349. *The Action of Nitrous Acid on Dimethylaniline-*p*-sulphonic Acid in Sulphuric Acid.*

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The products obtained in sulphuric acid (0·5N to 5·0N) at 14° are mainly 3-*nitro*-4-*dimethylaminobenzenesulphonic acid*, with smaller quantities of *p*-nitrophenylmethylnitrosoamine and *p*-nitrodimethylaniline. High concentrations of mineral acid slightly increase the yields of the first two products but decrease that of the last. Solubility data for the new sulphonic acid are recorded and its anilide is described.

Michler and Walder (*Ber.*, 1881, **14**, 2176) described briefly the action of nitrous acid on a dimethylanilinesulphonic acid of unmentioned orientation in mineral acid of unmentioned concentration; they isolated *p*-nitrodimethylaniline and a nitrodimethylanilinesulphonic acid. In the present investigation the starting point was pure dimethylaniline-*p*-sulphonic acid, a third product, 4-nitrophenylmethylnitrosoamine, was isolated, and the nitrosulphonic acid formed was shown to be 3-*nitro*-4-*dimethylaminobenzenesulphonic acid* by comparison with a snythetic specimen. The influence of sulphuric acid concentration on the course of the reaction, and the relative yields of the various products, were also noted.

The main action of nitrous acid (4 mols.) on dimethylaniline-*p*-sulphonic acid (1 mol.) in sulphuric acid at 14° was nuclear nitration, but was invariably accompanied by replacement of the sulpho-group by a nitro-group to the extent of about one-ninth of the whole. In high concentrations of mineral acid the *p*-nitrodimethylaniline so formed underwent nitrosation at the nitrogen atom to form 4-nitrophenylmethylnitrosoamine. Liberation of formaldehyde accompanied nitrosoamine formation and nitric oxide was evolved in all cases.

Increase in sulphuric acid concentration increased about equally the yields of 3-nitro-4-dimethylaminobenzenesulphonic acid and 4-nitrophenylmethylnitrosoamine, but decreased that of *p*-nitrodimethylaniline. Indeed the yields of the last two products stand in a reciprocal relationship to each other within the limits of experimental error. It is known that nitrous acid converts the latter into the former in mineral acid solution (Macmillan and Reade, J., 1929, 2863), and the formation of nitrosoamine at the expense of the amine

in the more strongly acid medium is probably due to the greater concentration of amine remaining dissolved (as its salt), *i.e.*, not removed from the sphere of action, in the more acidic solutions, thus facilitating the further action of nitrous acid.

Experimental.

*Preparation of Dimethylaniline-*p*-sulphonic Acid* (from a note by C. de B. Evans, P., 1895—96).—A mixture of dimethylaniline (121 g.) and 36N-sulphuric acid (102 g.) was heated for 4 hours at 180°, and the resulting syrup cooled and mixed with water. After basification with aqueous ammonia and removal of the excess of dimethylaniline by ether extraction, the sulphonic acid was obtained, after acidification, by evaporation until crystallisation began, and was recrystallised from 60—70 c.c. of hot water. Yield, 10—15 g.

Action of nitrous acid. A solution of the sulphonic acid (1 mol.) in 4N-sulphuric acid was cooled in ice, and aqueous sodium nitrite (4 mols.) added slowly with continuous stirring (resulting mineral acid concentration, 3·5N). After 17—18 hours the yellow precipitate was collected. Prolonged extraction with light petroleum separated this into two parts: (A) a portion soluble in light petroleum and other organic solvents and insoluble in water; (B) a portion insoluble in light petroleum and organic solvents generally, but recrystallisable from hot water.

(A), consisting of bright yellow needles giving a positive Liebermann nitroso-test, was separated into two substances by washing with 5N-hydrochloric acid. The filtrate on basification gave a yellow solid, which after recrystallisation from light petroleum was identified as *p*-nitrodimethylaniline, m. p. and mixed m. p. 162°. The residue, a nitrosoamine, melted sharply at 100° after repeated crystallisation from light petroleum. On boiling with 12N-hydrochloric acid and subsequent basification this yielded 4-nitromethylaniline, m. p. and mixed m. p. 152°. The nitrosoamine is 4-nitrophenylmethylnitrosoamine (Found: C, 46·2; H, 3·7. Calc.: C, 46·4; H, 3·8%).

