266. *Catalysis by Hydrogen Halides in the Gas Phase. Part V.*[1] *t-Pentyl Alcohol and Hydrogen Chloride.*

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A homogeneous, gas-phase, molecular decomposition of t-pentyl alcohol into 2-methylbut-2- and -1-ene, 3-methylbut-1-ene, and water, catalysed by hydrogen chloride in the temperature range 370—503°, is described.

Hydrogen bromide and hydrogen chloride catalyse the gas-phase dehydration of t-butyl alcohol at 315—422° and 328—454° respectively.[1] The similar dehydration of t-pentyl alcohol catalysed by hydrogen bromide [1] occurs at 308—415°. This reaction, catalysed by hydrogen chloride, is now described.

Experimental

The materials used and experimental procedures have been described in previous Parts.[1] As only a small correction for the equilibrium between pentenes and hydrogen chloride was necessary in the study [2] of the decomposition of t-pentyl chloride at 270—326°, it was neglected in the present work; $p_f/p_0 = 1{\cdot}91 \pm 0{\cdot}03$ (20 values). As t-pentyl alcohol undergoes uncatalysed decomposition [3] at a measurable rate above 480°, a small correction for this (*ca.* 10%) was made to the catalysed rates at 496° and 503°, where $t_{0\cdot5} < 5$ min. Under our conditions

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[1] Parts I, II, III, and IV, *J.*, 1960, 2836, 3087, 3090, 3920.
[2] Brearley, Kistiakowsky, and Stauffer, *J. Amer. Chem. Soc.*, 1936, **58**, 43.
[3] Schultz and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 395.

at 496° $10^3k_1 = 0{\cdot}27$ sec.$^{-1}$ for the uncatalysed reaction, a value slightly lower than that found by Schultz and Kistiakowsky.[3]

Although cyclohexene is a more effective inhibitor than propene,[4] it cannot be used above *ca.* 440° where its own decomposition commences. It was accordingly used at 439° and propene was used at 450° and 475°.

Products.—In two experiments t-pentyl alcohol (233 mm., 124 mg.; 251 mm., 134 mg.) and hydrogen chloride (106, 114 mm.) reacted to completion at 439°, giving $10^7k_1/p_{\rm HCl} = 58$, 57 sec.$^{-1}$ mm.$^{-1}$ respectively. The products were expanded directly into a 5-l. bulb containing magnesium perchlorate and calcium hydroxide. After *ca.* 15 min., the remaining gas was trapped and weighed (Found: 94, 109 mg. Theor. as pentene: 99, 107 mg.). The proportions of the various pentenes were estimated by gas chromatography within *ca.* 5% as described in Part IV[1] (Found: 2-methylbut-2-ene, 67, 70%; 2-methylbut-1-ene, 31, 28%; and 3-methylbut-1-ene, 2, 2%). The three methylbutenes were found in approximately similar proportions in several other experiments at various temperatures. The temperatures used did not cause the cracking of these hydrocarbons, for which 500—600° appears to be necessary. Retention times were identical with those of authentic samples and different from those of pent-1-ene and *cis*- and *trans*-pent-2-ene made from pentan-2-ol.

t-Pentyl alcohol (225 mm., 1·30 mmoles) and hydrogen chloride (60 mm.) reacted to completion at 475°. The products were separated at −80° and water, whose microanalysis showed very little carbon and chlorine, was estimated after adsorption on a drying agent (Found: 1·32 mmole).

Isomerisation of Methylbutenes.—2-Methylbut-2-ene (129 mm.) and hydrogen chloride (42 mm.) reacted at 393° for 3 hr. After removal of hydrogen chloride with magnesium perchlorate and calcium hydroxide as above the products were: 2-methylbut-2-ene 70%, 2-methylbut-1-ene 25%, and 3-methylbut-1-ene 5%. On similar treatment 2-methylbut-1-ene (148 mm.) and hydrogen chloride (101 mm.) gave 2-methylbut-2-ene 68%, 2-methylbut-1-ene 29%, and 3-methylbut-1-ene 3%. In similar experiments without hydrogen chloride no change of 2-methylbut-2- or -1-ene was found. The above compositions evidently correspond to that at equilibrium, as the equilibrium composition at 393° (see Part IV) calculated from tabulated data[5] is: 2-methylbut-2-ene 59·7%, 2-methylbut-1-ene 35·9%, and 3-methylbut-1-ene 4·4%. Considerable uncertainty attaches to these data which are based on incomplete spectroscopic measurements.[6]

RESULTS AND DISCUSSION

Whereas the uncatalysed decomposition of t-pentyl alcohol occurs only above *ca.* 480°, in the presence of hydrogen chloride pentenes and water are produced at measurable rates at 370—503° (Table 2), in a reaction apparently analogous to that with hydrogen bromide[1] at 308—415°, namely: $\mathrm{CMe_2Et{\cdot}OH + HCl \longrightarrow C_5H_{10} + H_2O + HCl}$. No gas uncondensed in liquid air or lower hydrocarbon was detected. The rate follows the relation, $-\mathrm{d[ROH]}/\mathrm{d}t = k_2\mathrm{[ROH][HCl]}$; *i.e.*, since [HCl] remains constant, individual runs are of the first order. At 410° the first-order rate constants are proportional to $p_{\rm HCl}$ for initial pressures of 63—398 mm. of hydrogen chloride and 85—344 mm. of t-pentyl

