

MAGNETIC SUSCEPTIBILITY OF IODIC ACID IN AQ. SOLUTION (CONSTITUTION OF IODIC ACID)

In a previous communication to *Current Science*¹ and in a detailed paper² it was pointed out that in the case of aqueous solutions of Iodic acid a number of properties, e.g., density, viscosity, parachor, refractive index, temperature coefficient of conductivity, all showed a remarkable similarity in their curves which exhibited breaks at 0.04 N and 0.09 N.

In the present investigation the magnetic susceptibility of the aqueous solution of the acid at different concentrations has been measured, and the mass susceptibility determined and plotted against concentration. The susceptibility measurements have been carried out previously by S. R. Rao and Sriraman³ by means of a Curie balance at concentrations ranging from 17 per cent. to 76 per cent. from which they concluded that "no systematic variation was obtained when the concentration was varied". In our case we used a modified form of Decker's balance with a special device for temperature control. The region of concentration investigated was between 0.01 N and 1.0 N, that is, below that of the previous workers. The following formulæ were used to evaluate firstly the susceptibility of the solution, and from that the mass susceptibility of the solute:—

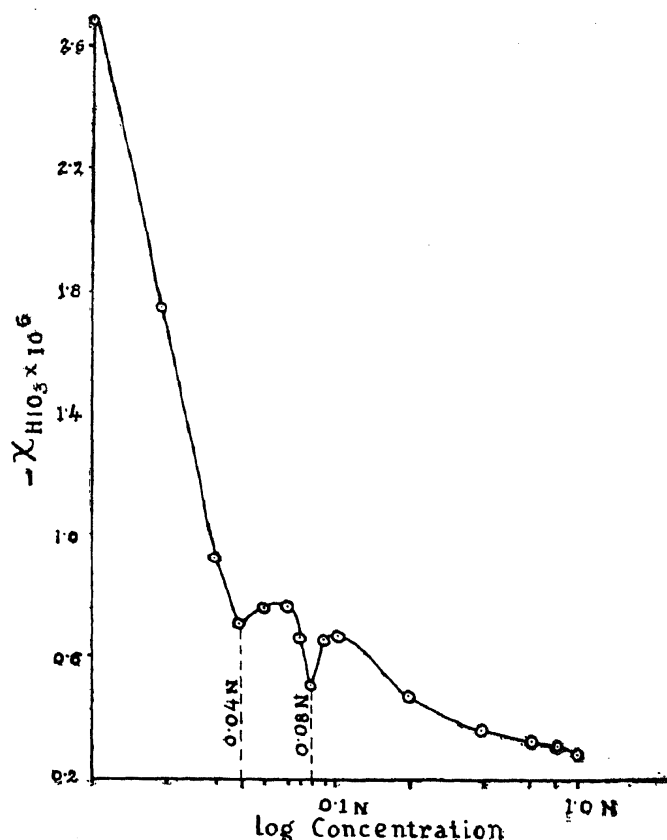
$$(1) \chi_{\text{sol}} \cdot \rho_{\text{sol}} = \chi_{\text{w}} \cdot \rho_{\text{w}} + (\chi_{\text{w}} \cdot \rho_{\text{w}} - \chi_{\text{a}} \rho_{\text{a}}) \cdot \frac{\theta_{\text{w}} - \theta_{\text{sol}}}{\theta_{\text{a}} - \theta_{\text{w}}}$$

$$(2) \chi_{\text{sol}} = C_{\text{s}} \cdot \chi_{\text{s}} + (1 - C_{\text{s}}) \chi_{\text{w}}$$

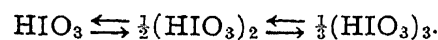
where χ_{sol} , χ_{w} , χ_{a} are the susceptibilities of the solution, water and air, ρ_{sol} , ρ_{w} , ρ_{a} are the densities of the solution concerned, water and air, and θ_{sol} , θ_{w} , θ_{a} are the deflections for solution, water and air respectively, and in the second equation C_{s} is the concentration, χ_{s} the mass susceptibility of the solute, and χ_{w} the mass susceptibility of water.

It will be observed that the curve shows two breaks at 0.04 N and 0.08 N. These correspond remarkably well with similar breaks in the curves obtained with other properties and were

explained as due to transition points arising



from the polymerisation of Iodic acid according to the scheme:



The detailed paper will appear elsewhere. Our thanks are due to Dr. K. N. Mathur for the construction of the magnetic balance which is of remarkable sensitivity.

M. R. NAYAR.

N. K. MUNDLE.

Lucknow University,
December 26, 1940.

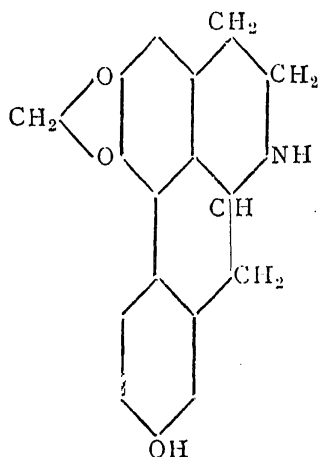
¹ *Curr. Sci.*, 1939, 8, 73.

