121. *Catalysis by Hydrogen Halides in the Gas Phase. Part VI.* Butan-2-ol and Hydrogen Bromide.*

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A homogeneous, molecular, gas-phase decomposition of butan-2-ol into but-1-ene, *cis*- and *trans*-but-2-ene, and water, catalysed by hydrogen bromide at 387—510°, is described. Comparison of the rate with that for propan-2-ol and hydrogen bromide shows that substitution at the β-carbon atom has only a minor effect.

Rates of gas-phase dehydration of various alcohols catalysed by hydrogen bromide have been determined (cf. previous Parts [1]), and indications are that substitution at the α-carbon atom affects the rate much more than does substitution at the β-carbon atom.

There are numerous references to the thermal decomposition of butan-2-ol on the surface of solids at temperatures even as low as 90°. Dehydration and dehydrogenation generally occur together and their proportions vary over wide limits depending on the nature of the catalyst, pressure of butan-2-ol, and temperature; in general, metals favour dehydrogenation, and acids or acidic oxides and halides dehydration. In the presence of hydrogen bromide, however, water and n-butenes are produced in the gas phase at measurable rates at 387—510°, and this reaction is now described.

Experimental

Materials.—Butan-2-ol (B.D.H.), fractionated through a 12 in. column of Fenske helices with a Whitmore–Lux head, had b. p. 96·1° (±0·1°)/677 mm. Weissberger *et al.*[2] give

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* Part V, *J.*, 1961, 1392.

[1] Parts I—V, *J.*, 1960, 2836, 3087, 3090, 3920; *J.*, 1961, 1392.

[2] Weissberger, Proskauer, Riddick, and Toops, " Organic Solvents," Interscience Publ., Inc., New York, 1955, p. 95.

96·5°/677 mm. (calc.). The hydrogen bromide, propene, and cyclohexene used have been described previously.[1]

Apparatus and Procedure.—The apparatus and procedures used were similar to those described in previous Parts.[1] The "blow-in" technique [1] was used always. In general 100—200 mm. each of the alcohol and hydrogen bromide were used. The surface was coated with the decomposition products of cyclopropane at 490°. The reaction was followed by means of the pressure increase. The value of p_f/p_0 was 1·87 ± 0·03 (mean of 16 values at various temperatures); a similar value (1·88) was obtained in the presence of propene. This value is comparable with 1·86 found by Maccoll and Thomas [3] under similar conditions in the pyrolysis of s-butyl bromide.

In the pyrolysis of s-butyl bromide at 300—350°, the equilibrium $Bu^sBr \rightleftharpoons n\text{-}C_4H_8 + HBr$ was found to lie well to the right, so that no allowance for it has been made at the temperatures used in this work, 387—510°.

Uncatalysed decomposition of the alcohol occurred at all temperatures used, and is probably induced by radicals formed in small quantities from the continuous decomposition of polymers in the surface coating. It was roughly of the first order for a small proportion of reaction, and a small correction (generally *ca.* 10%) for it was made to the catalysed rate constants. Propene inhibited this uncatalysed decomposition, and rates of the catalysed reaction at 440·3°, 474·4°, 487·8°, and 510·2° were measured in the presence of propene (up to 294 mm). Cyclohexene is a more effective inhibitor of radical chains than propene but it decomposes above 450° under our conditions. It has therefore been used at 435°, where it is reasonably stable.

Products.—In two experiments butan-2-ol (224 mm., 66·4 mg.; 148 mm., 43·8 mg.) reacted to completion with hydrogen bromide (255; 225 mm.) at 444·6°. The products were expanded directly into an evacuated 5-l. bulb containing magnesium perchlorate and calcium hydroxide, where water and hydrogen bromide were absorbed. The residue was trapped and weighed (Found: 48·8; 32·3 mg. Calc. as butene: 50·3; 33·2 mg.). Chromatography on a column like that described in Part III [1] gave peaks for but-1-ene (*ca.* 27%) and *cis*- and *trans*-but-2-ene (*ca.* 32% and 41%) which were completely separated. The equilibrium proportions at this temperature, calculated from the data given by Rossini *et al.*[4] are 21, 31, and 48%, respectively. As considerable inaccuracy can be ascribed to both the experimental and the calculated proportions it is likely that these values are comparable.

