616. *Catalysis by Hydrogen Halides in the Gas Phase. Part II.* t-Butyl Alcohol and Hydrogen Chloride.*

By K. G. Lewis and V. R. Stimson.

A homogeneous, molecular, gas-phase decomposition of t-butyl alcohol into water and isobutene, catalysed by hydrogen chloride at temperatures of 328—454°, is described.

Bell and Burnett[1] have shown that hydrogen bromide catalyses the decomposition of acetaldehyde in the gas phase at 430° 30 times faster than does hydrogen chloride. The uncatalysed gas-phase dehydration of t-butyl alcohol[2] into water and isobutene takes place above 500°. When catalysed by hydrogen bromide it occurs at 315—422° and is a homogeneous, molecular reaction (Part I *). The kinetics of this reaction, catalysed by hydrogen chloride at temperatures of 328—454°, are now described.

Experimental

The reactions were followed by observing the increase of pressure with time. Hydrogen chloride was prepared from hydrochloric and sulphuric acids; t-butyl alcohol and cyclohexene were prepared as described in Part I. The apparatus and procedure are also described in Part I. The " blow-in " technique was used in nearly all the runs. The value of p_f/p_0 was *ca.* 1·92. At the three highest temperatures a correction for the uncatalysed reaction amounting to not more than 5% of the rate was applied. Our results are presented in Tables 1—5.

Table 1. *Effect of hydrogen chloride on the rate at* 439·3°.

p_{HCl} (mm.)	p_{BuOH} (mm.)	10^5k (sec.$^{-1}$)	10^5k_1 * (sec.$^{-1}$)	$10^7k_1/p_{HCl}$ (sec.$^{-1}$ mm.$^{-1}$)
—	585	2·5	—	—
74	258	33	30	40
93	198	35	32	35
155	172	65	62	40
155	276	60	57	37
187	112	80	77	41
192	220	72	69	36
210	131	80	77	37
				Mean 38 ± 2

* k_1 is the first-order rate constant corrected for the uncatalysed reaction.

Table 2. *Variation of rate with temperature.*

Temp.	No. of runs	$10^7k_1/p_{HCl}$ (sec.$^{-1}$ mm.$^{-1}$)	k_1/p_{HCl} (sec.$^{-1}$ mole^{-1} c.c.)
454·4°	3	63	290
439·3	7	38	170
425·0	10	25	107
410·1	36	15·0	64
395·5	6	7·7	32
383·5°	3	5·5	23
371·1	5	3·0	12·0
357·0	2	2·3	9·0
341·1	2	1·13	4·3
328·2	2	0·67	2·5

Table 3. *Rates with added cyclohexene at* 410° *and water at* 371°.

$p_{C_6H_{10}}$ (mm.)	p_{HCl} (mm.)	p_{BuOH} (mm.)	$10^7k_1/p_{HCl}$ (sec.$^{-1}$ mm.$^{-1}$)
56	137	157	14·5
91	285	125	13·0
120	234	314	13·5
140	134	99	14·8
142	182	168	14·0
225	222	142	13·7
243	55	120	14·0
301	72	93	16·5

p_{H_2O} (mm.)	p_{HCl} (mm.)	p_{BuOH} (mm.)	$10^7k_1/p_{HCl}$ (sec.$^{-1}$ mm.$^{-1}$)
192	359	154	3·2
299	208	169	3·0

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* Part I, *J.*, 1960, 2836.

[1] Bell and Burnett, *Trans. Faraday Soc.*, 1939, **35**, 474.

[2] Schultz and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 395; Barnard, *Trans. Faraday Soc.*, 1959, **55**, 947.

TABLE 4. *Rates with hydrogen bromide and hydrogen chloride together at* 371°.

