Catalysed Gas Phase Decompositions. XXX*
Cyclopropane and Boron Tribromide

V. Raymond Stimson and Edward C. Taylor

Department of Physical Chemistry, University of New England,
Armidale, N.S.W. 2351.

Abstract

Boron tribromide in *c.* 10% proportion catalyses the isomerization of cyclopropane at 250–438°C in a homogeneous, molecular reaction. The rate is proportional to the pressures of cyclopropane and boron tribromide and follows the equation

$$k_2 = 10^{9 \cdot 30} \exp(-68020/8 \cdot 314T) \quad \text{s}^{-1} \text{ ml mol}^{-1}$$

Boron tribromide is *c.* 8 times as effective as boron trichloride.

Hitherto the catalysts we have used in the gas phase decompositions of basic organic compounds and in the isomerizations of olefins have been hydrogen halides and carboxylic acids which contain a hydrogen atom that might be made available to the transition state complex.[1,2] In particular, hydrogen bromide greatly increased the rate of isomerization of cyclopropane,[3] reducing the effective temperature from *c.* 500°C to 369–452°C and the activation energy from *c.* 270 to 162 kJ mol^{-1}. Recently, we have shown that boron trichloride, a Lewis acid, is a somewhat more powerful catalyst than hydrogen bromide in this isomerization.[4] The reaction took place at 360–470° with rate proportional to the pressures of substrate and catalyst and $E = 106 \cdot 6$ kJ mol^{-1} and $\log A = 11 \cdot 35$ (A in s^{-1} ml mol^{-1}). A polar transition state with an internal 1 → 2 shift of a hydrogen atom was proposed.

In solution reactions depending on Lewis acid catalysis, boron tribromide is also effective, and, on the basis of the heats of formation and dipole moments of the pyridine complexes and from the relative catalytic efficiency in alkylation and acylation reactions, it is judged to be a more powerful Lewis acid than boron trichloride.[5]

We now present results for the isomerization of cyclopropane catalysed by boron tribromide.

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[3] Ross, R. A., and Stimson, V. R., *J. Chem. Soc.*, 1962, 1602.

[4] Johnson, R. L., and Stimson, V. R., *Aust. J. Chem.*, 1975, **28**, 447.

[5] Olah, G. A., 'Friedel–Crafts and Related Reactions' Vol. 1, pp. 195, 229, 860 (Interscience: New York).

Experimental

Boron tribromide (B.D.H.) was purified on the line by trap-to-trap distillation. Thirty-eight mixtures in carbon dioxide ($2\cdot4$–$14\cdot5\%$) were used. The other materials and the general and analytical procedures have been described previously.[4] The vessel was conditioned regularly with cyclopropane. Control runs for 'zero' time at $352\cdot3°C$ showed that no significant amount of reaction took place during the manipulative or analytical procedures. Several runs at 315 and 401° taken to 99% completion gave $P_t/P_o = 0\cdot99\pm0\cdot01$. Propene was the only product found. No permanent gas was ever noted when the reaction was pumped out.

Rates

At $311\cdot0°C$ cyclopropane (119–326 mm) reacted with boron tribromide (15 ± 4 mm) in carbon dioxide to $10\cdot8$, $17\cdot5$, $33\cdot6$, $39\cdot0$, $43\cdot0$, $50\cdot6$, $50\cdot8$, $61\cdot2\%$ reaction with 10^5k_2 (s^{-1} mm^{-1}) $4\cdot4$, $5\cdot0$, $4\cdot9$, $4\cdot1$, $4\cdot7$, $4\cdot0$, $4\cdot3$, $5\cdot0$ (mean $4\cdot6\pm0\cdot4$), respectively. The progress of the reaction therefore follows the first-order form, and propene does not retard or reverse the reaction. Also, as the rate is maintained with $c.$ 10% of catalyst, there can be no significant loss of catalyst.

At $299\cdot3°$ cyclopropane ($21\cdot8$, $52\cdot2$, $81\cdot0$, $100\cdot6$ mm, variation: $4\cdot6$ times) reacted with boron tribromide (6 ± 1 mm) in carbon dioxide with 10^5k_2 (s^{-1} mm^{-1}) $3\cdot6$, $3\cdot9$, $4\cdot3$, $4\cdot2$ (mean $4\cdot0\pm0\cdot4$), respectively. Thus the reaction is first order in initial pressure of cyclopropane.

At $272\cdot7°$ cyclopropane (100 ± 10 mm) reacted with boron tribromide ($1\cdot4$, $2\cdot5$, $3\cdot6$, $8\cdot6$, $10\cdot5$, $10\cdot8$ mm, variation: $7\cdot7$ times) with 10^5k_2 (s^{-1} mm^{-1}) $1\cdot67$, $1\cdot69$, $1\cdot60$, $1\cdot79$, $1\cdot87$, $1\cdot88$ (mean $1\cdot75\pm0\cdot1$), respectively. Thus the rate is proportional to the pressure of boron tribromide.

