

**573.** *Catalysis by Hydrogen Halides in the Gas Phase.\**  
*Part I. t-Butyl Alcohol and Hydrogen Bromide.*

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A homogeneous, molecular, gas-phase decomposition of t-butyl alcohol into water and isobutene, catalysed by hydrogen bromide at 315—422°, is described. Possible mechanisms are discussed.

IN an attempt to find examples of acid-catalysis in the gas phase, Bell and Burnett<sup>1</sup> chose decompositions of molecules which contained a basic oxygen atom, *e.g.*, paraldehyde, dioxan, acetaldehyde. In general the results were not very conclusive—catalysis was not general and when it did occur the reactions were often seriously affected by the surface of the reaction vessel. A similar result was found by Winkler and Hinshelwood<sup>2</sup> for the reaction of methanol and hydrogen chloride in the gas phase. For the decomposition of acetaldehyde<sup>1b</sup> to carbon monoxide and methane at 430°, however, hydrogen bromide was found to be a powerful catalyst, the reaction was probably largely homogeneous and of first order, and its rate was roughly proportional to the pressure of hydrogen bromide. This result was also observed by Howlett and Barton<sup>3</sup> in their study of the decompositions of alkyl chlorides in the presence of acetaldehyde. Hydrogen bromide was found to be a more effective catalyst than hydrogen chloride by a factor of 20—40, and Bell and Burnett<sup>1b</sup> consider it probable that the catalysis may be attributed to its acidic properties.

\* Preliminary report, *Proc. Chem. Soc.*, 1958, 80.

<sup>1</sup> Bell and Burnett, *Trans. Faraday Soc.*, (a) 1937, **33**, 355; (b) 1939, **35**, 474.

<sup>2</sup> Winkler and Hinshelwood, *Trans. Faraday Soc.*, 1935, **31**, 1739.

<sup>3</sup> Howlett and Barton, *Trans. Faraday Soc.*, 1949, **45**, 735.

The thermal decomposition of *t*-butyl alcohol to water and isobutene has been studied by Schultz and Kistiakowsky<sup>4</sup> in the temperature range 505–551°. The reaction is homogeneous and unimolecular and has an activation energy of 65.5 kcal./mole. We now describe a catalysed<sup>5</sup> decomposition of this substance into the same products in the presence of hydrogen bromide; this occurs at temperatures of 315–425°, is homogeneous and molecular, and has a much lower activation energy (30.4 kcal. mole<sup>-1</sup>).

### EXPERIMENTAL

*Materials.*—*t*-Butyl alcohol, b. p. 82.1° ( $\pm 0.1^\circ$ )/751 mm., was obtained by fractionation of *t*-butyl alcohol (B.D.H.) through a 4-foot column of Fenske helices; its purity was checked by vapour chromatography. Hydrogen bromide was prepared from bromine and tetralin<sup>6</sup> and purified by several distillations through a trap at  $-80^\circ$ . Cyclohexene was freed from peroxides and fractionated.<sup>7</sup>

*Apparatus and Technique.*—The apparatus was similar to that described by Maccoll:<sup>8</sup> an aluminium-block furnace in which the temperature could be controlled to *ca.* 0.2° was used as a thermostat. The reactions were carried in all-glass vessels of *ca.* 250 c.c. capacity, the surfaces of which had been coated with the products of decomposition of allyl bromide. The course of a reaction was followed by observing the increase in pressure with time. Three vessels were used: (i) unpacked of surface : volume ratio 0.9 cm.<sup>-1</sup>, and (ii) reaction vessels of similar capacity, packed with concentric glass tubes at even spacings, having surface to volume ratios of 3.5 and 7 cm.<sup>-1</sup> severally. From time to time, especially with the packed vessels, control runs with *t*-butyl bromide<sup>9</sup> were carried out in order to ensure that the surface coatings were in good order. The heated capillary inlet to the vessel contained a U bend which could be heated or cooled.

