CCCLXXXVI.—*The Dihalides of Pyridine.*

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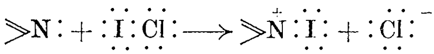
THE formation of dihalides by pyridine and other similar bases has been reported by many investigators (Hofmann, *Ber.*, 1879, **12**, 988; Dittmar, *Ber.*, 1885, **18**, 1612; Trowbridge and Diehl, *J. Amer. Chem. Soc.*, 1897, **19**, 558; Mouneyrat, *Compt. rend.*, 1903, **136**, 1470; Cremer and Duncan, this vol., p. 1857), but a systematic study of their formation, stability, and structure, as distinct from those of the perhalides, does not seem to have been undertaken.

All the possible dihalides of pyridine and chlorine, bromine, and iodine have now been prepared with the exception of the di-iodide, which could not be obtained from solution. The least stable is the dichloride, which is obtained as a white crystalline precipitate by mixing pyridine and chlorine in equimolecular amounts in carbon tetrachloride. It decomposes spontaneously in air, generally in the course of a minute or so after all the solvent has been removed from it. The most stable is the iodochloride, C_5H_5NICl, obtained first by Dittmar (*loc. cit.*) but in the best yield by using carbon tetrachloride as solvent. This compound and the *iodobromide* can be recrystallised from hot alcohol with only slight decomposition, but they decompose slowly in the presence of water and immediately in the presence of potassium iodide, liberating all their halogen. The *bromochloride* is not so stable and decomposes in hot alcohol, although quite stable in dry air. The *dibromide* is not so stable as the bromochloride and it decomposes readily in air. It seems that the di-iodide is formed in carbon tetrachloride solution, as is shown by the change in colour that occurs when pyridine is added to a solution of iodine, but all attempts to precipitate it failed.

An attempt was next made to study the extent of the dissociation of the compounds in solution by measuring the vapour pressure of the free halogen. For this purpose the dibromide was chosen as being the most likely to be highly dissociated (the dichloride was found to have many disadvantages for this purpose). Carbon tetrachloride was chosen as solvent, since the dibromide reacted with most other solvents, such as alcohol and acetone, in which it is more soluble. The vapour pressure of the bromine in a saturated solution of the dibromide in carbon tetrachloride (about 0·02*M*) was less than 0·002 mm. of mercury, and thus too small to be measured by the bubbling method, which was the one used. This proves that the dibromide exists in an inert solvent more or less completely as undissociated molecules.

In considering the structure of these dihalides, two possibilities suggest themselves. (*a*) One of the halogen atoms, the more electropositive one in the case of the mixed dihalides, co-ordinates itself with the nitrogen atom, forming a pyridinium ion and leaving the other halogen atom as an ion :



$$\gg N\!: + :\underset{\cdot\cdot}{\overset{\cdot\cdot}{I}}\!:\!\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\!: \longrightarrow \gg\overset{+}{N}\!:\!\underset{\cdot\cdot}{\overset{\cdot\cdot}{I}}\!: + :\!\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\!:^{-}$$

If this is the case, the substances would be electrolytes in a suitable solvent. This hypothesis explains why the iodochloride and the iodobromide are more stable than the dibromide, since the more electropositive iodine would co-ordinate more readily with the nitrogen. (*b*) One of the halogen atoms may be united to the nitrogen by the mechanism suggested by Bennett and Willis (J., 1929, 263), in which one halogen atom becomes 2-covalent owing to the absorption of two valency electrons into the core (Sidgwick, " The Electronic Theory of Valency," p. 292). This tendency increases from chlorine to iodine. But in view of the greater stability of the bromochloride compared with the dibromide, it seems probable that the less electropositive halogen would exert an influence on the halogen through which union occurs.

The measurement of the conductivity of the iodochloride (as the most stable of these dihalides) in a suitable solvent seemed a likely way of distinguishing between the possibilities. The choice of solvent was considerably limited by the small solubility of the compound in non-hydroxylic solvents such as nitrobenzene with fairly high dielectric constants. On the other hand it reacts slowly with cold alcohol and acetone with the development of the yellow colour of iodine. It is readily soluble in pure pyridine, giving a faint yellow solution, and therefore an attempt was made to measure its conductivity in this solvent. The results obtained were not conclusive, as the conductivity was very small and might well be due to traces of moisture in the solvent reacting with the dihalide, forming halogen acids. On the assumption that the conductivity is due to the ionisation of the substance itself, the abnormally low value of 2·3 is found for Λ_0. On the other hand, within the limits of experimental error, which was necessarily large in measuring such small conductivities, $1/\Lambda$ is a linear function of Λc, as would be the case if the iodochloride were a weak electrolyte. In any case, the substance must exist in solution in pyridine to a very large extent as undissociated molecules, and this brings it into line with some of the pyridine salts the conductivity of which was investigated by Wynne-Jones (this vol., p. 795). The most probable formula for these dihalides is therefore $C_5H_5N{:}I{:}Cl$, two of the valency electrons of the iodine atom being assumed to have entered the core.

An attempt to extend this work to other types of nitrogen compounds, so as to obtain more soluble dihalides and thus get more trustworthy conductivity measurements, has not yet been successful. The halogen compounds of the Schiff's bases (James and Judd, J., 1914, **105**, 1427) were found to be very unstable in the presence of moisture.

