Catalysis by Hydrogen Halides in the Gas Phase. Part XXVI.† Isopropylamine and Hydrogen Bromide

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The hydrogen bromide catalysed deamination of isopropylamine between 435 and 490 °C is described. Propene and ammonia are the major products of the decomposition. The reaction is believed to be homogenous, first order in both the acid and the substrate, and is molecular. The rate constant is expressed by the equation: $k_2 = 10^{12\cdot41} \exp(-33{,}115/RT)$ cm^3 mol^{-1} s^{-1} (where $R = 1\cdot987$ cal mol^{-1}; 1 cal = 4·187 J). A relatively smaller effect of α-methyl substitution in the hydrogen bromide catalysed deamination of amines as compared with that observed in the catalysed dehydration of alcohols is explained in terms of the greater basicity of amines.

In recent years there have been many studies of hydrogen halide catalysis of gas phase decomposition of alcohols, ethers, carboxylic acids, and esters.[1-3] Hydrogen chloride has been shown to catalyse the decarbonylation of dimethylformamide[4] into carbon monoxide and dimethylamine in the temperature range 335—415 °C. Also, in the presence of hydrogen bromide at 395—460 °C, t-butylamine[5] decomposes in the gas phase into ammonia and isobutene and the acid is not consumed. The reaction is homogeneous and molecular, and the stoicheiometry is:

$$Me_3CNH_2 + HBr \longrightarrow Me_2C{=}CH_2 + NH_3 + HBr \qquad (1)$$

The rate of reaction is proportional to the pressure of both t-butylamine and hydrogen bromide, *i.e.* the results fit the pseudo-first-order equation (2). This

$$\frac{-d[Bu^tNH_2]}{dt} = k_2[Bu^tNH_2][HBr]_0 \qquad (2)$$

reaction showed great similarity to the hydrogen halide catalysed decompositions of alcohols and ethers studied previously by Stimson *et al.*, so analogous transition states were proposed. With a view to studying the effect of α-methyl substitution we have now investigated the gas phase decomposition of isopropylamine and ethylamine, catalysed by hydrogen bromide.

EXPERIMENTAL

Isopropylamine and ethylamine (B.D.H. laboratory grade) were dried over anhydrous potassium hydroxide and fractionated through a 1 ft column. The constant boiling middle fractions of isopropylamine, b.p. 34 °C at 760 mmHg (lit.,[6] 33 °C at 760 mmHg), and ethylamine, b.p. 18 °C at 760 mmHg (lit.,[6] 16·1 °C at 760 mmHg; lit.,[7] 18·7 °C at 760 mmHg) were retained for use. Final purification in the vacuum system was affected by trap to trap distillation. Hydrogen bromide gas (Matheson) was dried by several distillations through a trap at −80 °C. Propene gas (Philips Petroleum Co. Inc.) was dried by passage through a column of calcium oxide. The apparatus and experimental procedures have been described previously.[5] Hydrogen bromide was introduced first into the reaction vessel and was followed by the amine. Propene was estimated by g.l.c. against isobutene as an internal standard, using a bis-2-methoxyethyl adipate column.[5] The progress of reaction was determined by measuring pressure increase as a function of time in a vessel coated with the products of decomposition of allyl bromide.[8] Reaction of ammonia and hydrogen bromide to form ammonium bromide has been shown to be not appreciable in the temperature range studied.[5] When isopropylamine (150·2 mmHg) was left in the reaction vessel for 30 min at 437·7 °C, no pressure increase occurred. However, at 490·9 °C the highest temperature in this work, $(dp/dt)_0/P_0$ obtained was approximately $0\cdot8 \times 10^{-4}$ s^{-1} and this is *ca.* 6% of the lowest catalysed rate constant. Also ethylamine did not decompose detectably at 460·0 °C, when left in the reaction vessel for 0·5 h, but when it reacted with hydrogen bromide at 460·0 °C, the pressure increased slowly. Ethylene was the major olefin of the catalysed decomposition.

RESULTS

Product analysis showed that propene and ammonia were the major products of the hydrogen bromide catalysed decomposition of isopropylamine. Trace amounts of hydrogen, ethylene, and up to a maximum of 8% methane were also observed. The ratio of final to initial pressure as obtained from six runs at one temperature gave an average value of 1·89. Therefore, in the temperature range 437—490 °C, the catalysed decomposition of isopropylamine is represented by reaction (3). A pressure–time curve and

$$Me_2CHNH_2 + HBr \longrightarrow MeCH{=}CH_2 + NH_3 + HBr \qquad (3)$$

its associated first order log plot are shown in the Figure. No induction periods were observed. The reaction was found to follow the first order rate law to *ca.* 20—40% decomposition of the amine depending upon the temperature and concentration of hydrogen bromide used. The pressure increase and the production of propene agree up to *ca.* 20% reaction (Table 1) after which deviations appear.