Two methods were used to introduce the reactants: (i) Hydrogen bromide was distilled into the U bend, then evaporated, and its pressure was measured; it was then condensed back into the vessel-side of the U bend, and *t*-butyl alcohol was distilled into the other arm. The U bend was then quickly warmed, the hydrogen bromide evaporating into the vessel first. The total pressure was then found by extrapolation of the pressure readings to zero time. (ii) Alternatively, *t*-butyl alcohol was distilled into the reaction vessel, and its pressure measured. Hydrogen bromide was then introduced from a reservoir at a higher pressure by quickly opening the outlet tap. Both methods gave the same result.

When cyclohexene was added the "distil-in" method (i) was used, a previously measured amount of cyclohexene being introduced with the *t*-butyl alcohol; when water was added, water and the alcohol were successively distilled into the reaction vessel, their pressure was measured, and then hydrogen bromide was introduced. Green and Maccoll<sup>7</sup> detected an equilibrium between cyclohexene, hydrogen bromide, and cyclohexyl bromide, lying well towards dissociation at 350°. At 410°, then, addition of cyclohexene is not likely to reduce the concentration of hydrogen bromide substantially. Cyclohexene has been used successfully as an inhibitor<sup>10</sup> up to 418°.

*Kinetic Measurements.*—As the pressure increased by an amount nearly equal to that of the *t*-butyl alcohol used, the pressure of this substance at time *t* was calculated from  $p_{\text{Bu}} = 2p_0 - p_t$ , where  $p_t$  is the total pressure at time *t*, and  $p_0$  the initial pressure. The reaction was found to follow the first-order rate law up to about 50% decomposition. The fall-away from first-order behaviour towards the end of the reaction is due, at least partly, to the fact that  $p_f/p_0 \sim 1.86 \pm 0.02$  (mean of 14 values at various temperatures) ( $p_f$  = final pressure). This ratio was apparently not changed by alterations in temperature or in the relative proportions of the reactants. A value of  $p_f/p_0$  of 1.8–1.9 has usually been found for the decompositions of the

<sup>4</sup> Schultz and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 395.

<sup>5</sup> Hinshelwood, "Kinetics of Chemical Change," Oxford, 1940, p. 240.

<sup>6</sup> Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1957, p. 182.

<sup>7</sup> Green and Maccoll, *J.*, 1955, 2449.

<sup>8</sup> Maccoll, *J.*, 1955, 965.

<sup>9</sup> Harden and Maccoll, *J.*, 1955, 2454.

<sup>10</sup> Maccoll and Thomas, *J.*, 1957, 5033.

alkyl bromides.<sup>11</sup> The difference between this value and that expected, *viz.*, 2.0, has been attributed to the dead space, polymerisation of the products, and establishment of an equilibrium, etc. The equilibrium between *t*-butyl bromide, isobutene, and hydrogen bromide has been measured<sup>12</sup> and makes it clear that at the temperatures used in this work the association of isobutene and hydrogen bromide is negligible. Calculation, using Allen's formula,<sup>13</sup> shows that a dead space of 5% would be necessary to reduce  $p_f/p_0$  to 1.87. The pyrolysis of isobutene<sup>14</sup> occurs at temperatures above 600° with an activation energy of *ca.* 55 kcal. mole<sup>-1</sup>, and its polymerisation<sup>15</sup> at these temperatures occurs only at high pressures. Steacie and Shane<sup>16</sup> found that *ca.* 0.1% of di-isobutene was formed in 60 min. at 400° at an initial pressure of 60 cm. of isobutene. Schultz and Kistiakowsky<sup>4</sup> found very little decomposition of isobutene at 505–551° under conditions similar to those of the present experiments. No induction periods were observed.

