80. *Catalysis by Hydrogen Halides in the Gas Phase. Part VIII.*[1] *Methyl t-Butyl Ether and Hydrogen Bromide.*

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A homogeneous, molecular, gas-phase decomposition of methyl t-butyl ether into isobutene and methanol, catalysed by hydrogen bromide at 258—371°, is described. It is faster than the corresponding reaction of t-butyl alcohol, and in general an increase in rate accompanies increased basicity of the oxygen atom. Methyl bromide is formed subsequently, probably by a heterogeneous reaction.

Gas-phase dehydration of alcohols catalysed by hydrogen halides has been observed in a number of cases.[1] It seems likely that this reaction is a general one and several mechanisms have been suggested (Part I [1]). They are such that it should be possible for an ether to undergo the same type of reaction. The results for the gas-phase decomposition of methyl t-butyl ether catalysed by hydrogen bromide are now presented.

Experimental

Materials and Procedure.—Methyl t-butyl ether, prepared by the method of Norris and Rigby [2] and refluxed over sodium, had b. p. 51·6° ± 0·1°/677·5 mm. after fractionation through 12 in. of Fenske helices. Gas chromatography showed no impurity. The other materials used and the general procedure have been described in previous Parts.[1] A surface coating formed by the pyrolysis of allyl bromide at temperatures >350° and the "blow-in" technique (Part I) were used. The equilibrium $i\text{-}C_4H_8 + HBr \rightleftharpoons t\text{-}C_4H_9Br$, has been measured [3] for temperatures up to 258°, where the extent of combination at the pressures used in this work is *ca.* 9%. As measurements of rate were made only at the beginning of the reaction and at higher temperatures (259—371°) and the accuracy of the rates is not great (*ca.* 5%; cf. Table 1), no corrections for the equilibrium were made. The value of p_f/p_0 found was 1·93 (64 observations under all experimental conditions). As free radicals are more likely to contribute to reaction at the higher temperatures, cyclohexene, a well-tested inhibitor of radical chains,[4] was used at 321°, 336°, 352°, and 361°. Green and Maccoll,[5] using similar experimental procedures, found that no correction for the equilibrium, Cyclohexene + HBr $\rightleftharpoons$ Cyclohexyl bromide, was necessary at 295—355°, so none was applied in the present case.

Products.—In a number of experiments the products of the reaction between methyl t-butyl ether and hydrogen bromide for times $t_{0{\cdot}1}$—$5t_{0{\cdot}5}$ and at temperatures 258—361° were expanded directly into an evacuated 5-l. bulb containing fresh magnesium perchlorate and powdered calcium hydroxide or sodium hydroxide pellets. After being kept for *ca.* 15 min. the remaining gas was trapped, separated into two fractions according to its volatility at −80°, and examined by gas chromatography. The products detected in these experiments were isobutene, methanol, and methyl bromide. At the higher temperatures the proportion of methyl bromide found decreased. To check the above procedure, methyl t-butyl ether (91 mm.) and hydrogen bromide (70 mm.), after 1 min. at 274°, were treated as described above; only methyl t-butyl ether and no reaction product was then found. This shows that reaction is not caused by the subsequent analytical treatment.

Estimation of Isobutene.—In two experiments methyl t-butyl ether (218, 116 mm.; 1·72, 0·91 mmole) and hydrogen bromide (163, 148 mm.) reacted to completion at 274°. The products were expanded directly into a 5-l. bulb containing magnesium perchlorate and calcium hydroxide; the materials volatile at −80° (isobutene and methyl bromide) were treated with an excess of bromine (5·04, 0·995 mmole) in acetic acid at room temperature. The remaining bromine was estimated by use of potassium iodide and standardised sodium thiosulphate

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[1] Maccoll and Stimson, *Proc. Chem. Soc.*, 1958, 80; Parts I—VI, *J.*, 1960, 2836, 3087, 3090, 3920; 1961, 1392; 1962, 653.

[2] Norris and Rigby, *J. Amer. Chem. Soc.*, 1932, **54**, 2095.

[3] Kistiakowsky and Stauffer, *J. Amer. Chem. Soc.*, 1937, **59**, 165; Howlett, *J.*, 1957, 2834.

[4] Maccoll and Thomas, *J.*, 1957, 5033; Thomas, *J.*, 1959, 1192; Harden and Maccoll, *J.*, 1959, 1197; Green, Maccoll, and Thomas, *J.*, 1960, 184.

[5] Green and Maccoll, *J.*, 1955, 2449.

solution (Found, as isobutene: 1·65, 0·85 mmole). To check the above procedure, isobutene (165 mg.) and bromine (534 mg.) were mixed in acetic acid at room temperature and the excess of bromine was estimated as above (isobutene found: 160 mg.). Although there was less than an equimolar amount of hydrogen bromide in the first of the above experiments, all of it could not have been converted into methyl bromide as the reaction reached completion.