Table 1. Variation of rate with temperature

Temp. (°C)	No. of runs	Cyclopropane (mm)	BBr_3 (mm)	10^5k_2 (s^{-1} mm^{-1})	$10^{-2}k_2$ (s^{-1} ml mol^{-1})
$438\cdot8$	3	138–150	$8\cdot2$– $9\cdot3$	$44\cdot1$	196
$433\cdot7$	3	105–136	$6\cdot2$–$13\cdot0$	$45\cdot2$	199
$425\cdot5$	3	81–122	$6\cdot9$– $8\cdot1$	$43\cdot3$	189
$409\cdot3$	3	162–168	$8\cdot1$–$12\cdot1$	$28\cdot1$	120
$401\cdot0$	5	116–152	$2\cdot8$–$13\cdot9$	$24\cdot9$	105
$381\cdot0$	4	116–140	$4\cdot6$– $6\cdot2$	$20\cdot9$	85
$371\cdot2$	3	131–159	$4\cdot0$– $6\cdot2$	$13\cdot6$	55
$363\cdot2^A$	2	119–137	$7\cdot1$– $9\cdot3$	$14\cdot6$	58
$362\cdot0$	4	123–152	$3\cdot5$– $7\cdot7$	$13\cdot0$	52
$349\cdot5$	3	132–161	$4\cdot6$– $6\cdot7$	$9\cdot4$	37
$342\cdot5$	5	142–165	$4\cdot1$– $9\cdot7$	$7\cdot8$	30
$330\cdot3$	3	133–154	$4\cdot5$– $4\cdot7$	$7\cdot2$	27
$320\cdot5$	2	134–144	$4\cdot0$–$18\cdot0$	$5\cdot54$	$20\cdot5$
$311\cdot0$	9	119–326	$10\cdot4$–$19\cdot2$	$4\cdot54$	$16\cdot5$
$302\cdot7$	5	131–155	$4\cdot6$–$13\cdot2$	$3\cdot73$	$13\cdot4$
$299\cdot3$	4	21–100	$5\cdot6$– $7\cdot0$	$4\cdot01$	$14\cdot3$
$296\cdot4^A$	2	125–167	$9\cdot7$–$10\cdot4$	$3\cdot62$	$12\cdot9$
$289\cdot5$	5	126–184	$4\cdot8$– $6\cdot9$	$2\cdot76$	$9\cdot7$
$281\cdot2$	3	138–164	$7\cdot0$–$13\cdot4$	$2\cdot49$	$8\cdot6$
$272\cdot7$	6	87–114	$1\cdot4$–$10\cdot8$	$1\cdot75$	$5\cdot9$
$266\cdot1$	5	119–165	$7\cdot8$–$11\cdot0$	$1\cdot68$	$5\cdot6$
$261\cdot2$	5	97–168	$4\cdot3$– $8\cdot2$	$1\cdot21$	$4\cdot0$
$258\cdot8^A$	4	151–164	$7\cdot5$–$21\cdot7$	$1\cdot11$	$3\cdot7$
$250\cdot0$	2	134–143	$6\cdot8$– $8\cdot3$	$1\cdot03$	$3\cdot4$

[A] In packed reaction vessel.

Results and Discussion

Boron tribromide in 2–14% proportion in carbon dioxide catalysed the isomerization of cyclopropane into propene at measurable rate in the temperature range

250–438°C. The progress of the reaction followed the first-order form and was not affected by the propene produced. The second-order rate constants were independent of initial pressures of substrate and catalyst for variations of 4·6 and 7·7 times, respectively. The rates were not affected by an eightfold increase in surface of the reaction vessel. We therefore consider the reaction to be homogeneous and molecular. Apart from random variations the variation of rate with temperature (Table 1) fits well on the straight line appropriate to the Arrhenius equation:

$$k_2 = 10^{9·30 \pm 0·2} \exp(-68020 \pm 2300/8·314T) \quad s^{-1} \, ml \, mol^{-1}$$

The values of A and E are low, particularly in comparison with those found with boron trichloride,[4] viz. $A = 2·3 \times 10^{11} \, s^{-1} \, ml \, mol^{-1}$ and $E = 106·6 \, kJ \, mol^{-1}$. The investigation has been carried out over quite a wide temperature range (189°); however, while the reliability of the rate is satisfactory and the plot showed no curvature, the individual rate constants are not of sufficient accuracy to test modifications of the Arrhenius equation.

Relative rates for catalysed isomerization of cyclopropane are: HBr, 1; BCl_3, 16; BBr_3, 140. Boron tribromide is a more effective catalyst than boron trichloride[4] by a factor of 8·8 times, as measured by the relative rates at 400°C, and this is consistent with the polar mechanism suggested.