*Reliability of the Rate Constants.*—In general, the consistency of reproduction of the rate constant was not good (Table 1), the variation being over a range of *ca.* 10%, which is slightly

TABLE I. *Effect of hydrogen bromide on the rate of dehydration of t-butyl alcohol at 370°.*

$p_{\text{HBr}}$ (mm.)	$p_{\text{BuOH}}$ (mm.)	$10^5 k_1$ (sec. <sup>-1</sup> )	$10^6 k_1/p_{\text{HBr}}$ (sec. <sup>-1</sup> /mm.)	$p_{\text{HBr}}$ (mm.)	$p_{\text{BuOH}}$ (mm.)	$10^5 k_1$ (sec. <sup>-1</sup> )	$10^6 k_1/p_{\text{HBr}}$ (mm. sec. <sup>-1</sup> )
23	316	20	8.7	64	273	55	8.6
39	247	31	8.0	68 (b)	238	52	7.7
40	71	33	8.3	92	341	74	8.1
46	243	33	7.2	99 (b)	210	92	9.3
48	331	43	8.9	104	315	75	7.2
55 (b)	361	43	7.8	113 (b)	504	87	7.7
63	374	56	8.9	276 (b)	273	223	8.1
Mean 8.2 ± 0.4							

Runs marked (b) were performed by using the "blow-in" technique (ii); otherwise the "distil-in" method (i) was used.

greater than is usually found in this type of work.\* In addition to the usual sources of error, *e.g.*, the nature of the surface, the dead space,  $p_f/p_0$  being less than 2, temperature control, determination of  $t_0$  and  $p_0$ , there is the difficulty of ensuring the proper mixing of the two reactants at the start of the reaction. However, within this rather large error-range similar rate constants have been found in a large number of experiments using different surface coatings.

At 410° and 422° corrections, never amounting to more than 4% of the rate, were necessary, in order to allow for the uncatalysed decomposition of *t*-butyl alcohol.

*Analysis of the Products.*—*t*-Butyl alcohol (316 mm., 126.5 mg.) and hydrogen bromide (27 mm.) were allowed to react to completion at 410°. The products were expanded directly into a 5-l. bulb containing magnesium perchlorate (10 g.) and calcium oxide (1 g.) and set aside for 3 hr., and the remaining gas was then trapped and weighed (Found: 97 mg., 101% as isobutene). This gas was identified as isobutene by vapour chromatography. Not even traces of hydrogen or hydrocarbon other than isobutene were detected. From a similar experiment the products were trapped at liquid-air temperature, and the system swept with dry nitrogen. Water was then determined by microanalysis and collection on magnesium perchlorate (Found: 29 mg. Calc.: 34 mg.; yield 86%).

\* *Note added in proof:* Barnard (*Trans. Faraday Soc.*, 1959, **55**, 947) has now verified the unimolecular nature of the *t*-butyl alcohol decomposition, but finds  $k_1 = 10^{11.51} \exp(-54,500/RT)$  sec.<sup>-1</sup>, the rate, frequency factor, and activation energy being lower than those found by Schultz and Kistiakowsky; Thomas (personal communication) has observed an activation energy of *ca.* 60 kcal. mole<sup>-1</sup>. These altered values do not effect the present arguments.

<sup>11</sup> For leading references see: Daniels and Goldberg, *J. Amer. Chem. Soc.*, 1957, **79**, 1314; Maccoll *et al.*, *J.*, 1955 *et seq.*

<sup>12</sup> Kistiakowsky and Stauffer, *J. Amer. Chem. Soc.*, 1937, **59**, 165; Howlett, *J.*, 1957, 2834.

<sup>13</sup> Allen, *J. Amer. Chem. Soc.*, 1934, **56**, 2053.

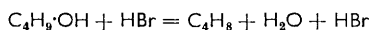
<sup>14</sup> Hurd, "The Pyrolysis of Carbon Compounds," Reinhold, New York, 1929, p. 78; Hurd and Spence, *J. Amer. Chem. Soc.*, 1929, **51**, 3561; Hurd and Blunck, *ibid.*, 1937, **59**, 1869.

<sup>15</sup> McKinley, Stevens, and Baldwin, *J. Amer. Chem. Soc.*, 1945, **67**, 1955.

<sup>16</sup> Steacie and Shane, *Canad. J. Res.*, 1938, **16**, B, 210.