Butan-2-ol (240 mm., 70·9 mg.) reacted to completion with hydrogen bromide (98 mm.) at 446·2°. The products were pumped through a U-bend at −80°, from which water was collected on an anhydrous calcium sulphate plug [5] (Found: 16·1 mg. Calc. 17·2 mg.).

In order to check that the extent of reaction could be inferred from the increase in pressure, butene, produced after various times at 446·2° and isolated as described above, was estimated by its reaction with bromine in glacial acetic acid, with the following result:

Time (min.)	94	62	35	23	10·5
Reaction (%) (by pressure increase)	82·7	78·1	56·8	40·4	25·9
Reaction (%) (by analysis)	84·5	80·2	56·4	38·4	27·9

RESULTS AND DISCUSSION

The gas-phase dehydration of butan-2-ol, catalysed by hydrogen bromide, occurs at measurable rates at 387—510°. A small amount of uncatalysed decomposition accompanies the reaction. The catalysed reaction is represented stoicheiometrically by the equation $Bu^sOH + HBr \longrightarrow n\text{-}C_4H_8 + H_2O + HBr$ and is of the first order in each reactant; *e.g.*, consistent first-order rate constants proportional to the pressures of hydrogen bromide were found for pressures of 83—376 mm. of butan-2-ol and 56—363 mm. of hydrogen bromide at 454·2° (cf. Table 1). No induction periods were observed.

The Arrhenius equation

$$k_2 = 5{\cdot}8 \times 10^{12} \exp(-34{,}900/\boldsymbol{R}T) \text{ (sec.}^{-1}\text{ c.c. mole}^{-1}\text{)}$$

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[3] Maccoll and Thomas, *J.*, 1955, 2445.

[4] Rossini *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, 1953.

[5] Lauder and Wilson, *Austral. J. Chem.*, 1961, **14**, 166.

represents the variation of rate with temperature (cf. Table 2), and the graph shows that the nature of the reaction is unaltered by addition of propene and cyclohexene. The reaction is homogeneous since increase by a factor of 8 in the surface : volume ratio of the reaction vessel had no significant effect on the rate (cf. Table 3). Additions of large amounts of propene (up to 294 mm.) and cyclohexene (up to 140 mm.), inhibitors of radical-chain mechanisms in similar reactions,[6] caused no change in the rate (cf. Tables 4 and 5, and Figure); hence the reaction is considered to be a molecular one.

TABLE 1.

Variation of rate with pressures of butan-2-ol and hydrogen bromide at 454·2°.

p(HBr) (mm.)	$p(\mathrm{Bu^sOH})$ (mm.)	10^5k (sec.$^{-1}$)	$10^7k_1/p_{\mathrm{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)	p(HBr) (mm.)	$p(\mathrm{Bu^sOH})$ (mm.)	10^5k (sec.$^{-1}$)	$10^7k_1/p_{\mathrm{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)
363	83	141	37	150	193	63	38
280	154	107	36	137	267	60	39
277	158	112	38	120	209	51	37
218	161	83	35	119	287	53	39
205	212	82	37	83	268	42	43
180	272	81	41	68	376	36	43
173	320	72	38	56	225	31	44
172	284	75	40				Mean 39 ± 2

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

TABLE 2.

Variation of rate with temperature.