			Found	Calculated		
p_{HBr} (mm.)	p_{HCl} (mm.)	p_{BuOH} (mm.)	10^5k_1 (sec.$^{-1}$)	10^5k_{HBr} (sec.$^{-1}$)	10^5k_{HCl} (sec.$^{-1}$)	10^5k_1 (sec.$^{-1}$)
84	60	263	63	69	1·8	71
96	67	205	90	79	2·0	81
12·7	287	128	18·0	10·4	8·6	19·0
5·7	129	296	8·3	4·7	3·9	8·6

TABLE 5. *Rates in packed vessels:* $10^7k/p_{\text{HCl}}$ (sec.$^{-1}$ mm.$^{-1}$).

	S/V (cm.$^{-1}$)				S/V (cm.$^{-1}$)				S/V (cm.$^{-1}$)		
Temp.	0·9	3·7	7·7	Temp.	0·9	3·7	7·7	Temp.	0·9	3·7	7·7
454°	63	65 ± 5	57 ± 5	410°	15·0	13·8 ± 1	23 ± 1	371°	3·0	3·5 ± 0·2	7·3 ± 0·2

Products.—After five half-lives at 454° the products from the reaction of t-butyl alcohol (426 mm., 163 mg.) and hydrogen chloride (66 mm., 12·5 mg.) were expanded directly into a 5 l. bulb containing magnesium perchlorate (10 g.) and barium oxide (1 g.). The residual gas was trapped and weighed (Found: 108·7 mg., 88% yield as isobutene). When chromatographed over Celite–acetoacetic ester this gas gave a single peak corresponding to that of isobutene [3] prepared from t-butyl alcohol. Molera and Stubbs [4] have shown that pyrolysis of isobutene commences at 580° so that no decomposition is likely under our conditions (<450°).

The reaction products from t-butyl alcohol (448 mm., 171 mg.) and hydrogen chloride (84 mm., 15·9 mg.), after seven half-lives at 454°, were trapped, isobutene was allowed to evaporate, and water in the residue, which also contained hydrogen chloride but no carbonaceous material, was estimated from the microanalysis (Found: 42·1 mg. Theor., 41·6 mg.).

Homogeneity of the Reaction.—Rates of reaction were also measured in vessels packed with concentric glass tubes so that the surface : volume ratios were 7·7 and 3·7 cm.$^{-1}$, *i.e.*, 8 and 4 times the value for the unpacked vessel. More than one surface of the type mentioned before was used at each temperature. About 7 values of the rate were obtained in each case. A value of p_f/p_0 = 1·89 was found. The rates (cf. Table 5) were less consistent, but, except for one case, comparable with those for the unpacked vessel, indicating that the reaction occurred mainly in the gas phase. At 371° in the vessel of surface : volume ratio (S/V) = 7·7 cm.$^{-1}$ the rate was high by a factor of 2·4, which is still not comparable with the increase in S/V, whereas very little increase in rate was found for the vessel of S/V = 3·7 cm.$^{-1}$ (factor = 1·16). In general, greater difficulty in obtaining a suitably " cured " surface has been experienced with hydrogen chloride-catalysed reactions than with similar reactions involving hydrogen bromide. Often after the vessel had been coated with allyl bromide it has been necessary to leave hydrogen chloride-catalysed reaction mixtures in it for several days before consistent values of the rate have been obtained. This has been especially the case with packed vessels. It seems likely that products of the allyl bromide decomposition remaining adsorbed on the surface can affect the rate of hydrogen chloride-catalysed reactions considerably, and this is a possible explanation of the high rate found for the case mentioned above.

Rates in the Presence of Cyclohexene.—Cyclohexene has been used as an inhibitor [5] up to 418°. In order to test for the presence of free radicals, rates with various pressures of cyclohexene were measured at 410°. No significant reduction in rate was found (Table 3). Reactions involving free radicals are more likely to be present at the higher temperatures, and if another reaction of this type occurred above 410°, a change in activation energy might be expected. The reaction appears to be a molecular one between 328° and 454°.