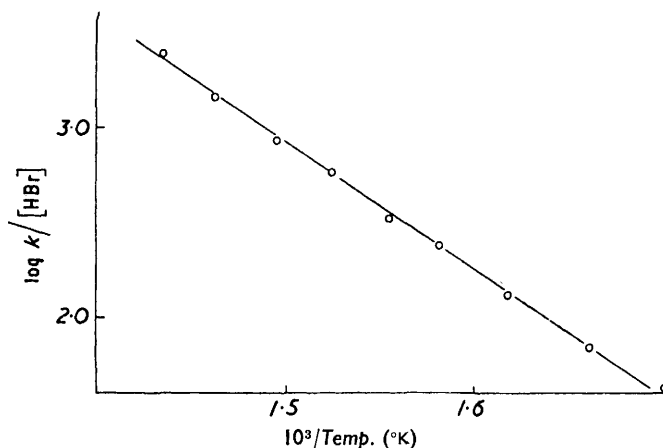
## RESULTS AND DISCUSSION

Hydrogen bromide catalyses the decomposition of t-butyl alcohol at 217—422° at measurable rates, whereas the uncatalysed decomposition does not occur at an appreciable rate below 450°. The reaction is stoichiometrically



The reaction follows the rate equation  $-d[\text{Bu}^t\text{OH}]/dt = k_2[\text{Bu}^t\text{OH}][\text{HBr}]$ . Individual runs are of the first order and the first-order rate constants so obtained are proportional to the pressure of hydrogen bromide, without significant variation, for pressures of 71—500 mm. of the alcohol and 23—270 mm. of hydrogen bromide (Table 1). The reaction is homogeneous between 315° and 422°, since increases of surface : volume ratio by factors

*The Arrhenius plot between 315° and 422°.*



of 4 and 8 do not alter the rate significantly (Table 2). However, at temperatures below 315° a heterogeneous reaction appears; at 267° about half, and at 217° probably all, of

TABLE 2. Rates in packed vessels.

Temp.	No. of runs	$10^7 k_1 / p_{\text{HBr}}$ (mm. sec. <sup>-1</sup> )	Ratio of rates in packed and unpacked vessels	Temp.	No. of runs	$10^7 k_1 / p_{\text{HBr}}$ (mm. sec. <sup>-1</sup> )	Ratio of rates in packed and unpacked vessels
		$S/V = 3.5 \text{ cm.}^{-1}$				$S/V = 7 \text{ cm.}^{-1}$	
370°	3	78	0.95	370°	4	130	1.6
315	3	12.8	1.09	315	4	18	
267	3	6.2	2.2	267	4	10	
217	3	2.8	3.4	217	2	7.5	9

$S$  = Surface;  $V$  = volume.

the reaction takes place on the surface. Evidently the heterogeneous reaction has the same kinetic form as the homogeneous reaction, for, at 267°, the first-order rate constant is proportional to the pressure of hydrogen bromide, for pressures of 53—536 mm. of hydrogen bromide and 124—537 mm. of t-butyl alcohol (14 runs).

The Arrhenius equation, obeyed between 315° and 422° (see Table 3 and Figure), gives  $k_2 = 9.22 \times 10^{12} \exp(-30,400/RT)$  mole<sup>-1</sup> ml. sec.<sup>-1</sup>. As Schultz and Kistiakowsky give  $k_1 = 4.8 \times 10^{14} \exp(-65,500/RT)$  sec.<sup>-1</sup> for the uncatalysed decomposition at temperatures above 500°, the catalysis is accompanied by a marked decrease in activation energy. Below 315° the Arrhenius plot curves towards lower activation energies and  $E$

for the surface reaction is probably *ca.* 10 kcal. mole<sup>-1</sup>. Bell and Burnett have calculated that the energy required for the formation of a reasonable dipole is 5 kcal. mole<sup>-1</sup> less at the surface of the reaction vessel than in the gas phase.

