778. Catalysis by Hydrogen Halides in the Gas Phase. Part IV.* t-Pentyl Alcohol and Hydrogen Bromide.

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A homogeneous, gas-phase, molecular decomposition of t-pentyl alcohol into pentenes and water, catalysed by hydrogen bromide in the temperature range 308—415°, is described. The three methylbutenes are produced, their proportions have been measured, and the significance of this is discussed.

THE homogeneous, gas-phase, molecular decompositions of t-butyl alcohol into isobutene and water, catalysed by hydrogen bromide and by hydrogen chloride, have been described in Parts I and II.[1] The close resemblance of the reactions in solution of t-pentyl compounds to those of t-butyl compounds is well known, and several examples have also been observed in the gas-phase, *viz.*, the uncatalysed dehydrations of the alcohols[2] at 480—550°, the dehydrochlorinations of the chlorides[3] at 270—350°, the dehydrobrominations of the bromides[4] at 220—280°, and the elimination of acetic acid from the acetates[5] at *ca.* 260°. In all cases these are molecular reactions and the t-pentyl compound reacts slightly faster than does the t-butyl compound. The kinetics of the gas-phase elimination of water from t-pentyl alcohol catalysed by hydrogen bromide are now described (see Tables 1—4).

TABLE 1. *The effect of hydrogen bromide on the rate at* 359·1°.

p_{HBr} (mm.)	37	60	79	92	96	96	103	121	243
$p_{\text{C}_5\text{H}_{11}\cdot\text{OH}}$ (mm.)	127	182	183	138	164	125	152	180	200
10^5k (sec.$^{-1}$)	37	62	85	100	99	97	113	125	266
$10^7k/p_{\text{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)	100	103	107	108	103	101	109	103	109
								Mean	105 ± 3

EXPERIMENTAL

Materials.—t-Pentyl alcohol, fractionated through a column of Fenske helices (12″) fitted with a Whitmore–Lux head, had b. p. 99·0° ± 0·2°/675 mm. and n_D^{20} 1·4061. Weissberger

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* Part III, Ross and Stimson, *J.*, 1960, 3090.

[1] Part I, Maccoll and Stimson, *J.*, 1960, 2836; Part II, Lewis and Stimson, *J.*, 1960, 3087.

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

[3] Brearly, Kistiakowsky, and Stauffer, *J. Amer. Chem. Soc.*, 1936, **58**, 43.

[4] Harden and Maccoll, *J.*, 1955, 2454; Harden, *J.*, 1957, 5024.

[5] Rudy and Fugassi, *J. Phys. Chem.*, 1948, **52**, 357; Emovon and Maccoll, "Theoretical Organic Chemistry," Butterworths, London, 1959, p. 243.

et al.[6] give b. p. 99·0°/675 mm. (calc.), n_D^{20} 1·4058. Hydrogen bromide and cyclohexene were prepared as described in Part I. The pentenes used for identifying the products, *viz.*, 2-methylbut-2-ene, 2-methylbut-1-ene, and 3-methylbut-1-ene, obtained from Phillips Petroleum Company, were 99% pure.

Procedure (cf. Parts I—III).—The reaction was followed by observation of the increase in pressure (p_0 and p_f are initial and final pressures): $p_f/p_0 = 1{\cdot}92 \pm 0{\cdot}01$ (22 values), which is a reasonable result for this type of apparatus (cf. Part I). From consideration of the corresponding case of isobutene, an equilibrium between the pentenes and hydrogen bromide is to be expected at lower temperatures; however, as no significant correction for it was necessary in the decomposition of t-pentyl bromide [4] at 233—269°, it was believed to have a negligible effect at 308—415°. Decomposition of t-pentyl alcohol alone was not observed at 415°, and this agrees with the results of Schultz and Kistiakowsky, so that no corrections for uncatalysed reaction were necessary.

Products.—In two runs, t-pentyl alcohol (239, 167 mm.; 136·6, 95·3 mg.) reacted to completion with hydrogen bromide (46, 67 mm.) at 393°. The products were expanded directly into a 5-l. bulb containing magnesium perchlorate and calcium hydroxide. After some time the remaining gas was trapped and weighed (Found: 107·4, 76·1 mg. Theoretical yield as pentene: 108·5, 75·8 mg.).

t-Pentyl alcohol (201 mm., 112·2 mg.) and hydrogen bromide (47 mm.) reacted to completion at 408°. The products were trapped and swept out with dry nitrogen at room temperature. Water in the residue, which contained no carbonaceous material but some hydrogen bromide, was estimated from the microanalysis (Found: 23·9 mg. Theoretical yield: 23·0 mg.).

