617. *Catalysis by Hydrogen Halides in the Gas Phase. Part III.* Isopropyl Alcohol and Hydrogen Bromide.*

By R. A. Ross and V. R. Stimson.

A homogeneous, molecular, gas-phase decomposition of isopropyl alcohol into water and propene catalysed by hydrogen bromide in the temperature range 369—520° is described.

WHEREAS t-butyl alcohol decomposes by itself in the gas-phase at measurable rates at temperatures of 487—620° with a high activation energy, its decomposition into isobutene and water is catalysed by both hydrogen bromide at 315—422° and hydrogen chloride at 328—454° (Parts I and II [1]). These reactions are homogeneous and molecular. In the decomposition of isopropyl alcohol over pumice at 615°, Nef [2] found acetone and hydrogen and small amounts of other products as well as propene and water, and numerous subsequent investigations with catalytic surfaces have shown that dehydration and dehydrogenation generally accompany one another in various proportions. Barnard [3] states that a chain reaction is carried on by hydrogen atoms formed by the splitting of the bond on the secondary carbon atom. Under the conditions of our experiments decomposition occurs above 450°; acetone and a gas uncondensed at liquid-air temperature, presumably hydrogen, are produced in addition to the main products, propene and water. Although it is not the case for ethanol,[4] it is probable that for isopropyl alcohol a unimolecular reaction analogous to those studied by Schultz and Kistiakowsky [5] for t-butyl and t-pentyl alcohol produces propene and water, and another type of reaction, occurring at the same time, acetone and hydrogen. In the presence of hydrogen bromide, however, a catalysed decomposition into propene and water only, presumably analogous to those referred to above for t-butyl alcohol, occurs at temperatures above 369°, and this reaction is now described.

EXPERIMENTAL

Materials.—Isopropyl alcohol (" AnalaR "), fractionated through 1 ft. of Fenske helices with a Whitmore-Lux head, had b. p. 79·5° (±0·1°)/669·7 mm. Weissberger [6] gives 79·3°/670 mm. (calc.). Propene, prepared [7] from isopropyl alcohol, sulphuric acid, and aluminium sulphate, was passed through potassium hydroxide pellets and purified by trap-to-trap distillation through a U-bend at −80°. Hydrogen bromide, hydrogen chloride, and cyclohexene were prepared as described in Parts I and II. Ethanol was of spectroscopic-reagent grade.

Procedure.—The reaction takes place with an increase in pressure and was followed by the procedure described in Part I. The " blow-in " technique was used in nearly all runs. In general, initial pressures of *ca.* 100—200 mm. of isopropyl alcohol and hydrogen bromide were used. The value of p_f/p_0 was 1·86 ± 0·02 (mean of 23 values at various temperatures); this value is of the same order as those found for similar reactions in this type of apparatus (for a discussion see Part I). A similar value for p_f/p_0 was obtained in the presence of cyclohexene and of propene. In their studies of the decompositions of isopropyl bromide and n-propyl bromide Maccoll and Thomas and Agius and Maccoll found evidence of an equilibrium reaction involving propene and hydrogen bromide.[8] It lay well towards decomposition at 300—380°,

---

* Part II, preceding paper.

[1] Part I, Maccoll and Stimson, *J.*, 1960, 2836.

[2] Nef, *Annalen*, 1901, **318**, 206.

[3] Barnard, *Trans. Faraday Soc.*, 1959, **55**, 947.

[4] Freeman, *Proc. Roy. Soc.*, 1958, **245**, *A*, 75.

[5] Schultz and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 395.

[6] Weissberger, Proskauer, Riddick, and Toops, " Organic Solvents," Interscience, New York, 1955, p. 93.

[7] Kistiakowsky, Ruhoff, Smith, and Vaughan, *J. Amer. Chem. Soc.*, 1935, **57**, 876.

[8] Maccoll and Thomas, *J.*, 1955, 979; Agius and Maccoll, *J.*, 1955, 973.

and no allowance for it was necessary. At temperatures of 370—520° then, it may be safely neglected. Above 450° the proportion of uncatalysed reaction becomes significant. At these temperatures its rate was measured over various times by the increase in pressure; on the assumption that it follows the first-order relationship, which is not strictly true, a rate constant was found and an appropriate correction made to the total rate to obtain the rate constant of the catalysed reaction. These corrections were *ca.* 40, 20, 20, 10, 6, 5, and 5% of the uncatalysed rates at 520°, 500°, 480°, 468°, 459°, 450°, and 440° respectively. These figures are not definite because the rate varies with the amount of hydrogen bromide present. The magnitude of this correction at 520°, and the general irreproducibility of the uncatalysed reaction, made it unprofitable to study the catalysed reaction at temperatures above 520°. The values of k_1/p_{HBr} varied over *ca.* 10% but were consistent within this rather large error; for instance, at 440° with about 20 different pot coatings, 52 runs gave a mean value of 15·0 ± 0·5 sec.$^{-1}$ mm.$^{-1}$ for the rate constant. Our results are summarised in Tables 1—6.