TABLE 3. Variation of rate with temperature.

Temp.	No. of runs	$10^7 k_1/p_{\text{HBr}}$ (mm. sec. <sup>-1</sup> )	$k_1/p_{\text{HBr}}$ (sec. <sup>-1</sup> mole <sup>-1</sup> ml.)	Temp.	No. of runs	$10^7 k_1/p_{\text{HBr}}$ (mm. sec. <sup>-1</sup> )	$k_1/p_{\text{HBr}}$ (sec. <sup>-1</sup> mole <sup>-1</sup> ml.)
422.7°	3	570	2460	344.4°	2	33	128
410.4	3	340	1440	328.5	3	18.3	69
396.6	5	207	860	315.0	4	11.7	43
383.4	5	138	570	267.0	14	2.8	9.5
370.6	13	82	330	217.2	4	0.83	2.5
359.1	2	60	236				

TABLE 4. Rates with added cyclohexene at 410° and water at 370°.

$p_{\text{C}_6\text{H}_{10}}$	$p_{\text{HBr}}$	$p_{\text{BuOH}}$	$10^6 k_1/p_{\text{HBr}}$ (mm. sec. <sup>-1</sup> )	$p_i/p_0$	$p_{\text{H}_2\text{O}}$	$p_{\text{HBr}}$	$p_{\text{BuOH}}$	$10^6 k_1/p_{\text{HBr}}$ (mm. sec. <sup>-1</sup> )	$p_i/p$
66	27	413	37		35	147 (b) *	164	7.3	
160	24	313	35		256	174 (b)	191	8.3	1.90
180	27	212	35	1.86	382	60 (b)	145	7.0	
205	38	269	31						
206	24	80	27						

\* (b): see Table 1.

Addition of cyclohexene (66—206 mm.) has no marked effect on the rate at 410° (see Table 4). As cyclohexene is a powerful inhibitor of the chain mechanisms in decompositions of alkyl bromides proceeding by dual unimolecular-radical chain mechanisms,<sup>17</sup> its lack of effect suggests a molecular mechanism in this case. Addition of water (35—382 mm.) has no effect on the rate at 370° (Table 4).

Apparently similar reactions, faster with hydrogen iodide and slower with hydrogen chloride, have been observed but not confirmed. The former case is complicated, however, by the production of iodine, which may arise from isobutene and hydrogen iodide in a manner analogous to that found by Holmes and Maccoll for propene.<sup>18</sup>

Three mechanisms for the reaction seem inherently likely: (i) *t*-Butyl bromide and water might be formed by the reaction  $\text{Bu}^t\text{OH} + \text{HBr} = \text{Bu}^t\text{Br} + \text{H}_2\text{O}$ . Under the conditions of the present experiments *t*-butyl bromide<sup>9</sup> decomposes into isobutene and hydrogen bromide at measurable rates at temperatures of 230—280° with an activation energy of 42 kcal. mole<sup>-1</sup>, so that at 315°, the lowest temperature where the reaction is homogeneous, its decomposition would be instantaneous, and thus the concentration of hydrogen bromide and the first-order increase in pressure unimpaired. A four-centre transition state (IA) for reaction (i) is not likely because of the steric resistance to approach of a large bromine atom to the central carbon atom of a *t*-butyl group. On this side of the *t*-butyl alcohol molecule the bromine must approach under the influence of the similarly electronegative oxygen rather than of the carbon, reaching the van der Waals radius of the former when the internuclear distance from the latter is still 3.98 Å, if an undistorted molecule is considered. Moreover, the valency forces of the central carbon atom are not favourably disposed towards additional bonding on this side.<sup>19</sup> As Meer and Polanyi<sup>20</sup> have pointed out, the dipole field of the *t*-butyl alcohol molecule will cause the most likely approach of hydrogen bromide to be as in (IB). The consequences of such a reaction scheme lead to a greater energy discrepancy than is found for case (iii) (below).