Pentenes.—The gas–liquid chromatography apparatus described in Part III adequately separated 2-methylbut-2-ene, 2-methylbut-1-ene, and 3-methylbut-1-ene for which typical retention times were 17·9, 13·9, and 8·9 min., respectively. A quantitative estimation of them to an accuracy of *ca.* ±2% was made by measuring the areas under the curves, *e.g.*, a mixture of composition 2-methyl-but-2-ene (74%) and -but-1-ene (26%), measured by pressures, was prepared. Analysis as described above gave 2-methyl-but-2-ene (75%) and -but-1-ene (25%).

t-Pentyl alcohol (256 mm.) and hydrogen bromide (42 mm.) reacted to completion at 393° ($10^7k/p_{\text{HBr}} = 280$ sec.$^{-1}$ mm.$^{-1}$). The products, after being kept over calcium hydroxide and magnesium perchlorate, were chromatographed (Found: 2-methylbut-2-ene, 68; 2-methylbut-1-ene, 28; 3-methylbut-1-ene, 4%). Similar results (±2%) were found from a number of runs.

Isomerisation of the Methylbutenes.—2-Methylbut-2-ene (144 mm.) and hydrogen bromide (57 mm.) reacted for 5 min. at 393°. After the treatment described above, the products were 2-methylbut-2-ene (69%), 2-methylbut-1-ene (27%), and 3-methylbut-1-ene (4%).

2-Methylbut-1-ene (150 mm.) and hydrogen bromide (58 mm.) reacted for 5 min. at 393°. After treatment as described above, the products were 2-methylbut-2-ene (71%), 2-methylbut-1-ene (25%), and 3-methylbut-1-ene (4%). After 40 min. alone at 393°, 2-methylbut-1-ene was unchanged.

No other products were found. If straight-chain pentenes had also been formed in their equilibrium proportions, *cis*- and *trans*-pent-2-ene would have been produced in easily detectable amounts.[8] Such a reaction would have involved the breaking of the skeletal structure. Under our conditions the isomerisation occurs at temperatures above 230° and 290° with hydrogen bromide and hydrogen chloride, respectively. The kinetics of this reaction are being investigated and it appears that at 393° in the presence of hydrogen bromide isomerisation is instantaneous.

Rates with Added Inhibitor.—The addition of cyclohexene (up to 300 mm.) to the present reaction mixtures caused no significant change in rate (Table 3) at 370° or 408°. A value of $p_f/p_0 = 1{\cdot}90 \pm 0{\cdot}03$ (10 values) was found.

Homogeneity of the Reaction. —Rates were measured at 344° and 314° in a vessel packed with concentric glass tubes at even spacings (*ca.* 3 mm.) having surface : volume ratio of 7·7 cm.$^{-1}$, *i.e.*, a value 8 times that of the unpacked vessel. Values of $10^7k/p_{\text{HBr}}$ of 77 and 32 sec.$^{-1}$ mm.$^{-1}$, respectively, were found (Table 4), and these rates are 10% and 30% higher than those found in the unpacked vessel. In view of the increase in surface area these increases in rate are not significant and the reaction can be considered essentially homogeneous above 314°. A few runs

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[6] Weissberger, Proskauer, Riddick, and Toops, " Organic Solvents," Interscience, New York, 1955, p. 102.

performed at temperatures below 314° indicate that the Arrhenius plot curves towards lower activation energies below 300°, and this, taken in conjunction with the 30% increase in rate at 314°, may mean the incursion of a heterogeneous reaction below 300°. Similar behaviour was found in the case of t-butyl alcohol and hydrogen bromide.