TABLE 1. *Variation of rate at 480° with pressure of hydrogen bromide.*

p_{HBr} (mm.)	p_{PrOH} (mm.)	10^5k * (sec.$^{-1}$)	$10^7k_1/p_{\mathrm{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)
75	197	43	42
99	148	58	46
100	234	55	43
131	239	73	47
151	163	82	46
—	175	12	—

* k is the observed rate constant; k_1 has been corrected for the uncatalysed reaction.

TABLE 2. *Variation of rate with temperature.*

Temp.	No. of runs	$10^7k_1/p_{\mathrm{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)	k_1/p_{HBr} (sec.$^{-1}$ c.c. mole^{-1})
520·0°	4	122	600
500·0	8	85	410
480·0	5	45	211
468·1	22	36	166
459·9	5	31·3	143
449·8	5	21·0	95
440·2°	52	15·0	67
425·0	5	9·1	40
410·2	3	5·8	24·8
400·0	5	3·7	15·7
385·0	4	2·42	9·9
369·6	2	1·22	4·9

TABLE 3. *Rates with cyclohexene at 440°.*

$p_{\mathrm{C_6H_{10}}}$ (mm.)	p_{HBr} (mm.)	p_{PrOH} (mm.)	10^5k_1 * (sec.$^{-1}$)	$10^7k_1/p_{\mathrm{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)
25	176	196	24·3	13·8
40	206	134	32·1	15·6
89	225	141	37·2	16·5
116	163	197	22·8	14·0
160	220	104	36·3	16·5
176	133	118	21·3	16·0
231	125	109	21·8	17·4
250	120	207	17·5	14·6
282	60	139	9·2	15·3
			Mean	15·5 ± 1

* k_1 is corrected for the uncatalysed reaction.

TABLE 4. *Rates with propene.*

Temp.	$p_{\mathrm{C_3H_6}}$ (mm.)	p_{HBr} (mm.)	p_{PrOH} (mm.)	10^5k_1* (sec.$^{-1}$)	$10^7k_1/p_{\mathrm{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)
490°	154	142	180	97	68
500	264	99	284	83	84
500	260	186	212	175	94
500°	206	144	132	145	101
500	155	135	125	127	94

* k_1 is corrected for the uncatalysed reaction.

TABLE 5. *Rates of dehydration catalysed by hydrogen chloride at 440°.*

p_{HCl} (mm.)	p_{PrOH} (mm.)	10^5k * (sec.$^{-1}$)	$10^7k_1/p_{\mathrm{HCl}}$ (sec.$^{-1}$ mm.$^{-1}$)
178	119	2·4	0·7
207	163	2·2	0·5
234	314	2·3	0·5
283	277	2·9	0·6
285	134	3·1	0·7
346	189	3·3	0·6
—	192	1·2	—

* k is the observed rate constant; k_1 has been corrected for the uncatalysed reaction.

TABLE 6. *Rates in a packed vessel of S/V = 7·7 cm.$^{-1}$.*

Temp.	p_{HBr} (mm.)	p_{PrOH} (mm.)	10^5k_1 (sec.$^{-1}$)	$10^7k_1/p_{\text{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)	Temp.	p_{HBr} (mm.)	p_{PrOH} (mm.)	10^5k_1 (sec.$^{-1}$)	$10^7k_1/p_{\text{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)
440·2°	144	163	23·0	16·0	400·0°	73	246	3·0	4·1
	152	177	23·0	15·1		129	255	5·2	4·0
	156	245	25·8	16·5		140	193	6·7	4·8
	203	223	33·0	16·2		229	173	9·5	4·1
	204	250	37·2	18·2		253	224	9·7	3·8
			Mean	16·4		280	149	11·0	3·9
								Mean	4·1

k_1 for 440·2° is corrected for the uncatalysed reaction.