Reaction of Methanol with Hydrogen Bromide.—The reaction products obtained from methanol (126 mm., 0·99 mmole) and hydrogen bromide (247 mm.) after 22 hr. at 274° were expanded directly into a 5-l. bulb containing magnesium perchlorate and calcium hydroxide. After being kept for 15 min. the residue was trapped and weighed (Found: 97 mg., 1·02 mmoles as methyl bromide, the only product by gas chromatography). In a similar experiment with methanol (117 mm., 0·93 mmole) and hydrogen bromide (161 mm.), the products were slowly pumped directly through a plug of granulated dried calcium sulphate,[6] trapped in liquid air, and returned for 15 min. to a 5-l. bulb containing magnesium perchlorate and calcium hydroxide; then methyl bromide only (0·89 mmole) remained. Water (0·98 mmole) was collected from the calcium sulphate plug by heating it. Similar experiments for times of 1—3 hr. showed that reaction was not then complete. With methanol (173 mm., 1·18 mmoles) and hydrogen bromide (323 mm.) at 361° for 60 hr., only methyl bromide (1·12 mmoles) was found; thus decomposition does not occur under these conditions. Methyl bromide, by itself and in the presence of hydrogen bromide, decomposes at 400—500°, temperatures well above those used in this investigation, with loss of volatile material.[7] During the formation of methyl bromide no permanent gas was produced and no change in pressure $>1\%$ occurred, so that the increase in pressure due to the ether decomposition should not be impaired by this reaction; however, as hydrogen bromide is consumed the rate of the ether decomposition will fall. As the latter reaction was generally followed to $< t_{0\cdot5}$, this was not a serious complication.

Uncatalysed Decomposition.—At temperature >430° methyl t-butyl ether decomposes at measurable rates into isobutene, methanol, and small amounts of isobutane and gas uncondensed in liquid air. Isobutane is one of the products of the likely radical decomposition of the ether as a result of homolysis of the t-butyl–oxygen bond, *e.g.*,

$$\begin{aligned} \mathrm{Bu^tOMe} &\longrightarrow \mathrm{Bu^{t}\cdot + MeO\cdot} \\ \mathrm{Bu^{t}\cdot + Bu^tOMe} &\longrightarrow \mathrm{Isobutane + Bu^tO{\cdot}CH_2{\cdot}} \\ \mathrm{Bu^tO{\cdot}CH_2{\cdot}} &\longrightarrow \mathrm{Bu^{t}\cdot + Other\ Products} \end{aligned}$$

as t-butyl radicals produce isobutane by hydrogen abstraction and disproportionation.[8] Isobutene may arise from molecular or radical decomposition. Over most of the temperature range used for the catalysis there was also a small amount of decomposition not directly due to the hydrogen bromide added, and this may have been caused by hydrogen bromide adsorbed on the surface and radicals or atoms slowly but continuously produced from the surface coating. While detracting from the accuracy of the results this did not seriously interfere with the investigation.

Gas Chromatography.—In addition to the column described in Part III, a 5-ft. column of 40% w/w silicone M.S. 550 on Celite 545 was also used at 72°. Typical retention times for the latter were: isobutene, 160; methanol, 185; methyl bromide, 257; methyl t-butyl ether, 530 sec.

RESULTS AND DISCUSSION

Whereas uncatalysed gas-phase pyrolysis of methyl t-butyl ether does not occur below 430°, its decomposition in the presence of hydrogen bromide has been followed in the temperature range 258—371°. Below 250° the rates became unreliable, presumably owing to incursion of a surface reaction. This type of behaviour has been found in a number of other cases (cf. previous Parts). Initially isobutene and methanol are produced. A subsequent reaction between methanol and hydrogen bromide, giving methyl bromide and water, occurs at a comparable rate. For the analogous case of hydrogen chloride and

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

[7] Meissner and Schumacher, *Z. phys. Chem.*, 1939, *A*, **185**, 435; Whittingham, *Discuss. Faraday Soc.*, 1947, **2**, 175.

[8] Birrell and Trotman-Dickenson, *J.*, 1960, 4218.

methanol at 450°, Winkler and Hinshelwood[9] showed that methyl chloride and water were produced in a heterogeneous reaction and it is likely that the reaction with hydrogen bromide is similar.

The rate of the catalysis at 305° is proportional to the initial pressure of hydrogen bromide for pressures of 47—322 mm. of hydrogen bromide and 101—284 mm. of the ether (cf. Table 1).

The Arrhenius equation

$$k_2 = 6{\cdot}7 \times 10^{11} \exp\left(-25{,}600/\boldsymbol{R}T\right) \text{ sec.}^{-1} \text{ c.c. mole}^{-1}$$

describes the variation of rate in the temperature range 258—371° (Table 2).

TABLE 1.

