229. *The Mechanism of the Bucherer Reaction. Part II. Isolation of Bisulphite Compounds from Naphthionic Acid.*

By W. A. Cowdrey.

The product of the reaction between naphthionic acid and sodium bisulphite has been isolated and separated into two pure compounds.

The major constituent, $C_{20}H_{24}O_{16}NS_4Na_3$, appears to be the *tetrahydrate* of the di-bisulphite compound of 4 : 4′-dinaphthylamine-1 : 1′-disulphonic acid (A). The connection between this substance and its simple analogue, iminomethanesulphonic acid, prepared from the formaldehyde-bisulphite compound and ammonia by Raschig, is discussed, and its formation is correlated with the common occurrence of dinaphthylamines as by-products in the Bucherer reaction.

The other *compound*, $C_{10}H_{10}NS_2Na,1\frac{1}{2}H_2O$, is either the monosodium salt of the bisulphite compound of naphthionic acid (IV), or the sodium ammonium salt of the bisulphite compound of 1-naphthol-4-sulphonic acid (V).

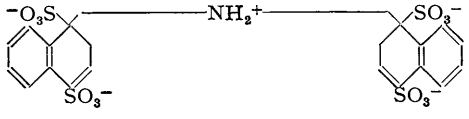
A detailed scheme for the mechanism of the Bucherer reaction as applied to the conversion of naphthylamines into naphthols is proposed, based on this work and the kinetic study reported in Part I.

As early as 1904 Bucherer showed that very soluble bisulphite compounds were formed during the reaction between naphthylamine derivatives and sodium bisulphite, but few such substances have as yet been isolated in a pure condition from simple monohydroxy- or monoamino-naphthalene derivatives, and directions given for their preparation are often vague (cf. Woroshtzow, *Ann. Chim.*, 1917, **7**, 50). The compounds which Bucherer himself prepared (*J. pr. Chem.*, 1904, **69**, 80) were not isolated pure and no analytical examination of them is reported (see Friendländer, *Ber.*, 1921, **54**, 620). Fuchs and his co-workers describe the preparation and analysis of bisulphite compounds from a number of aminonaphthols and polyhydroxy-naphthalene and -benzene derivatives (*Ber.*, 1921, **54**, 245; 1922, **55**, 658; 1920, **53**, 886), but the majority of these are necessarily complex and some of them do not correspond to the intermediates formed in the Bucherer process because they are not completely hydrolysed to the parent substance by alkali.

A notable exception in this connection appeared to be the compound described by Woroshtzow (*Ber.*, 1929, **62**, 57) from 2-naphthol-1-sulphonic acid, but on repetition this work has been found incorrect. Purified 2-naphthol-1-sulphonic acid, when converted into its disodium salt and treated with sulphur dioxide in concentrated aqueous solution, does not in fact yield a crystalline bisulphite compound in the manner described. The method outlined by Woroshtzow for preparing sodium 2-naphthol-1-sulphonate by sulphonating β-naphthol actually gives mainly the 2-naphthol-6-sulphonate. This forms a very soluble disodium salt, and a sparingly soluble monosodium salt which reacts with iodine in neutral or alkaline solution and was probably mistaken for a bisulphite compound.

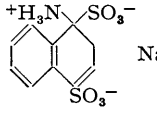
The kinetic investigation described in Part I showed that a bisulphite compound was formed during the rate-determining stage of the reaction between sodium naphthionate and sodium bisulphite which was stable in presence of excess of bisulphite below 100°. The precise nature of this substance, and in particular whether it still contains any of the original nitrogen, has never been established, although it is made regularly on an industrial scale as an intermediate in the conversion of naphthionic acid into 1-naphthol-4-sulphonic acid (cf. D.R.-P. 109,102; U.S.P. 1,880,701). From the mechanism suggested by Fuchs and Stix (see Part I) the product of the reaction would be expected to consist of a mixture of naphthylamine- and naphthol-bisulphite compounds, and this investigation was carried out to obtain more definite information about the composition of the equilibrium mixture.

It was found that the reaction product freed from inorganic salts could be separated into a mixture of two substances, both of which have been prepared in a pure condition. The main *constituent* (A) crystallises in colourless spherulites and has the composition $C_{20}H_{24}O_{16}NS_4Na_3$. It is soluble in about its own weight of water but almost insoluble in organic solvents, and it does not react with acidified iodine. On boiling with aqueous sodium hydroxide the whole of its nitrogen is evolved as ammonia, and at the same time half of its sulphur becomes available as sulphite. It is almost certainly the di-bisulphite compound of the dinaphthylamine derivative with the following structure:

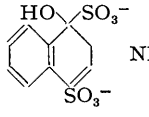


$Na_3,4H_2O$ (A)