(B) crystallised from hot water in pale yellow needles. It appeared to be a sulphonic acid, but gave only small precipitates, on addition of barium chloride and calcium chloride to neutralised solutions. Reduction of the acid with tin and hydrochloric acid yielded a product, which, after diazotisation, coupled with β-naphthol. Attempts to remove the sulphonic acid group by superheated steam or by fusion yielded no result (Found: NO_2, 19·1; C, 39·0; H, 4·1; N, 11·4; S, 13·4. *3-Nitro-4-dimethylaminobenzenesulphonic acid* requires NO_2, 18·7; C, 39·0; H, 4·1; N, 11·4; S, 13·0%).

The nitrous acid experiment was repeated in 5N- and in 0·5N-mineral acid; no new precipitate was obtained. In each case treatment of the filtrate yielded no new product, except a trace of formaldehyde in the experiments (conc. acid) where nitrosoamine was formed: this was detected by distilling over 10 c.c. from the filtrate, which gave positive reactions to Schiff's and Schryver's tests.

Synthesis of 3-Nitro-4-dimethylaminobenzenesulphonic Acid.—4-Chloro-3-nitrobenzenesulphonic acid (10 g.), prepared from *o*-chloronitrobenzene by Fischer's method (*Ber.*, 1891, **24**, 3187), was dissolved in 75 c.c. of alcohol with sufficient water to keep it in solution at the b. p., 0·05 g. of freshly prepared copper powder and 25 g. of 33% aqueous dimethylamine added, and the mixture heated under reflux for 3—4 hours. The orange solution was filtered hot, acidified to Congo-paper with hydrochloric acid, and evaporated on the steam-bath until crystallisation set in on cooling. After decolorisation by charcoal and recrystallisation from a little water, 3-nitro-4-dimethylaminobenzenesulphonic acid was obtained in pale golden needles, which appeared identical with the product (B). Both specimens gave the same *sulphonanilide*, m. p. and mixed m. p. 182°, as follows: Equal weights (about 2 g.) of the sodium salt of the sulphonic acid and phosphorus pentachloride were heated on the water-bath for 2 hours, excess of aniline added, and heating continued for 1½—2 hours. The mixture was then cooled and after filtration the precipitate was washed with ether to remove the excess of aniline and with water to remove chlorides and unchanged sodium salt, dried, and crystallised from hot alcohol (charcoal), forming lustrous white plates (Found: C, 52·3; H, 4·6; N, 13·0. $C_{14}H_{15}O_4N_3S$ requires C, 52·3; H, 4·7; N, 13·1%), readily soluble in methyl alcohol, acetone, glacial acetic acid and hot ethyl alcohol, slightly in benzene, carbon disulphide and hot water, and insoluble in ether and chloroform.

Influence of Mineral Acid Concentration on Yields of Products.—4 G. of dimethylaniline-*p*-sulphonic acid were dissolved in water, and concentrated sulphuric acid added. A solution containing 5·492 g. of sodium nitrate was then added, the reaction mixture being cooled in ice.

The total volume of solution in each case was 100 c.c., and the resulting mineral acid concentrations varied from 0·5N to 5N. The mixture was kept for 17—18 hours and then submitted to filtration. The precipitate was extracted with light petroleum, and the residue, consisting of nitro-sulphonic acid, dried and weighed. The petroleum solution was evaporated to dryness; the residue, after being washed with cold 5N-hydrochloric acid, was washed on to a sintered glass crucible, dried, and weighed along with the small further quantity of nitrosoamine isolated from the filtrate. The acid solution, containing *p*-nitrodimethylaniline, was neutralised with sodium hydroxide solution and the precipitate was dried and weighed, along with the small further quantity obtained by treatment of the filtrate by concentration and neutralisation.

Solubility data for 4-nitrophenylmethylnitrosoamine in 5N-hydrochloric acid were obtained from figures by R. L. Mitchell (Ph.D. Thesis, Aberdeen, 1934).

Solubility of 3-Nitro-4-dimethylaminobenzenesulphonic Acid in 100 c.c. of Sulphuric Acid of Various Concentrations at 14°.

H_2SO_4, N	0·5	1	2	3	4	5
Solubility, g.	0·5710	0·5660	0·547	0·5217	0·4823	0·4100

The results were calculated as g.-mols. of product derived from 1 g.-mol. of initial material.

	Yields (corrected for solubilities).		
Acid, N.	3-Nitro-4-dimethylamino-benzenesulphonic acid.	4-Nitrophenylmethyl-nitrosoamine.	*p*-Nitrodimethyl-aniline.
0·5	0·319	0·0037	0·052
1	0·320	0·0207	0·0336
2	0·333	0·0277	0·0263
3	0·360	0·0487	0·005
4	0·379	0·0547	—
5	0·380	0·0547	—

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