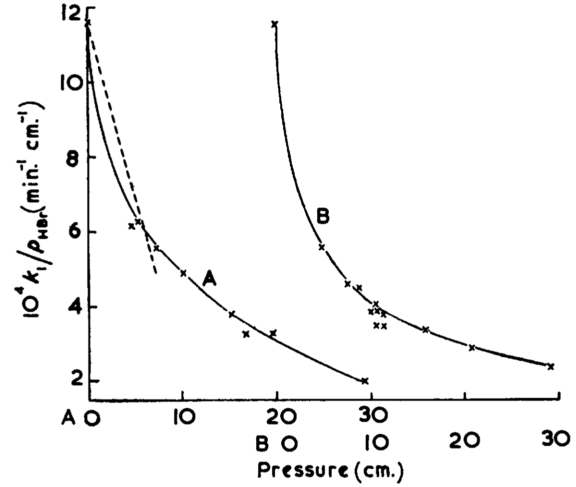


FIG. 4. Rates with added propene (A) and isobutene (B); p_{Cp} ~11 cm., p_{HBr} ~15 cm.

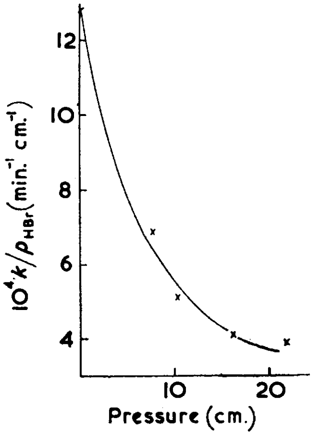


FIG. 5. Variation of rate with added isobutene in packed vessel. p_{Cp} ~10 cm., p_{HBr} ~20 cm.

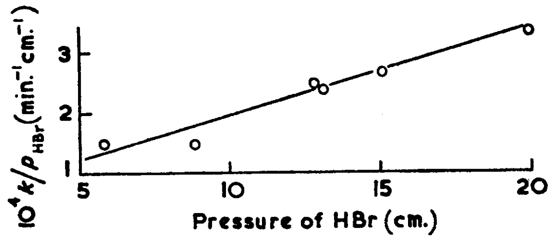


FIG. 6. Variation of retarded rate in the presence of *ca.* 23 cm. of isobutene at 402·6° with pressure of hydrogen bromide.

The kinetic scheme

$$\text{Cyclopropane} + \text{HBr} \xrightarrow{\text{Fast}} \text{n-Propyl bromide} \xrightarrow{\text{Slow}} \text{Propene} + \text{HBr}$$

is not consistent with the experimental observations, and reversal to form cyclopropane is not likely. However, a scheme

$$\text{Cyclopropane} + \text{HBr} \xrightarrow{\text{Slow}} \text{n-Propyl bromide} \xrightarrow{\text{Slow}} \text{Propene} + \text{HBr}$$

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[14] Ingold, *Proc. Chem. Soc.*, 1957, 279; Maccoll, " Theoretical Organic Chemistry," Butterworths Scientific Publns., London, 1959, p. 230.

is kinetically feasible. The decomposition of n-propyl bromide[10] occurs by a radical chain-mechanism of order 1·5 for temperatures 300—380°, and the rate is given by

$$k_{1\cdot5} = 7\cdot24 \times 10^{10} \exp(-33{,}800/\boldsymbol{R}T) \text{ mole}^{-\frac{1}{2}} \text{ c.c.}^{\frac{1}{2}} \text{ sec.}^{-1}.$$

In the presence of large amounts of propene (*ca.* 200 mm.) the radical-chain mechanism is inhibited, leaving a unimolecular reaction[15] whose rate is given by

$$k_1 = 7\cdot94 \times 10^{12} \exp(-50{,}700/\boldsymbol{R}T) \text{ sec.}^{-1}$$

for temperatures 350—390°. Calculations from these equations show that the half-life of, say, 25 mm. of n-propyl bromide at 369°, 402°, 452° is as follows: uninhibited 69, 22, 3; fully inhibited 300, 44, 3 min., respectively. Under the conditions of our experiments then, n-propyl bromide exists for times ($t_{0\cdot5}$, say, 100, 30, 3 min.) comparable with those used. n-Propyl bromide cannot have been present in large quantity during reaction, but a small amount could have escaped detection.

Possible Heterolytic Mechanism.—In view of the suggestion[14] that gas-phase reactions can be heterolytic, n-propyl bromide is not a necessary intermediate for the reaction, which might involve the cyclopropyl cation. Cyclopropane possesses the necessary basicity to make the reaction

$$\text{Cyclopropane} + \text{HBr} \longrightarrow \overbrace{(\text{Cyclopropane H})^{+}(\text{Br})}^{-} \longrightarrow \text{Propene} + \text{HBr}$$

feasible,[3-9] in which case this reaction is akin to those described in previous Parts.[16] Such a cation has been used to explain the reactions of cyclopropane and substituted cyclopropanes in solution and in electron-impact studies.[17] If the ion-pair transition-state complex exists for longer than the time between collisions it could be destroyed on attack by a molecule with affinity for hydrogen bromide similar to that of cyclopropane, *e.g.*, an olefin, and this may be the origin of the retardation.

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[15] Maccoll and Thomas, *J.*, 1957, 5033.

[16] Maccoll and Stimson, *Proc. Chem. Soc.*, 1958, 80; *J.*, 1960, 2836; Lewis and Stimson, *J.*, 1960, 3087; Ross and Stimson, *J.*, 1960, 3090; Stimson and Watson, *J.*, 1960, 3920; *J.*, 1961, 1392; *Chem. and Ind.*, 1961, 207; Failes and Stimson, *J.*, 1962, 653.

[17] Lawrence and Tipper, *J.*, 1955, 713; Edwards and Lesage, *Chem. and Ind.*, 1960, 1107; Skell and Starer, *J. Amer. Chem. Soc.*, 1960, **82**, 2971; Silver, *ibid.*, p. 2971; Rylander and Meyerson, *ibid.*, 1956, **78**, 5799.