The other *compound* (B) separates in crystals of the anorthic system having the form of four-sided prisms terminated by four-faced truncated pyramids, with a composition corresponding to $C_{10}H_{13}O_{7\cdot5}NS_2Na$, *i.e.*, $C_{10}H_{10}O_6NS_2Na,1\frac{1}{2}H_2O$. Its properties are very similar to those of (A). Two structures are possible for this compound on the available evidence, *viz.*,



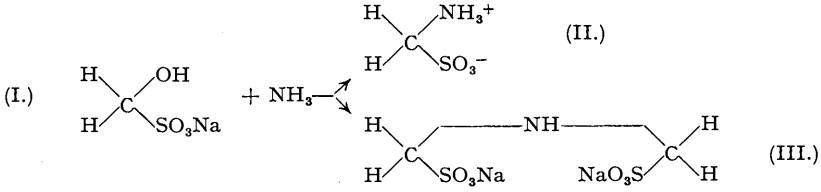
$Na,1\frac{1}{2}H_2O$ and



$NH_4,Na,\frac{1}{2}H_2O$ (B)

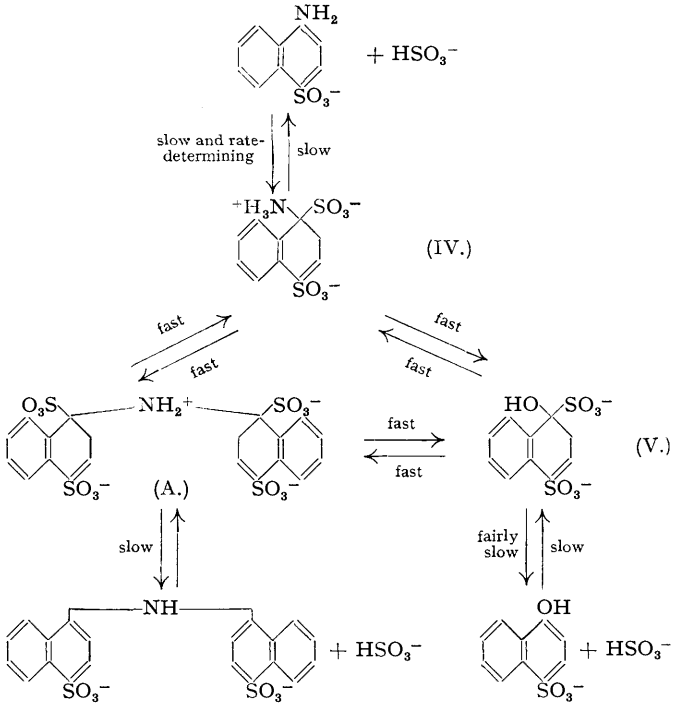
which correspond to the bisulphite compounds of the naphthylamine and naphthol respectively. Compound (A) can, moreover, readily be converted into (B) by treatment with ammonium iodide in concentrated aqueous-alcoholic solution, even in presence of strong acid. This means either that the sodium ammonium salt of the naphthol bisulphite compound is rather more sparingly soluble and separates in preference to the disodium or diammonium salt, or alternatively but less probably that compound (A) actually reacts with ammonium ion to form the naphthylamine bisulphite compound. So far it has not been possible to decide definitely between the two possible structures for compound (B).

Concerning the formation of compound (A), it is of interest to recall Raschig and Prahl's work (*Ber.*, 1926, **59**, 859; *Annalen*, 1926, **448**, 265) on the reaction between the formaldehyde-bisulphite compound (I) and ammonia in connection with the mechanism of the Bucherer reaction. Below 10° the main product was aminomethanesulphonic acid (II), but above this temperature the iminomethanesulphonate (III) was chiefly formed.



Compound (III) is, of course, the simple analogue of substance (A) isolated from naphthionic acid, whilst (B) corresponds to either (I) or (II). The properties of (III) are actually similar to those of compound (A) in that they both evolve their nitrogen as ammonia and their sulphur as sulphite on alkaline hydrolysis.

Taken in conjunction with the kinetics outlined in Part I, the reaction between naphthionic acid and sodium bisulphite can be represented by the following detailed scheme :



It is interesting to note that this scheme accounts for the known occurrence of dinaphthylamine compounds as by-products (and even in some cases as main products) in the treatment of naphthylamines with sulphites or bisulphites (cf. Bucherer and Stohmann, *J. pr. Chem.*, 1905, **71**, 441; Bayer and Co., D.R.-P. 114,974).

Experimental.

Attempt to Prepare the Bisulphite Compound of 2-Naphthol-1-sulphonic Acid.—Crude sodium 2-naphthol-1-sulphonate was obtained from two different commercial sources (Messrs. B.D.H. and I.C.I. Dyestuffs Division) and purified by conversion into and recrystallisation of the aniline salt (cf. Forster and Keyworth, *J. Soc. Chem. Ind.*, 1927, **46**, 25T). Both samples of aniline salt had m. p. 178—179°, as compared with the recorded 182°. The purified aniline salt (27 g.) was converted into the monosodium salt by dissolving it in water (50 c.c.) and 2N-sodium hydroxide (90 c.c.), the aniline being extracted with ether. After being neutralised with concentrated hydrochloric acid and filtered through carbon, the sodium salt (15 g.) was salted out with A.R. sodium chloride (35 g.).