Variation of rate with pressure of hydrogen bromide at 305·8°.

p_{HBr} (mm.)	p_{BuOMe} (mm.)	10^5k (sec.$^{-1}$)	$10^7k/p_{\mathrm{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)	p_{HBr} (mm.)	p_{BuOMe} (mm.)	10^5k (sec.$^{-1}$)	$10^7k/p_{\mathrm{BHr}}$ (sec.$^{-1}$ mm.$^{-1}$)
47	284	15·2	32·4	157	231	54	34·4
86	185	30·7	35·7	159	101	55	34·6
95	172	33·5	35·2	170	179	56	33·0
99	116	36·6	36·9	286	148	102	35·6
106	165	35·0	33·0	322	179	116	35·9
108	152	37·5	34·8				Mean 34·7 ± 1·0

TABLE 2.

Variation of rate with temperature.

Temp.	No. of runs	$10^7k/p_{\mathrm{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)	k/p_{HBr} (sec.$^{-1}$ c.c. mole^{-1})	Temp.	No. of runs	$10^7k/p_{\mathrm{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)	k/p_{HBr} (sec.$^{-1}$ c.c. mole^{-1})
371·2°	5	372	1490	305·8°	11	34·7	126
361·2	11	258	1020	290·3	10	21·4	75
352·2	12	172	670	274·2	12	12·8	43·6
336·8	20	115	437	258·9	10	7·5	24·9
321·0	13	65	241				

TABLE 3.

Rates in packed vessels ($10^7k/p_{\mathrm{HBr}}$; sec.$^{-1}$ mm.$^{-1}$).

Temp.	S/V = 0·9 cm.$^{-1}$	S/V = 3 cm.$^{-1}$	No. of runs	S/V = 7·5 cm.$^{-1}$	No. of runs
352°	172	192 ± 10	6	188 ± 15	5
305	34·7	36 ± 2	5	50 ± 3	7
259	7·5	8·5 ± 0·5	6		

TABLE 4.

Rates with added cyclohexene.

Temp.	No. of runs	$p_{\mathrm{C_6H_{10}}}$ (mm.)	p_{HBr} (mm.)	p_{BuOMe} (mm.)	$10^7k/p_{\mathrm{HBr}}$ (sec.$^{-1}$ mm.$^{-1}$)
361·2°	4	149—205	76—93	86—150	244 ± 10
352·2	6	83—267	54—111	119—152	183 ± 8
336·8	10	33—359	37—122	122—175	115 ± 8
321·0	8	18—363	64—173	141—328	64 ± 3

Since no substantial increase in rate was observed when vessels with surface : volume ratios up to 8 times that of the unpacked vessel were used (Table 3), the reaction is believed to be essentially homogeneous. The reaction is considered to be a molecular one, as additions of cyclohexene (up to 363 mm.) do not reduce the rate (Table 4).

The corresponding gas-phase reaction between t-butyl alcohol and hydrogen bromide (Part I) occurs at measurable rates in the temperature range 315—422°, with an activation energy of 30·4 kcal./mole and pre-exponential factor of 9·2 × 10^{12}, so that reaction for the

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[9] Winkler and Hinshelwood, *Trans. Faraday Soc.*, 1935, **31**, 1739.

ether is somewhat faster with smaller values for both Arrhenius parameters; the relative rates at **340°**, the middle of the common temperature range, are **4** : 1. However, even with the largest pressure of hydrogen bromide used as catalyst, decomposition of the ether is still slower than that of t-butyl bromide.[10] The value of E for the latter is **42** kcal./mole, but the decomposition of the ether could not be followed to a temperature low enough for its rate to overtake that of t-butyl bromide.

Each of the three possible mechanisms which were suggested for the catalysed decomposition of t-butyl alcohol (Part I), *viz.*, (i) formation and subsequent decomposition of the alkyl halide, (ii) elimination *via* a six-membered ring transition state, and (iii) formation of a gas-phase ion-pair with subsequent elimination, is consistent with the experimental results for methyl t-butyl ether. Each depends to some extent on the basicity of the oxygen atom, the last (iii) most directly. The basic character of ethers towards hydrogen halides in solution is well known,[11] and the basicity increases with variation of the alkyl substitutent in the order, primary < secondary < tertiary. The infrared spectra of mixtures of ethers and hydrogen halides in the gas phase also indicate that hydrogen bonding takes place, and the manner in which the intensity changes with variation of the pressures of the components implies that 1 : 1 complexes are formed.[12]

For the decompositions of alcohols and ethers catalysed by hydrogen bromide studied so far, the rate order is $EtOH < Pr^iOH < Bu^tOH < CMe_2Et{\cdot}OH < Bu^tOMe$, and this corresponds with the order of increasing basicity of the oxygen atom.

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[10] Harden and Maccoll, *J.*, 1955, 2454.

[11] Gerrard and Mecklen, *Chem. Rev.*, 1959, **59**, 1105.

[12] Arnold, Bertie, and Millen, *Proc. Chem. Soc.*, 1961, 121.