Temp.	510·2°	487·8°	474·4°	474·4°	467·2°	454·2°	446·2°
No. of runs	2 *	5 *	5 *	7	10	16	11
$10^7k_1/p_{\mathrm{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)	233	111	78	74	68	39	35
k_1/p_{HBr} (sec.$^{-1}$ c.c. mole^{-1})	1140	527	364	345	314	177	157
Temp.	440·3°	435·8°	424·6°	413·6°	404·1°	387·4°	
No. of runs	4 *	10	11	4	8	3	
$10^7k_1/p_{\mathrm{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)	25·3	22·5	18·7	9·8	8·2	3·8	
k_1/p_{HBr} (sec.$^{-1}$ c.c. mole^{-1})	113	99	81	42	35	15·6	

* With addition of propene.

TABLE 3.

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

Temp.	No. of runs	p(HBr) (mm.)	$p(\mathrm{Bu^sOH})$ (mm.)	$10^7k/p_{\mathrm{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)
446·2°	12	63—221	150—219	39 ± 3
424·6	10	101—180	133—206	20 ± 2

TABLE 4.

Rates with added propene at 474·4°.

$p(\mathrm{C_3H_6})$ (mm.)	p(HBr) (mm.)	$p(\mathrm{Bu^sOH})$ (mm.)	10^5k_1 (sec.$^{-1}$)	$10^7k_1/p_{\mathrm{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)
183	103	190	85	83
214	103	168	75	73
217	191	120	144	75
252	193	89	158	82
294	102	147	78	76
				Mean 78 ± 4

TABLE 5.

Rates with added cyclohexene at 435·8°.

$p(\mathrm{C_6H_{10}})$ (mm.)	p(HBr) (mm.)	$p(\mathrm{Bu^sOH})$ (mm.)	10^5k_1 (sec.$^{-1}$)	$10^7k_1/p_{\mathrm{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)
108	132	193	27	20
125	118	192	22	19
140	62	129	13	21

The three possible butenes, *viz.*, but-1-ene, *cis*- and *trans*-but-2-ene, were produced in approximately their equilibrium proportions. Since the methylbutenes from the similar decomposition of t-pentyl alcohol were isomerised in the presence of hydrogen bromide or hydrogen chloride to their equilibrium mixture (Parts IV and V [1]), the present proportions

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

may be the result of subsequent isomerisation, even though n-butenes are not expected to be as reactive as methylbutenes. At present then, it is not possible to say in what proportion the various butenes were produced from the elimination.

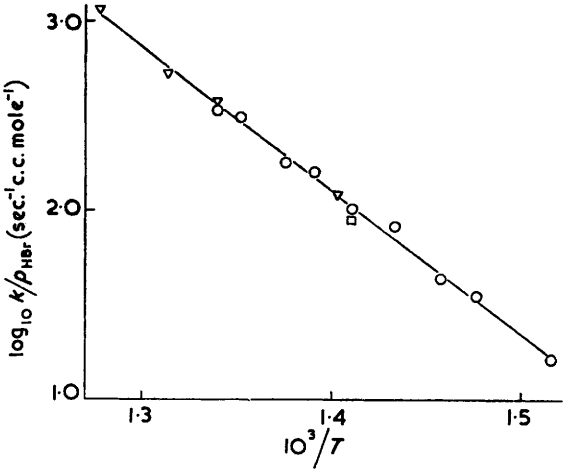

FIG. 1. ○ Bu^sOH and HBr. △ With added propene. □ With added cyclohexene.

The rate of hydrogen bromide-catalysed dehydration of butan-2-ol is only 1·9 times that of propan-2-ol at 430°, *i.e.*, substitution of a methyl group at the β-position of the alcohol has very little effect on the rate of reaction. This result agrees with that observed for the tertiary alcohols, where the relative rate for t-pentyl : t-butyl alcohol is 1·8 : 1 (365°), and contrasts markedly with the effect of substitution at the α-position, *e.g.*, t-butyl : isopropyl and t-pentyl : 2-butyl alcohol, where the relative rates are 62 : 1 (400°) and 57 : 1 (400°), respectively.

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