² M. R. Nayar Srivastava, Sen, Ramgopal & Sharma, *Z. anorg. u. allg. Chem.*, 1939, 240, 217.

³ *Phil. Mag.*, 1937, 24, 1030.

SYNTHESIS OF dl, ANALOBINE-O-METHYL ETHER (dl-2, METHOXY-5, 6 METHYLENE DIOXY-NOR-APORPHINE)

ANALOBINE, an alkaloid obtained from *Asimina triloba* was assigned the following constitution by Manske¹ on the basis of analytical data:



1,2, hydroxy-5, 6-methylene dioxy nor-aporphine

Its synthesis was undertaken not only because it was felt that a rigid proof of its structure was desirable but also because of the great interest attached to phenolic aporphines. It was proposed to synthesise 2, benzyloxy-5, 6-methylene dioxy noraporphine, and after debenylation resolve the inactive phenolic aporphine into the active forms. This procedure would eliminate the complications that would ensue with a free hydroxyl group at the isoquinoline ring closure stage.^{2,3,4}

The starting materials were Homopiperonylamine⁵ and 2, nitro-5, benzyloxy-phenyl acetic acid. The acid could not be prepared in good yield by the method of Perkin for 2, nitro-5, methoxy-phenyl acetic acid⁶ because the yield of the intermediate 2, nitro-5, benzyloxy-phenyl pyruvic acid by condensation of 2, nitro-5, benzyloxy-toluene with ethyl oxalate was poor. It could, however, be prepared in good yield on the lines of the method of Gulland, Ross and Smellie² for 2, nitro-4, hydroxy-3, methoxy-phenyl acetic acid. *m* aldehydo-*p* nitro phenyl carbonate⁷ with hippuric acid and acetic anhydride gave the azlactone (m.p. 162°) of 2, nitro-5, hydroxy-benzaldehyde. This, with alcoholic HCl under pressure at 100°, gave 2, nitro-5, hydroxy-phenyl pyruvic acid (m.p. 194°, 70 per cent.) which was then oxidised with H₂O₂ to 2, nitro-5, hydroxy-phenyl acetic acid (m.p. 199°, 90 per cent.), and benzylated to 2, nitro-5, benzyloxy-phenyl acetic acid (m.p. 165°, 80 per cent.). The acid chloride prepared by the action of thionyl chloride, on addition to homopiperonylamine gave the amide (m.p. 145°-146°) in good yield. This was converted to 2', nitro-5', benzyloxy-1, benzyl-3, 4-dihydro-

6, 7-methylene dioxy-isoquinoline in 80 per cent. yield by PCl₅ in CHCl₃ at room temperature for 7 days (Picrate, m.p. 190°-191°). On reduction with Zn and HCl (d, 1.16) at 100°, the benzyloxy group was not disturbed, and 2', amino-5', benzyloxy-1, benzyl-1, 2, 3, 4-tetrahydro-6, 7-methylene dioxy-isoquinoline was obtained. This was extremely unstable in air. Picrate, m.p. 159°. Further work is in progress on the ring closure to the phenanthrene derivative.

Meanwhile the synthesis has been achieved of *dl*-2, methoxy-5, 6-methylene dioxy nor-aporphine starting from homopiperonylamine, and 2, nitro-5, methoxy-phenyl acetic acid. The amide (m.p. 182°-183°) was converted by PCl₅ and CHCl₃ at room temperature for 48 hours in 70 per cent. yield to the dihydro isoquinoline derivative (m.p. 166°-167°, Picrate m.p. 218°), and reduced to the amino tetrahydro isoquinoline derivative in 80 per cent. yield (hydrobromide, m.p. 244°). Diazotisation followed by boiling in methanol gave *dl*-2, methoxy-5, 6-methylene dioxy-nor-aporphine in 10 per cent. yield (B. hydrochloride—m.p. 305° from alcohol B.HCl. H₂O from water, m.p. 278°). It is proposed to resolve it into the active forms and compare the *l* form with Artabotrine⁷ and also Analobine O methyl ether.¹ Failing a resolution, the product obtained by a Gadammer ring cleavage on the synthetic aporphine will be compared with those obtained by a similar process on the natural alkaloids. Dr. Manske and the Institute of Medicinal Chemistry (where the late Dr. Barger worked) have been written to for specimens of the alkaloids for comparison. My grateful thanks are due to Prof. Dey for his valuable help and guidance in this investigation.

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Presidency College,
Madras,
January 1, 1941.

¹ *Can. J. Res.*, 1938, 16, 76.

² Gulland, Ross and Smellie, *J.C.S.*, 1931, 2885.

³ Douglas and Gulland, *ibid.*, 2893.

⁴ Kondo and Ishiwata, *Ber.*, 64, 1533.

⁵ Buck and Perkin, *J.C.S.*, 1924, 1693.

⁶ *J.C.S.*, 1924, 296

⁷ Mason, *J.C.S.*, 1925, 1196.

⁸ Barger and Sargent, *J.C.S.*, 1939, 991.