TABLE 1

Progress of the reaction

% Reaction by pressure increase	9·0	15·5	27·8	**50·3**
% Reaction by production of propene	9·5	14·6	25·0	**43·0**

At a constant pressure of hydrogen bromide (*ca.* 150 mmHg) the first order rate coefficients did not depend upon

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† Part XXV, D. A. Karaitis, V. R. Stimson, and J. W. Tilley, *Austral. J. Chem.*, 1973, **26**, 761.

[1] A. Maccoll and V. R. Stimson, *J. Chem. Soc.*, 1960, 2836; *Proc. Chem. Soc.*, 1958, 80.

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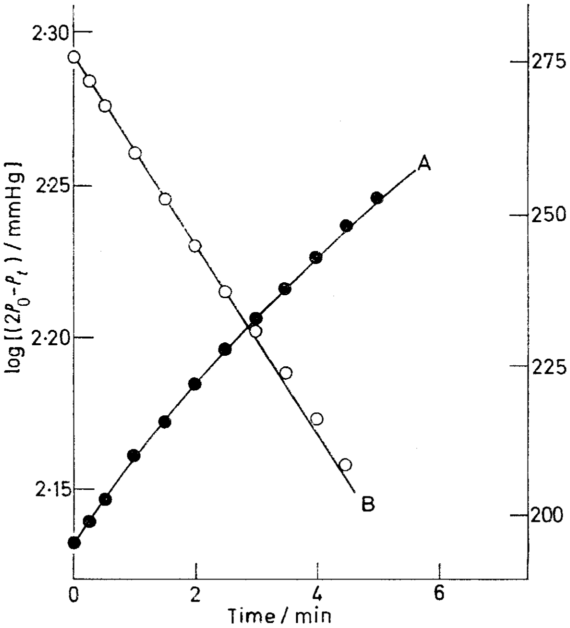
[5] A. Maccoll and S. S. Nagra, *J. Chem. Soc.* (*B*), 1971, 1865.

[6] 'Handbook of Chemistry and Physics,' 45th edn., The Chemical Rubber Co., Cleveland, Ohio, 1964.

[7] H. A. Taylor, *J. Phys. Chem.*, 1930, **34**, 2761.

[8] A. Maccoll and J. H. S. Green, *J. Chem. Soc.*, 1955, 2449.

the initial pressure of isopropylamine (60—240 mmHg), thus showing that the decomposition is first order in amine. The first order rate coefficients are directly proportional to the pressure of hydrogen bromide (Table 2). Therefore, the reaction is also first order in the catalysing acid.



The pressure–time curve A and the corresponding log plot B

TABLE 2

Variation of first order rate coefficients with pressure of hydrogen bromide

P(HBr)/ mmHg *	P(Isopropylamine)/ mmHg	10^4k_1/ s^{-1}	10^6k_2/ s^{-1} $mmHg^{-1}$
50·6	129·0	4·0	7·7
80·0	179·5	5·6	7·0
113·7	144·0	8·7	7·6
117·2	199·0	9·3	8·0
150·1	104·2	10·5	7·0
152·6	134·4	11·0	7·2
153·6	152·5	12·5	8·0
187·5	165·0	14·2	7·6
203·8	199·0	14·0	6·9
210·0	133·1	14·9	7·0
241·0	169·0	16·8	7·1
308·9	146·0	21·4	6·8

* 1 mmHg = 133·3 N m^{-2}.

No significant change in the rates was observed when the runs were carried out in the presence of isobutene and toluene (Table 3), which suggests that the decomposition is molecular. This is also supported by the absence of induction periods in the pressure–time curves. When the catalysis was done in a packed vessel with a surface to volume ratio of 5 relative to the normal vessel, the rates were not affected.

The catalytic decomposition of isopropylamine was studied over the temperature range of 55 °C and the second rate constants obtained are listed in Table 4.

These values were fitted by least squares method to the Arrhenius equation (4). The error in E (95% confidence limit) was ±1333 cal mol^{-1} and that in log A (95% confidence limit) was ±0·39 cm^3 mol^{-1} s^{-1}.

$$k_2 = 10^{12\cdot42}\exp(-33{,}115/RT)\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1} \qquad (4)$$

In the decomposition of ethylamine catalysed by hydrogen bromide, the individual first order rate coefficients were found again to be roughly proportional to the pressure of the catalysing acid. A value of 2·1 × 10^{-6} s^{-1} $mmHg^{-1}$ was found for the catalysed rate constant of ethylamine at 460·0 °C. Owing to the slowness of this reaction no further measurements were performed. Stimson and Ross [9] found a value of $10^7 \times k_1/P_{HBr}$ = 2·0 s^{-1} $mmHg^{-1}$ for the hydrogen bromide catalysed dehydration of ethyl alcohol.

