833. *The Basic Properties of Azines. Part I. Potentiometric and Conductometric Titration of Dimethylketazine with Hydrogen Chloride in Acetone.*

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Conductometric and potentiometric measurements on solutions of mixtures of dimethylketazine and hydrogen chloride in anhydrous and moist acetone support the view that these solutions contain azinium ions as postulated by Pugh and his co-workers.

THE formulation by Pugh and his co-workers [1-3] of a number of compounds prepared by them as complex salts of ketazines and aldazines was based almost entirely on analytical results, the only exception being Morrison's demonstration [4] that solutions of some of these compounds in aqueous acetone were good conductors of electricity. Gilbert [5] considered that dimethylketazine (*NN'*-di-isopropylidenehydrazine) did not act as a base, but the results described in this paper support the contrary view. Attempts to prepare crystalline halides and a sulphate of this base, which might be more suitable than the complex salts for crystallographic examination, were unsuccessful,[3] and it therefore seemed desirable to enquire whether the properties of solutions which might be expected to contain such salts supported the hypothesis that azinium ions were present.

Although dimethylketazine is hydrolysed extensively by small amounts of water, Gilbert [5] has shown that in excess of acetone the equilibrium

$$N_2H_4 + 2Me_2CO \rightleftharpoons Me_2C{:}N{\cdot}N{:}CMe_2 + 2H_2O$$

is displaced in favour of the azine, so that conversion of hydrazine into the ketazine is almost complete. Some electrochemical properties of solutions in acetone containing mixtures of dimethylketazine with hydrogen chloride have therefore been studied.

Preliminary potentiometric titrations [6] indicated the presence in moist acetone solution of a basic substance which, if stable in water, would have $pK_b \sim 9$. Comparison with hydrazine ($pK_{b,1}$ 6·1, $pK_{b,2}$ 16·1) [7] suggests that this is probably the ketazine and that its second ionisation constant must be extremely small, so that it will behave as a mono-acid base. Since the possibility of hydrolysis to hydrazine or a hydrazone could not be excluded in those titrations, solutions of the base in anhydrous acetone and in acetone containing 0·2%, 0·65%, and 1·0% of water were titrated potentiometrically with solutions of hydrogen chloride in the same solvents. The titration curves are shown in Fig. 1. Specific conductances in anhydrous acetone were also measured, both the concentration of base and the ratio of hydrogen chloride to base being varied, and the conductometric curves shown in Fig. 2 were constructed by an indirect procedure.

The potentiometric titration curve in anhydrous acetone shows an inflexion when 1 mole of acid has been added per mole of base, and no further inflexion could be obtained, even when addition of hydrogen chloride was continued beyond twice this quantity. A single inflexion is also shown on titration in 99·8% acetone, but the base appears weaker than in the anhydrous solvent. The appearance of a second inflexion on the addition of an appreciable amount of water indicates the replacement of a mono-acid base by a di-acid base, and is consistent with the hydrolysis of dimethylketazine to hydrazine. The

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[1] Pugh and Stephen, *J.*, 1952, 4138; 1953, 354.
[2] Pugh, *J.*, 1953, 3445.
[3] Sohn, Marks, and Pugh, *J.*, 1955, 1753.
[4] Morrison, quoted in ref. 2.
[5] Gilbert, *J. Amer. Chem. Soc.*, 1929, **51**, 3394.
[6] Hotz and Spong, *Chem. and Ind.*, 1960, 392.
[7] Schwarzenbach, *Helv. Chim. Acta*, 1936, **19**, 178.

possible production of acetone hydrazone under these conditions would appear to be excluded because, although it might behave as a mono-acid base, it would be expected to be stronger than the azine and not weaker.

The shapes of the conductometric titration curves in anhydrous acetone are typical of those obtained for neutralisation of a weak mono-acid base by a weak acid (see Fig. 2). Over the portion of the curve where insufficient acid for neutralisation has been added, the conductance depends on the concentration of ions produced by equivalent neutralisation of the base, and the slope should therefore be steeper at higher concentrations of base than at lower, as is observed. The variation of the slope indicates that the products of the reaction are ionic in character.

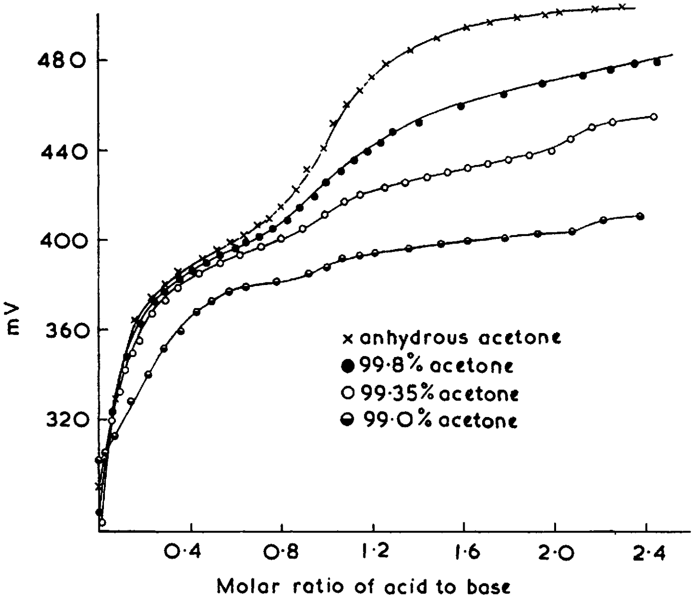

FIG. 1. Potentiometric titration of dimethylketazine with hydrogen chloride in acetone.