RESULTS AND DISCUSSION

The decomposition of t-butyl alcohol in the gas phase is catalysed by hydrogen chloride at measurable rates at temperatures of 328—454° (cf. Table 1), which are considerably lower than those for the uncatalysed decomposition,[2] *viz.*, 505—550°. The reaction is stoicheiometrically:

$$\text{t-C}_4\text{H}_9\text{·OH} + \text{HCl} \longrightarrow \text{iso-C}_4\text{H}_8 + \text{H}_2\text{O} + \text{HCl}$$

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[3] Hurd and Spence, *J. Amer. Chem. Soc.*, 1929, **51**, 3561.
[4] Molera and Stubbs, *J.*, 1952, 384.
[5] Maccoll and Thomas, *J.*, 1957, 5033.

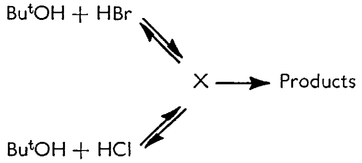
Isobutene was the only hydrocarbon found in the products and no gas uncondensed in liquid air was detected. The reaction is substantially homogeneous and follows the rate equation

$$-d[Bu^tOH]/dt = k_2[Bu^tOH][HCl]$$

e.g., individual runs were of the first order and the first-order rate constants so obtained were proportional to the initial pressure of hydrogen chloride (cf. Table 1). At 410°, 36 runs with a range of initial pressures of 110—358 mm. of the alcohol and 43—496 mm. of hydrogen chloride gave $10^7k_1/p_{HCl} = 15{\cdot}0 \pm 0{\cdot}8$ sec.$^{-1}$ mm.$^{-1}$. The rate of the reaction follows the Arrhenius equation $k_2 = 2{\cdot}0 \times 10^{12} \exp(-32{,}700/\boldsymbol{R}T)$ sec.$^{-1}$ c.c. mole^{-1} between 328° and 454°. The activation energy is slightly higher than that found for the same reaction catalysed by hydrogen bromide, *viz.*, 30·4 kcal./mole, and very much lower than that for the uncatalysed decomposition,[2] *viz.*, 65·5 or 54·5 kcal./mole. In the temperature range 328—423° the rate with hydrogen bromide is *ca.* 26 times as fast as that with hydrogen chloride, a value very close to that found by Bell and Burnett [1] for the relative rates of catalysis of the decomposition of acetaldehyde, *viz.*, 30.

Additions of cyclohexene (56—301 mm.), a very effective inhibitor of free-radical mechanisms in the closely related decompositions of alkyl bromides,[5] had no significant effect on the rate at 410° (cf. Table 2), which suggests that the reaction is a molecular one. Additions of water (192 and 299 mm.) had no effect on the rate at 371° (cf. Part I).

The kinetic features of the gas-phase dehydrations of t-butyl alcohol catalysed by hydrogen bromide and hydrogen chloride are very similar, and it seems likely that they occur by analogous mechanisms. Possible mechanisms for the former have been discussed in Part I. The fact that the rate constant with hydrogen chloride is less than that with hydrogen bromide is consistent with each of them. In the presence of hydrogen chloride and hydrogen bromide together, the two catalysed reactions occur independently: with comparable pressures of each catalyst the effect of hydrogen bromide is preponderant, and with comparably effective quantities of each the rates are additive (cf. Table 4). These facts eliminate possible mechanisms which contain an equilibrium with a common intermediate (X) with fast reversible steps, *e.g.*,



Evans and Polanyi [6] have suggested that the gaseous polymerisation of isobutene in the presence of Friedel–Crafts catalysts and water is initiated by the formation of a t-butyl cation and is carried on by a carbonium-ion mechanism. Hydrogen chloride, however, is ineffective as a catalyst for this reaction. In the present experiments the major product was isobutene; no evidence of polymerisation was observed, but a small amount would have escaped detection.

The authors thank Dr. Allan Maccoll for his interest, and The Chemical Society and I.C.I.A.N.Z. for grants for equipment.

UNIVERSITY OF NEW ENGLAND,
ARMIDALE, N.S.W., AUSTRALIA.

[*Received, November* 17*th*, 1949.]

[6] Evans and Polanyi, *J.*, 1947, 252.