TABLE 3

Effect of added inhibitor at 470·0 °C

Additive	(%)	P_0 (Isopropylamine)/ mmHg	P(HBr)/ mmHg	10^6k_2/ s^{-1} $mmHg^{-1}$
		152·5	59·7	10·0
		165·0	303·1	10·2
Isobutene	20·8	168·2	145·0	10·3
Isobutene	80·5	157·3	127·0	9·8
Isobutene	120·5	180·3	131·2	9·7
Toluene	10·8	148·2	111·3	10·0
Toluene	109·1	132·0	195·8	10·8

TABLE 4

Temperature dependence of the second order rate constants

T/°C	10^6k_2/ s^{-1} $mmHg^{-1}$	$10^{-2}k_2$/ cm^3 mol^{-1} s^{-1}
437·9	3·94	1·75
447·7	5·40	2·43
460·0	7·30	3·34
470·0 *	10·03	4·65
480·5	13·90	6·53
490·9	18·80	8·96

* Packed vessel study.

DISCUSSION

The various possible transition states for the hydrogen bromide catalysed decomposition of amines have been discussed previously [5] and a polar transition state has been favoured. The thermal decomposition of ethylamine [7] between 500 and 540 °C and isopropylamine [10] between 490 and 540 °C have been studied by Taylor. He concluded that these decompositions were essentially homogeneous, unimolecular reactions and involved the production of ammonia and the corresponding olefin. The energies of activation for ethylamine and isopropylamine were 43·4 and 42·6 kcal mol^{-1} respectively. It is clear from the present work that the hydrogen bromide catalysed decomposition of isopropylamine occurs at lower temperatures and requires less energy of activation, *e.g.* 33·1 kcal mol^{-1}. This again shows a similarity to the hydrogen halide catalysed decompositions of alcohols and ethers. Some suitable comparisons are made in Tables 5 and 6.

The effect of α-methylation (Table 6) in the hydrogen bromide catalysed dehydration of alcohols is much greater than that observed in the catalysed deamination of amines. This can be explained in terms of the basicity of amines as compared with that of alcohols.

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[9] R. A. Ross and V. R. Stimson, *J. Chem. Soc.*, 1960, 3090.

[10] H. A. Taylor, *J. Phys. Chem.*, 1932, **36**, 670.

TABLE 5

Comparison of hydrogen bromide catalysed decompositions of alcohols and amines

Compound	E/kcal mol^{-1}	log A/ cm^3 mol^{-1} s^{-1}	Ref.
Bu^tOH	30·4	12·96	1
Pr^iOH	33·2	12·00	9
Bu^tNH_2	29·3	12·21	5
Pr^iNH_2	33·1	12·41	This work

TABLE 6

Relative rates of hydrogen bromide catalysis of amines and alcohols

Compound	Ethyl	Isopropyl	t-Butyl
Alcohol [10]	1	2·0	1000
Amine	1	3·5	34·0
$\frac{k_2\text{ (Amine)}}{k_2\text{ (Alcohol)}}$	14	2·3	0·4

An increasing basic strength in nitrogeneous bases is related to the readiness with which they are prepared to take up protons and therefore to the availability of the unshared electron pair on nitrogen. In aqueous solution, K_a for the amines is 12—14 orders of magnitude greater than that of the corresponding alcohols. Unfortunately, the pK_a values of these compounds in non-aqueous media are not available in the literature. However, the values of K_a in water are sufficient to illustrate the much higher basicity of the amines than the alcohols. Therefore, since nitrogen is already more basic in the amines, the α-methyl substitution would not be expected to increase the rate to the same extent as it would in the case of alcohols. From Table 6 it is also obvious that the hydrogen bromide catalysed decomposition of ethylamine is *ca.* 14 times faster than that of ethyl alcohol,[9] and the catalysis rate of isopropylamine is *ca.* 2·3 times faster than that of isopropyl alcohol. This again is a consequence of the higher basicity of nitrogen than oxygen which will facilitate the attack of a proton. It is interesting to note (Table 6) that the catalysed decomposition of t-butylamine is *ca.* 2·5 times slower than that of t-butyl alcohol. This is because the α-methyl substitution from isopropyl to t-butyl alcohol increases the rate by a factor of 50; whereas the α-methyl substitution in the corresponding amines increases the rate by a factor of 10 only. The weaker basicity of alcohols as compared with the amines has been associated with the increased *s* character of the orbitals containing the unshared electrons. Thus these lone pairs of electrons in the alcohols are rendered less available for bonding to a proton in comparison with those of the amines.

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