If the formation of the transition state depends merely on the polar conjunction of the two molecules, and the time for this process is of the order of the time between collisions,

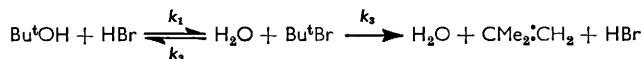
<sup>17</sup> Green and Maccoll, ref. 8; Maccoll and Thomas, *J.*, 1957, 5033.

<sup>18</sup> Holmes and Maccoll, *Proc. Chem. Soc.*, 1957, 175.

<sup>19</sup> Cowdrey, Hughes, Ingold, Mastermann, and Scott, *J.*, 1937, 1252.

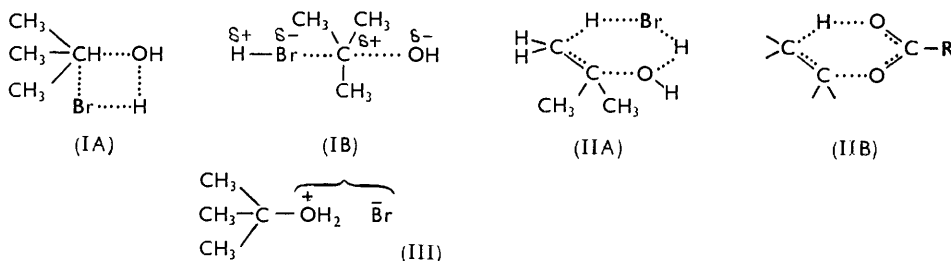
<sup>20</sup> Meer and Polanyi, *Z. phys. Chem.*, 1932, B, 19, 164.

water ( $\mu = 1.84$ ), a molecule more polar than t-butyl alcohol ( $\mu = 1.66$ ), might be expected to destroy the transition state before reaction could take place. Experimentally, water produced in the reaction, or added initially, has no effect on the rate (Table 4). This fact also rules out the scheme



with  $k_2 \gg k_1$  and  $k_3$ . While reaction (i) is kinetically feasible, the detailed mechanism by which it might take place gives rise to considerable difficulty.

(ii) A six-membered ring transition state (IIA) may be envisaged whereby the bromine atom makes a nucleophilic attack on a hydrogen attached to  $\text{C}_\beta$  by means of its lone-pair electrons, while the oxygen atom is protonated by the hydrogen atom. The polarity of the hydrogen bromide molecule fits such a scheme. This transition state is somewhat analogous to that proposed<sup>21</sup> for the pyrolysis of esters (IIB). Contributing factors to the transition state (IIA) would be: the energy of heterolytic dissociation of hydrogen bromide, the basicity of the oxygen atom in t-butyl alcohol, the nucleophilic power of the bromine atom, and the energy of dissociation of the  $\beta$ -carbon-hydrogen bond.



(iii) Protonation at the oxygen atom of t-butyl alcohol by the hydrogen bromide accompanied by ion-pair formation (III). Recent reviewers<sup>22</sup> of the unimolecular gas-phase eliminations of alkyl halides have emphasised their close resemblance to the corresponding reactions in solution and have proposed a heterolytic mechanism accompanied by ion-pair formation. The energy discrepancy in the present case is considerable. Whereas 312 kcal. are required for the heterolysis of hydrogen bromide,<sup>1b</sup> the major energy contributions to this transition state are: the activation energy, 30 kcal.; the formation of an O—H bond, *ca.* 100 kcal.; and the coulombic energy of an ion-pair, say, 3 Å separation, 110 kcal. A continuous range of possible transition states may be envisaged between (II) and (III).

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<sup>21</sup> Rudy and Fugassi, *J. Phys. Chem.*, 1948, **52**, 357; Warwick and Fugassi, *ibid.*, 1948, **52**, 1314; Maccoll, *J.*, 1958, 3398.

<sup>22</sup> Ingold, *Proc. Chem. Soc.*, 1957, 279; Maccoll, *ibid.*, 1958, 301; Maccoll, "Theoretical Organic Chemistry," p. 230, Butterworths, London, 1959.