TABLE 1. *Variation of rate at* 410° *with pressure of hydrogen chloride.*

$p_{\rm HCl}$ (mm.)	$p_{\rm ROH}$ (mm.)	10^5k_1 (sec.$^{-1}$)	$10^7k_1/p_{\rm HCl}$ (sec.$^{-1}$ mm.$^{-1}$)	$p_{\rm HCl}$ (mm.)	$p_{\rm ROH}$ (mm.)	10^5k_1 (sec.$^{-1}$)	$10^7k_1/p_{\rm HCl}$ (sec.$^{-1}$ mm.$^{-1}$)	$p_{\rm HCl}$ (mm.)	$p_{\rm ROH}$ (mm.)	10^5k_1 (sec.$^{-1}$)	$10^7k_1/p_{\rm HCl}$ (sec.$^{-1}$ mm.$^{-1}$)
63	92	12·6	20·0	168	126	33	19·7	235	97	48	20·4
76	237	15·5	20·4	194	167	34	17·6	287	138	58	20·2
97	207	19·4	20·0	196	163	36	18·4	398	89	73	18·3
109	344	23·0	21·1	208	137	42	20·2			Mean	19·8 ± 0·6
133	85	27	20·3	215	103	45	20·9				

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

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

[6] Kilpatrick, Prosen, Pitzer, and Rossini, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 559.

alcohol (Table 1). The Arrhenius equation $k_2 = 6{\cdot}7 \times 10^{12} \exp(-34{,}000/\boldsymbol{R}T)$ (sec.$^{-1}$ c.c. mole^{-1}) describes the rate between 370° and 503°.

At 410° the rate of catalysis by hydrogen bromide is 27 times that with hydrogen chloride, and this ratio is approximately the value of their relative catalytic powers in the other cases so far studied. It also agrees with their approximate relative catalytic effects (20—40 : 1) on the decomposition of acetaldehyde and that predicted from the energies of gas-phase heterolytic dissociation of the hydrogen halides.[7] As for t-butyl alcohol, the activation energy for the reaction with hydrogen chloride is a few kcal. higher than with hydrogen bromide.

TABLE 2. *Variation of rate with temperature.*

Temp.	503·9°	496·2°	486·6°	475·0°	463·6°	450·2°	439·2°	410·0°	370·3°
No. of runs	4	5	7	8	7	10	19	13	4
$10^7k_1/p_{HCl}$ (sec.$^{-1}$ mm.$^{-1}$)	330	270	220	175	115	85	57	19·8	4·3
k_1/p_{HCl} (sec.$^{-1}$ c.c. mole^{-1}	1620	1300	1050	820	530	384	254	85	17·2

TABLE 3. *Rates with added cyclohexene at* 439° *and propene at* 450° *and* 475°.

Temp.	No. of runs	$p_{C_6H_{10}}$ (mm.)	p_{HCl} (mm.)	p_{ROH} (mm.)	$10^7k_1/p_{HCl}$ (sec.$^{-1}$ mm.$^{-1}$)
439°	6	43—300	129—202	117—192	54 ± 4
		$p_{C_3H_6}$			
450	7	9—356	94—185	104—194	91 ± 7
475	7	29—280	50—132	86—237	180 ± 9

TABLE 4. *Rates in packed vessels,* $10^7k/p_{HCl}$ (sec.$^{-1}$ mm.$^{-1}$).

Temp.	S/V 1·0 cm.$^{-1}$	S/V 3·6 cm.$^{-1}$	No. of runs	S/V 9 cm.$^{-1}$	No. of runs
370°	4·3	5·6 ± 0·4	6	6·8 ± 0·5	5
410	19·7	23 ± 1	7	26 ± 1	5
450	82	94 ± 2	7	100 ± 9	7

As increase of the surface : volume ratio of the reaction vessel does not significantly affect the rate (Table 4), the reaction is considered to be homogeneous. Indications that a heterogeneous reaction also occurs at *ca.* 340° were noted but not investigated; this behaviour has also been found in the cases of other alcohols.[1] As no induction periods were observed, and additions of up to 300 mm. of cyclohexene or propene, effective inhibitors of free-radical chains in similar systems,[4] had no effect on the rate (Table 3), the reaction is believed to be molecular.

The pentenes produced are 2-methylbut-2- and -1-ene, and 3-methylbut-1-ene in approximately their equilibrium proportions. Whereas the first two are usually found in the decompositions of t-pentyl compounds, the third must have been produced subsequently, presumably by catalysed isomerisation which occurs in our conditions. This may also account for the proportions. Preliminary measurements on the rate of isomerisation show that it is comparable with that of the decomposition, so that the proportion in which the pentenes are produced initially is not known.

TABEL 5. *Comparative rates of gas-phase reactions of t-pentyl and t-butyl compounds.*

Reaction	Temp.	Factor	Ref.
Uncatalysed dehydrn. of alcohols	505°	2·3	3
Dehydrochlorin. of chlorides	313	2·2	2
Dehydrobromin. of bromides	240	3·2	[a]
Elimin. of AcOH from acetates	260	1·4	8
Dehydrn. of alcohols catalysed by HBr	315—383	2·0	1
Dehydrn. of alcohols catalysed by HCl	340—440	1·5	1

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

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

The rate is 1·4—1·5 times as fast as that of the corresponding reaction of t-butyl alcohol. Evidently the effect of substitution at the β-carbon atom is much smaller than that produced by substitution at the α-carbon atom[1] where the rate increases by a factor of *ca.* 60. The relative rates of the gas-phase reactions of t-pentyl and t-butyl compounds that are known to be homogeneous, molecular reactions are listed in Table 5. In all cases the t-pentyl compound reacts faster by a factor of *ca.* 2. In view of the quite different types of mechanism proposed for the decompositions of the alkyl halides and acetates[8] no conclusions about the mechanism of the catalysed reactions can be drawn by use of analogy.

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[8] Maccoll, " Theoretical Organic Chemistry," Butterworths, London, 1959, p. 230.