225. *The Ionisation of Amines in Alcohol: a Possible Slow Reaction.*

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The intention of the present work was to make a quantitative investigation of the slow increase of electrical conductivity found by Jones and Hughes (J., 1934, 1197) to follow dilution of stock solutions of ammonia in methyl and ethyl alcohols. Concentrated solutions of ammonia in benzene were added to methyl alcohol; the bases diethylamine, *iso*butylamine, benzylamine, and piperidine were added in liquid form to ethyl alcohol. The solvent alcohol was contained in a conductivity cell, and the change of conductivity of the solution with time was followed after mixing was complete, the first reading being made about 90 seconds after the addition.

The qualitative observations of Jones and Hughes were confirmed in every case; a slow increase in conductivity was observed which was virtually complete after 10 minutes in methyl alcohol and after 40 minutes in ethyl alcohol. After the first 2 minutes, the reaction followed a first-order course, but during that time a more rapid change occurred accounting for about $\frac{2}{3}$ of the total change observed in the reaction. Continuous stirring was essential to the smooth course of the reaction, and the reproducibility of the curves and of dissociation constants was not good. The fact that this effect was not reduced noticeably by using a cell having unplatinised plates removes the possibility of much heterogeneous reaction on the plates. The reproducibility of the curves was improved, and the effect of stirring decreased, by coating the walls of the cell with highly purified paraffin wax.

Another cause of uncertainty lay in the small concentration (*ca.* $10^{-4}M$) of carbon dioxide present in the best alcohol that could be prepared: an excess of a strong base (potassium methoxide or ethoxide) was always added to the alcohol to convert this into methyl or ethyl carbonate, but the difficulty in estimating the carbon dioxide accurately leads to error in the excess of strong base ion initially present. In the later experiments, the carbon dioxide was assumed to have such a concentration as would give a consistent dissociation constant for the amine estimated from two parallel runs in the same batch of solvent.

Jones and Hughes ascribed these changes to slow ionisation processes. In view of the relative constancy of velocity constants in waxed cells (see table, in which K is the dissociation constant of the base and k is the velocity constant) with four different amines, and of the great precautions taken to exclude impurities (such as carbon dioxide from the air) it seems difficult to resist this conclusion. The facts that the changes involve an increase of conductivity, and that Jones and Hughes found that the reaction $H_2O + OR' \longrightarrow OH' + ROH$ led to a decrease of conductivity, being borne in mind, two possibilities present themselves. (i) The primary ionisation of the amine involves the residual water present in the alcohol (to about $10^{-3}M$), followed by the slow reaction $OH' + ROH \longrightarrow H_2O + OR'$. This would account for both the fast and the slow stage: the magnitude of the slow change seems rather large to be explained thus. (ii) The slow stage is a genuine slow ionisation of the amine which, if the non-existence of compounds of the type $R{\cdot}NH_3{\cdot}OH$ is assumed, might be due to one of three processes:

(1) $B + EtOH \longrightarrow BH^{\cdot} + OEt'$.

(2) $2EtOH \xrightarrow{\text{slow}} EtO' + EtOH_2^{\cdot}$; $EtOH_2^{\cdot} + B \xrightarrow{\text{rapid}} EtOH + BH^{\cdot}$.

(3) As (2), but with the first stage fast and the second slow.

The velocity constants for these processes are given in the table. Their uniformity for process (3) suggests the controlling stage to be the ionisation of the alcohol. Calculation on this assumption of the rate of the reverse reaction $RO' + ROH_2^{\cdot} \longrightarrow 2ROH$ gives $1{\cdot}1 \times 10^{11}$ and $0{\cdot}7 \times 10^{11}$ for ethyl and methyl alcohol respectively: the closeness of these values to each other and to the collision number (*ca.* 10^{11}) gives further support to mechanism (3); but no explanation of the initial fast reaction can be given on this basis.

It seems, however, that this is likely to be a case of an ionic reaction occurring with measurable velocity, of interest in view of modern theories of acid and basic catalysis.

				k (g.-mols./l./min.).		
Base.	Cell.	Concn. of base $\times 10^3$.	$K \times 10^7$.	(1) $\times 10^{-2}$.	(2).	(3) $\times 10^6$.
Diethylamine	Glass	3·22	4·8	2·21	0·037	0·44
	,,	5·34	5·0	10·1	0·078	2·79
	Waxed	5·10	0·72	29·8	0·051	1·13
	,,	11·24	0·72	6·2	0·016	0·51
*iso*Butylamine	Glass	5·71	5·3	10·1	0·062	3·04
	,,	21·5	3·8	6·7	0·055	5·52
	Waxed	4·66	1·16	24·0	0·048	1·29
	,,	9·32	1·16	9·9	0·030	1·06
Benzylamine	Glass	6·09	3·01	6·0	0·030	1·08
	,,	19·0	3·15	3·9	0·023	2·28
	Waxed	5·22	1·53	12·4	0·051	0·99
	,,	15·7	1·53	3·9	0·028	0·95
Piperidine	Glass	5·07	3·6	15·9	0·159	2·86
	,,	25·0	2·8	5·3	0·085	3·74
	Waxed	6·39	1·91	13·6	0·058	2·30
	,,	12·15	1·90	2·8	0·012	0·65

EXPERIMENTAL.

Reactions were carried out in a 20 c.c. cell of the type described by Hartley and Barrett (J., **1913**, 103, 786). Resistances were measured by means of a drum bridge, current being supplied by a valve oscillator. Measurements were made at 25° ± 0·01°. Solvent alcohol was made up in batches, an excess of potassium ethoxide added from a weight pipette, and the carbon dioxide in the solvent estimated as described by Jones and Hughes. Liquid bases were added from a capillary micropipette calibrated directly by titration. The mobilities of base kations were determined approximately from the conductivity of their hydrochlorides at an ionic concentration of $2 \times 10^{-4}N$: account was taken of alcoholysis.

The concentration of the amines ranged from 10^{-3} to $10^{-2}N$, and the excess of ethoxide ion was about $2 \times 10^{-4}N$.

Materials.—Diethylamine was from Kahlbaum. *iso*Butylamine, benzylamine, and piperidine were A.R. products (B.D.H.) redistilled. Ethyl alcohol was prepared by the method of Woolcock and Hartley (*Phil. Mag.*, 1928, **5**, 1134). Paraffin wax was purified by successive boiling with acid, alkali, distilled water, conductivity water, and conductivity alcohol; it appeared to be free from any soluble electrolyte.

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