Inhibitors.—Cyclohexene decomposes at temperatures above 450° under our conditions; hence its use as an inhibitor is restricted to temperatures below this value. Propene is not such an effective inhibitor [9] in this type of reaction, and with two other components present it is difficult to introduce a completely effective amount (probably >200 mm.). Ingold and Stubbs [10] have shown that polymerisation and pyrolysis of propene occur at temperatures above 500° and 570° respectively; however, it was found to be suitable for use with our conditions. No change in pressure was observed and no permanent gas was produced when propene (243 mm.) was left in the reaction vessel for 20 min. at 500°. When it was then passed through the gas-chromatography column, only one peak was obtained, and this corresponded to propene. It was therefore used as an inhibitor at 490° and 500°. At 490° the uninhibited rate, calculated from the Arrhenius equation, is 65×10^{-7} sec.$^{-1}$ mm.$^{-1}$ and at 500° it is 85×10^{-7} sec.$^{-1}$ mm.$^{-1}$ (measured). Propene, in the amounts added (up to 264 mm.), caused no reduction in rate (cf. Table 4).

Homogeneity of the Reaction.—At 440° and 400° runs were carried out in a vessel packed with concentric glass tubes at *ca.* 3 mm. spacings and having a surface : volume ratio 7·7 cm.$^{-1}$, *i.e.*, 8 times that for the unpacked vessel. Several pot coatings were used. The value of p_f/p_0 was found to be 1·87. The rates (cf. Table 6) are less consistent and slightly higher (*ca.* 10%) than those found in the unpacked vessel, but the difference is not significant.

Products.—Isopropyl alcohol (246 mm., 71·2 mg.; 198 mm., 57·3 mg.) reacted to completion (p_f/p_0 = 1·86) with hydrogen bromide (152, 148 mm.) at 468°, when 12% of the reaction was uncatalysed. About 96% of the products were expanded directly into an evacuated 5-l. bulb containing magnesium perchlorate to absorb the water produced. The residual propene and hydrogen bromide were pumped into a tap-vessel and weighed (Found: 104, 97 mg. Theor.: 109, 98 mg.).

Isopropyl alcohol (190 mm., 55·0 mg.; 187 mm., 54·2 mg.) reacted to completion (p_f/p_0 = 1·83, 1·85) with hydrogen bromide (63, 129 mm.) at 468°, 25% and 12% of the reaction, respectively, being uncatalysed. The products were treated as above except that both magnesium perchlorate and calcium hydroxide were used to absorb water and hydrogen bromide, respectively. The residual propene was pumped into a tap-vessel and weighed (Found: 34, 41 mg. Theor.: 39, 38 mg.)

Isopropyl alcohol (265 mm., 76·7 mg.) and hydrogen bromide 226 mm.) reacted to completion (p_f/p_0 = 1·86) at 468°; 10% of the reaction was uncatalysed. The products were trapped and swept with dry nitrogen at $-40°$. Water in the residue, which contained some dissolved hydrogen bromide, was estimated from the microanalysis (Found: 25 mg. Theor.: 23 mg.).

Propene (338, 236 mm.) was left in the pot for 40 and 300 min. at 480° and 440°, respectively, the average half-lives for the reaction being 20 and 50 min., respectively. These samples showed only one peak when chromatographed, and this is consistent with the findings of Hurd and Meinert [11] and of Ingold and Stubbs [10] that the decomposition of propene commences at 575—600°. Isopropyl alcohol (379, 384 mm.) reacted to completion with hydrogen bromide (108, 106 mm.) at 468° and 440°, 20% and 8% of the reaction, respectively, being uncatalysed. The products were expanded directly into a 5 l. bulb containing magnesium perchlorate and calcium hydroxide. After some time the residual gas was chromatographed. A major peak

---

[9] Maccoll and Thomas, *J.*, 1957, 5033.
[10] Ingold and Stubbs, *J.*, 1951, 1749.
[11] Hurd and Meinert, *J. Amer. Chem. Soc.*, 1930, **52**, 4978.

corresponding to propene was found, with *ca.* 10% and 5%, respectively, of additional peaks in the C_2 and C_3 region, which presumably arise from the uncatalysed reaction.

After 25 min. at 500° (30% reaction), the products of the uncatalysed decomposition of isopropyl alcohol (340 mm.) were trapped and acetone was estimated [12] as the 2,4-dinitrophenylhydrazone (yield: *ca.* 0·2 mol.). In an identical reaction, but with the alcohol at 117 mm., the products were trapped and distilled from −80° to −190°. These volatile materials were passed through the gas-chromatography column (Found: propene, *ca.* 75; propane, *ca.* 20; C_2 hydrocarbons, *ca.* 5%).

Vapour-phase Chromatography.—The column consisted of 10 feet of 5-mm. diam. 30% (w/w) acetonylacetone on Celite 545. Nitrogen flow-rates of *ca.* 3 l./hr. at room temperature were used. The column had an efficiency of *ca.* 1600 plates and completely separated propane and propene, for which typical retention times were 167 and 196 sec., respectively.