RESULTS AND DISCUSSION

In marked contrast to the uncatalysed decomposition,[2] which does not occur at a measurable rate below 487°, the gas-phase dehydration of t-pentyl alcohol catalysed by hydrogen bromide occurs at measurable rates in the temperature range 308—415°. The reaction is stoicheiometrically $\text{t-C}_5\text{H}_{11}\cdot\text{OH} + \text{HBr} \longrightarrow \text{C}_5\text{H}_{10} + \text{H}_2\text{O} + \text{HBr}$. No gas uncondensed at liquid-air temperature was detected. The reaction is of first order in both t-pentyl alcohol and hydrogen bromide, since individual runs were of the first order and the rate constants were proportional to the pressure of hydrogen bromide: *e.g.*, at 344° sixteen consistent values of k/p_{HBr} were obtained with initial pressures of 88—413 mm. of the alcohol and 24—319 mm. of hydrogen bromide. The rate follows the Arrhenius equation $k_2 = 1{\cdot}02 \times 10^{12} \exp(-27{,}100/\boldsymbol{R}T)$ sec.$^{-1}$ c.c. mole^{-1}, and is 1·6—2·0 times that of the similar reaction of t-butyl alcohol. Results are summarised in Tables 1 and 2.

The reaction is essentially homogeneous, as the small increase in rate which occurs when a packed vessel is used is not comparable with the increase in surface : volume ratio (Table 4). Addition of cyclohexene (9—320 mm.), an effective inhibitor of radical chains in the decompositions of alkyl bromides,[7] has no significant effect on the rate at 370° and 408° (Table 3). There were no indications of induction periods. These facts, coupled with the low activation energy (27·1 kcal./mole), make it likely that the reaction is a molecular one.

TABLE 2. *Variation of rate with temperature.*

Temp.	415·1°	408·9°	392·5°	383·5°	370·8°	365·2°	359·1°	344·6°	328·7°	314·8°	308·6°
No. of values	4	7	7	10	9	8	9	16	6	11	5
$10^7 k/p_{\text{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)	600	515	308	232	160	130	105	69	42	24·2	22·3
k/p_{HBr} (sec.$^{-1}$ mole^{-1} c.c.)	2580	2190	1280	950	640	520	415	265	157	88	80

TABLE 3. *Rates with added cyclohexene.*

Temp.	370·8°	370·8°	370·8°	370·8°	370·8°	370·8°	408·9	408·9°	408·9°	408·9°	408·9°
$p_{\text{C}_6\text{H}_{10}}$ (mm.)	24	118	120	148	166	320	9	56	82	239	301
p_{HBr} (mm.)	132	133	122	68	210	99	48	43	43	85	91
$p_{\text{C}_5\text{H}_{11}\cdot\text{OH}}$ (mm.)	116	114	105	175	96	63	115	120	105	141	111
$10^7 k/p_{\text{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)	161	153	151	151	156	144	530	500	500	480	530

TABLE 4. *Rates in a packed vessel* ($S/V = 7{\cdot}7$ cm.$^{-1}$).

Temp.	344·6°	344·6°	344·6°	344·6°	344·6°	344·6°	314·8°	314·8°	314·8°	314·8°	314·8°	314·8°
p_{HBr} (mm.)	55	60	72	73	77	99	113	156	164	182	191	237
$p_{\text{C}_5\text{H}_{11}\cdot\text{OH}}$	145	178	151	200	151	154	186	117	152	85	145	95
$10^5 k$ (sec.$^{-1}$)	40	45	58	55	65	75	35	52	52	65	63	70
$10^7 k/p_{\text{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)	73	75	80	75	84	76	31	33	32	36	33	30

The olefins which result from the elimination under these conditions are 2-methylbut-2-ene, 2-methylbut-1-ene, and 3-methylbut-1-ene in approximately equilibrium proportions (cf. Table 5). However, this proportion is the result of their subsequent

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

[8] Calculated from data given by Rossini *et al.*, " Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, 1953. The estimated error allows for a variation of 10% in the proportions of the major components.

TABLE 5. *Proportion (%) of methylbutenes in equilibrium.*[8]

Temp. (° K)	300	400	500	600	700	800
2-Methylbut-1-ene	11·1	19·8	26·9	33·2	38·0	42·0
3-Methylbut-1-ene	0·2	0·8	1·8	3·2	4·8	6·5
2-Methylbut-2-ene	88·7	79·4	71·3	63·6	57·2	51·5

isomerisation in the presence of hydrogen bromide which also accounts for the presence of 3-methylbut-1-ene. The proportions in which the olefins are produced from the catalysed dehydrations and the rates per branch are not known.

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