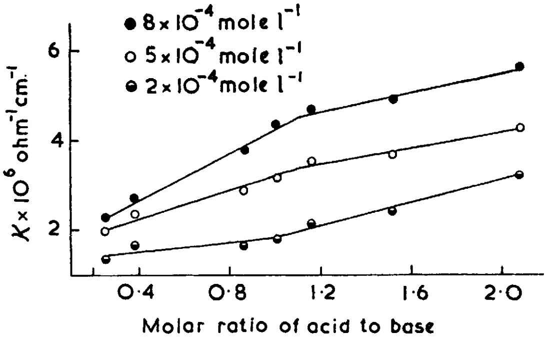

FIG. 2. Conductometric titration of dimethylketazine with hydrogen chloride in acetone.

On account of the low dissociation constant of the acid,[8] the slopes of the titration curves should be less after the equivalence point is passed than before, and this is observed with the two higher concentrations. With the lowest concentration, however, the reverse is the case, and the slopes of the three curves are approximately the same instead of varying with concentration in the usual way. A possible explanation might be sought in a

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[8] Everett and Rasmussen, *J.*, 1954, 2812.

suggestion advanced by Mackor[9] that hydrogen chloride dimerises in acetone, and this possibility is being further explored. Preliminary observations indicate an even higher degree of polymerisation, and if this occurred head to tail, H–Cl • • • H–Cl • • • in equilibrium with depolymerisation products, both the apparent weakness of the acid and the constancy of slope may be accounted for by displacement of the equilibrium in favour of the shorter molecules as the solution is diluted.

EXPERIMENTAL

B.D.H. " AnalaR " acetone was dried by a method similar to that of Dippy and Hughes[10] (cf. Reynolds and Kraus[11]) with modified apparatus which permitted transfer of acetone from the reflux side to the distillation side without exposure to the external atmosphere. All handling of the solvent and solution was in a dry-box containing nitrogen, free from moisture but saturated with acetone, at a pressure slightly above atmospheric.

Hydrogen chloride was prepared by treating silicon tetrachloride with distilled water.[12] The gas was dried [$Mg(ClO_4)_2$] and then passed through a trap immersed in solid carbon dioxide–acetone, after which it was allowed to bubble through an ice-cooled acetone saturator. A sample was removed for gravimetric chloride analysis, and the solution diluted to the required concentration.

Dimethylketazine was made from hydrazine hydrate and acetone.[13]

Potentiometric Titration.—E.m.f.'s were measured by using a chloranil electrode in conjunction with an acetone–saturated lithium chloride–calomel electrode[14] and a Pye Universal pH and millivoltmeter. The chloranil electrode was prepared from an equimolar mixture of tetrachlorobenzoquinone and tetrachloroquinol, which had been dried (P_2O_5) in a vacuum desiccator for 3 weeks before use. A special burette, which balanced the pressures throughout the system on the addition of the hydrogen chloride solution, was used, and the liquid in the titration vessel was stirred with nitrogen saturated with dry acetone. All joints and stopcocks were lubricated with Fisher " Nonaq " grease, which was found to be unaffected by acetone within the time required for these experiments.

Conductometric Titration.—Solutions of dimethylketazine in acetone were mixed with calculated quantities of hydrogen chloride, diluted to 50 ml., and sampled for gravimetric chloride analysis. A series of dilutions was made from each of these mixtures, and the chloride analysis repeated on the last, the solutions being discarded if this did not agree with the calculated value. The resistance of the solutions so prepared were measured on a Jones-type bridge, with a Daly and Smith[15] cell immersed in a circulating-oil thermostat, which was in turn enclosed in an air thermostat. The temperature was maintained at 25 ± 0·01° c.

The specific conductances for each series of dilutions were then plotted against the concentration of dimethylketazine, and interpolated values for $2·0 \times 10^{-4}$, $5·0 \times 10^{-4}$, and $8·0 \times 10^{-4}$ mole $l.^{-1}$ read off. These were plotted against the molar ratio of acid to base, and the titration curve shown in Fig. 2 was constructed.

The authors acknowledge their debt to the later Professor W. Pugh, whose work led to the initiation of this investigation. Grateful acknowledgment is also made to African Explosives and Chemical Industries Ltd. for a Research Studentship (to M. C. B. H.) and to the Council of the University of Cape Town for grants for apparatus and chemicals.

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CAPE TOWN. [*Received, April 19th*, 1962.]

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[9] Mackor, quoted in ref. 8.
[10] Dippy and Hughes, *J.*, 1954, 953.
[11] Reynolds and Kraus, *J. Amer. Chem. Soc.*, 1948, **70**, 1709.
[12] Partington, " Textbook of Inorganic Chemistry," Macmillan, London, 1947, p. 192.
[13] Curtius and Thun, *J. prakt. Chem.*, 1891, **44**, 161.
[14] Arthur and Lyons, *Analyt. Chem.*, 1952, **24**, 1422.
[15] Daly and Smith, *J.*, 1953, 2779.