Catalysis by Hydrogen Chloride.—Attempts to observe a similar reaction catalysed by hydrogen chloride, as was found for t-butyl alcohol, were made at 440°. Pressures up to 350 mm. of hydrogen chloride were used but even then the proportion of uncatalysed reaction was *ca.* 50%. The value obtained for $10^7k/p_{\text{HCl}}$ (sec.$^{-1}$ mm.$^{-1}$), *viz.*, 0·6 (6 runs), is probably accurate to about 20%. In view of the difficulties involved, no control runs or determinations of the products were made. However, it can be inferred that a reaction with hydrogen chloride does occur. It is probably analogous to that with hydrogen bromide and slower by a factor of *ca.* 25.

Catalysed Decomposition of Ethanol.—A possible catalysed pyrolysis of ethanol was investigated briefly. At 472°, where the uncatalysed reaction was slow, hydrogen bromide substantially increased the rate of decomposition, as measured by the change in pressure. The rate constant of the uncatalysed reaction was 20—50% of that for the catalysed reaction, whose rate constant was roughly proportional to the pressure of hydrogen bromide for p_{HBr} = 72—267 mm. A value of $10^7k_1/p_{\text{HBr}} = 2{\cdot}0 \pm 0{\cdot}4$ sec.$^{-1}$ mm.$^{-1}$ (13 runs) was found; this rate is *ca.* 1/20 that for isopropyl alcohol. Owing to the large proportion of uncatalysed reaction and the slowness of the catalysed reaction, no other measurements were made for ethanol.

RESULTS AND DISCUSSION

The gas-phase decomposition of isopropyl alcohol, catalysed by hydrogen bromide, occurs at measurable rates in the temperature range 369—520°. The reaction is stoicheiometrically

$$\text{iso-}C_3H_7OH + HBr \longrightarrow C_3H_6 + H_2O + HBr$$

and is of first order in both isopropyl alcohol and hydrogen bromide, *e.g.*, first-order rate constants are proportional to the pressure of hydrogen bromide for initial pressures of 56—373 mm. of the alcohol and 43—355 mm. of hydrogen bromide at 440°. At 420° the reaction is slower than that of t-butyl alcohol and hydrogen bromide by a factor of *ca.* 60. The Arrhenius equation $k_2 = 10^{12.00} \exp(-33{,}200/\boldsymbol{R}T)$ sec.$^{-1}$ c.c. mole^{-1} describes the variation of rate with temperature. The activation energy, 33·2 kcal./mole, is slightly higher than that found for t-butyl alcohol and hydrogen bromide, *viz.*, 30·4 kcal./mole.

Chains, carried on by free radicals, are not involved in the reaction since addition of cyclohexene (25—280 mm.) at 440°, where the catalysed reaction is *ca.* 95% of the total reaction, does not change the rate significantly, and at 500°, propene, produced in the reaction or introduced at the beginning, does not affect the rate. The reaction is homogeneous, since no significant increase in rate is observed when it takes place in a vessel with surface : volume ratio 8 times that of the unpacked vessel.

Apparently similar reactions occur with isopropyl alcohol and hydrogen chloride (>440°) and with ethanol and hydrogen bromide (>470°). Experimental difficulties have prevented their complete investigation.

The catalyses of the dehydrations of t-butanol by both hydrogen bromide (315—422°) and hydrogen chloride (328—454°) occur at temperatures well below those for the uncatalysed decomposition (>500°) and can be fully studied (Parts I and II). However, for isopropyl alcohol, a small amount of uncatalysed decomposition occurs in the same

---

[12] Siggia, " Quantitative Organic Analysis," Wiley, New York, 1954, p. 31.

temperature range (>450°) as that for catalysis by hydrogen bromide (370—520°). Even so, evidence that a slower and probably similar reaction takes place with hydrogen chloride was obtained. For ethanol the catalysed decompositions are evidently slower still, and catalysis by hydrogen bromide in this case does not take place at measurable rates below 470°, where uncatalysed decomposition is also occurring at a comparable speed. A rough value for the comparative rates of catalysis by hydrogen bromide is:

$$\text{t-butyl} : \text{isopropyl} : \text{ethyl alcohol} = 1 : 2 \times 10^{-2} : 1 \times 10^{-3}.$$

The authors thank Dr. Allan Maccoll for his interest in this work, The Chemical Society and I.C.I.A.N.Z. for grants for equipment, and Mr. E. J. Watson for the gas-chromatography results.

University of New England,
Armidale, N.S.W., Australia.

[*Received, November* 16*th*, 1959.]