EXPERIMENTAL.

All the dihalides were prepared by slowly adding the calculated volume of a *M*-solution of the halogen in carbon tetrachloride to a definite volume of a *M*-solution of pyridine in the same solvent. Owing to the possible formation of the perhalide, slightly more than the calculated quantity of pyridine was used. The dihalide was precipitated immediately; it was separated, washed with the solvent, and dried in a vacuum. The yields were 80—90%, except in the case of the dichloride (yield, about 40%).

The titratable halogen was determined by treating the compound with a few c.c. of concentrated potassium iodide solution, adding rather less than an equal volume of alcohol, shaking the mixture until a clear solution was obtained, and titrating this with *N*/10-thiosulphate without an indicator.

Pyridine dichloride was obtained as a white crystalline precipitate which decomposed rapidly when the solvent was removed from it. It liberated chlorine and hydrogen chloride, often in dense white fumes, and left an oil containing pyridine and another substance not yet identified. The highest m. p. found was 47°, but this varied according to the rate of heating. Because of the extreme instability of the dichloride no analysis was attempted.

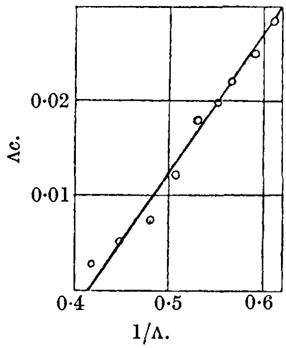
Pyridine dibromide, a red crystalline solid, decomposing slowly in moist air and smelling strongly of bromine, decomposed in alcohol, acetone, etc., and could not be recrystallised; m. p. 62—63° (Found : Br, 67·1; I equiv., 120·2. $C_5H_5NBr_2$ requires Br, 66·9%; I equiv., 119·5).

Pyridine bromochloride, a white crystalline solid, decomposing very slowly in moist air, could not be recrystallised; m. p. 107—108° (Found: Br, 40·8; Cl, 17·8; I equiv., 98·1. C_5H_5NClBr requires Br, 41·1; Cl, 18·3%; I equiv., 97·3).

Pyridine iodochloride was obtained after recrystallisation from alcohol as pale yellow needles, m. p. 134°, very sparingly soluble in benzene and carbon tetrachloride, slightly more soluble in nitrobenzene, and readily soluble in hot alcohol, cold acetone, and cold pyridine (Found: I, 52·7; Cl, 15·2; I equiv., 121·2. Calc. for C_5H_5NClI: I, 52·6; Cl, 14·7%; I equiv., 120·7).

Pyridine iodobromide, after recrystallisation from alcohol, consisted of golden-yellow needles, m. p. 116—117°. It is very similar to the iodochloride in all its properties (Found: I, 44·9; Br, 27·5; I equiv., 143·1. C_5H_5NBrI requires I, 44·4; Br, 28·0%; I equiv., 143·0).

FIG. 1.



Measurement of the Vapour Pressure of a Solution of the Dibromide in Carbon Tetrachloride at 0°.—Dry air was aspirated through a solution of bromine in carbon tetrachloride containing an excess of pyridine over that required for the formation of the dibromide, the solution being in a modified form of Arnold wash-bottle. The bromine was then absorbed by bubbling through potassium iodide solution. The maximum concentration of bromine possible, without precipitation occurring, is about 0·02*M*. On aspirating 4 l. of air through carbon tetrachloride containing 0·02 mol./l. of bromine and 0·1 mol./l. of pyridine, kept at 0°, the iodine liberated was equivalent to about 0·1 c.c. of 0·0113*N*-thiosulphate solution. The vapour pressure of the bromine in the solution is thus less than 0·002 mm. of mercury. The vapour pressure of a 0·02*M*-solution of bromine in the same solvent at 0° was found to be 0·2624 mm. Hence the dissociation of the dibromide in solution in carbon tetrachloride must be extremely small.

The Conductivity of Pyridine Iodochloride in Pyridine at 25°.—B.D.H. Pure pyridine was dried by standing over sticks of potassium hydroxide for a week and was then fractionally distilled through an 18-inch column. The fraction, b. p. 115—115·8° (corr.), was redistilled, and a fraction of b. p. 115·2—115·6° used for the conductivity measurements.

The cell used was of the type described by Hartley and Barrett (J., 1913, **103**, 789). Small amounts of a concentrated solution of the iodochloride from a weight burette were added to the pyridine in the cell, dry air being passed through the cell during each addition. All measurements were made at 25°.

Results.—The conductivity of the solvent was found to be 11×10^{-7} mho. The equivalent conductivity for each concentration is given in the table, *c* being expressed in g.-equivs. per litre.

$c \times 10^3$ ...	1·16	2·31	3·53	6·20	9·58	10·95	12·52	14·80	17·40
Λ	2·396	2·234	2·083	1·970	1·888	1·813	1·765	1·691	1·637

In the diagram the values of $1/\Lambda$ are plotted against Λc. It will be seen that $1/\Lambda_0$ is 0·415, which gives the extremely low value of 2·4 for Λ_0. It seems, therefore, fairly conclusive that the substance is not a weak electrolyte and that the conductivity is due to reaction with traces of water present in the solvent.

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