The monosodium salt (3 g.) was converted into disodium salt by dissolving it in boiling 90% alcohol (50 c.c.) and adding 50% aqueous sodium hydroxide (1 c.c.); it was filtered off and washed with cold alcohol (50 c.c.).

The disodium salt was dissolved in water (12 c.c.), and the solution saturated with sulphur dioxide. The solution, initially almost colourless, became bright yellow, but no solid separated even after several weeks' standing and repeated resaturation with the gas.

Re-examination of Woroshtzow's Preparation.—On repeating the preparation of disodium 2-naphthol-1-sulphonate outlined by Woroshtzow (*Ber.*, 1929, **62**, 61) and treating it with sulphur dioxide in aqueous solution, a crystalline solid separated in the way described. This reacted with iodine in neutral or alkaline solution and also formed sparingly soluble barium, copper, zinc, and mercury salts as claimed. However, conversion of the supposed disodium 2-naphthol-1-sulphonate into aniline salt gave needles, m. p. 262—263°, which is approximately that recorded by Forster and Keyworth (*loc. cit.*) for the aniline salt of 2-naphthol-6-sulphonic acid.

A purified sample of monosodium 2-naphthol-6-sulphonate was converted into disodium salt with 50% sodium hydroxide using alcohol, and on dissolving this in water and passing sulphur dioxide into the solution, the sparingly soluble monosodium salt separated in fine needles. Monosodium 2-naphthol-6-sulphonate reacts with iodine in neutral or alkaline solution, but not in acid medium; this would explain Woroshtzow's results on the supposed dissociation of the bisulphite compound. Finally, 2-naphthol-6-sulphonic acid forms sparingly soluble salts with the four metals mentioned above.

Isolation of Bisulphite Compounds from Naphthionic Acid.—Purified sodium naphthionate (130 g.) was dissolved in a warm solution of sodium bisulphite prepared by saturating sodium carbonate (212 g.) in water (800 c.c.) with sulphur dioxide. The solution was kept at 80° for 18 hours whilst a slow stream of sulphur dioxide was passed through it. At this stage no unchanged naphthionic acid was detected on acidification. The solution was cooled, made strongly acid to Congo-red with concentrated hydrochloric acid (300 c.c.), and a fast stream of nitrogen was passed through the solution, which was kept strongly acid, until all the sulphur dioxide was removed according to a test titration with iodine. Some inorganic salts were filtered off; the filtrate was evaporated to 250 c.c. under reduced pressure below 60°, and its pH was adjusted to 3·0 by addition of solid sodium hydrogen carbonate. Concentration and filtering from inorganic salts was continued until a thick syrupy residue remained, and this was stirred with about three times its volume of absolute alcohol. The mixture of bisulphite compounds slowly separated in two different types of large crystals, which were filtered off, air-dried, and separated from each other easily by hand picking.

The aggregates of needles (A) (approx. 85 g.) were recrystallised by dissolving them in water (85 c.c.) and adding absolute alcohol (260 c.c.) (Found : C, 32·82; H, 3·43; N, 2·12; S, 17·33; Na, 9·62. $C_{20}H_{16}O_{12}NS_4Na_3,4H_2O$ requires C, 32·82; H, 3·31; N, 1·91; S, 17·50; Na, 9·44%). On heating with aqueous sodium hydroxide, ammonia was evolved corresponding to 1·95% of N, and sulphite was formed which, on iodine titration, was equivalent to 8·50% of S.

The other type of crystal (B) (about 12 g.) (Found : C, 33·93; H, 4·20; S, 18·30; N, 3·49; Na, 6·40. $C_{10}H_{10}O_6NS_2Na,1\frac{1}{2}H_2O$ requires C, 33·89; H, 3·70; N, 3·95; S, 18·08; Na, 6·50%) with alkali yielded ammonia corresponding to 3·93% of N, and sulphite equivalent to 9·01% of S.

Conversion of Compound (A) into Compound (B).—The compound A (10 g.) was dissolved in water (10 c.c.), and a solution of ammonium iodide (10 g.) in absolute alcohol (20 c.c.) was added. On standing for 12 hours, compound B (5·0 g.) separated (Found : C, 33·12; H, 4·01; S, 18·73; Na, 6·60; N, available as ammonia, 3·64; S, available as sulphite, 8·94%). A further crop of the same material was obtained from the filtrate by adding more alcohol.

This experiment was repeated in presence of constant b. p. hydriodic acid (1 c.c.), and gave substantially the same results.

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