

169. *Sulphites of Azo-compounds containing Two Hydroxyls.*

By ALBERT THEODORE KING.

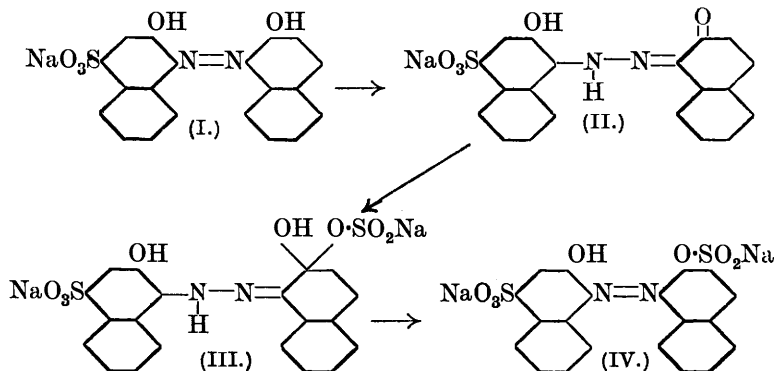
IN discussing the evidence in support of his view of the structure of the azo-sulphites, as opposed to that of Spiegel (*Ber.*, 1885, **18**, 1479), Voroschtsov (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1669) observes that with compounds containing two azo-linkings and one hydroxy-group, Spiegel's formula would allow of the formation of a disulphite by addition at each azo-linking, whereas according to the Voroschtsov formula only a monosulphite could be formed. He found that in the case of 1-naphthol-2:4-disazoaniline only a monosulphite is formed.

Conversely he predicts that compounds with one azo-linking and two active hydroxy-groups should form a monosulphite according to Spiegel's formula, and a disulphite according to the Voroschtsov formula, but he did not investigate this point experimentally.

Consideration will show, however, that the latter prediction is only realisable if, contrary to his view, the mono-addition product first formed loses a water molecule so that the product can re-assume the azo-linking.

Taking as a concrete example 4-sulpho-2-hydroxy- α -naphthalene-azo- β -naphthol (Eriochrome Blue Black R.C., Geigy), it will be seen that the assuming of the ketonised form by one of the β -naphthol nuclei automatically prevents the other from so doing (except by an

entirely different and improbable mechanism involving a quinquevalent nitrogen atom).



Thus in the first place the reaction can only proceed as far as the monosulphite, as shown, for example, in (III). (It is assumed that the addition takes place on the coupled β -naphthol group.) If this loses water to give (IV), the second hydroxy-group can then ketonise and a further bisulphite molecule can be added. If, however, the additive form shown in (III) is retained, the second hydroxy-group cannot ketonise and no further addition can occur.

It therefore appeared of interest to investigate this point experimentally. The above compound has been found to yield a *monosulphite*, which is readily isolated from reaction in warm bisulphite solution. It shows abnormal behaviour, however, in that though it dissolves in warm bisulphite, and from solutions heated even up to 60° crystallises unchanged, when the temperature is raised to about 70° a rapid deposition of the original dye takes place and the reversion is practically complete, notwithstanding the presence of a large excess of alkali bisulphite.

No indication could be obtained of any formation of a disulphite. Similar behaviour is shown by 4-sulpho-5-nitro-2-hydroxy- α -naphthaleneazo- β -naphthol (Eriochrome Black A, Geigy).

On the contrary, 5-sulpho-2-hydroxybenzeneazo- β -naphthol (Solochrome Violet R), which contains similarly oriented hydroxy-groups, only one of which, however, is naphtholic, yields a *monosulphite* which crystallises unchanged from bisulphite solution heated even to boiling point.

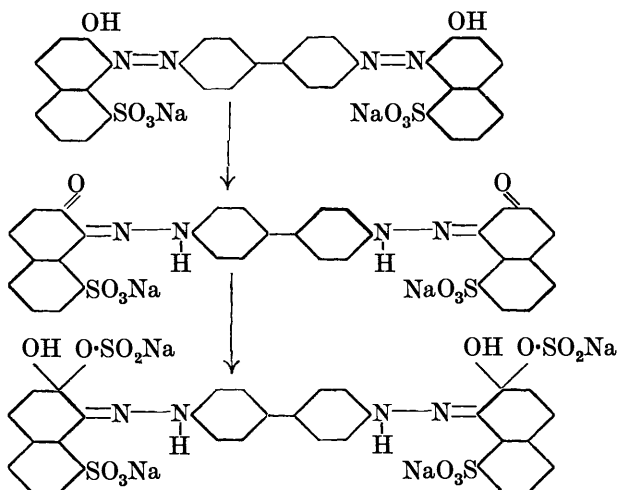
Also the bisulphite compounds of a number of other mono-azo-derivatives containing only one β -naphthol group (J., 1929, 601) do not exhibit this reversion, which is thus apparently associated in some way with the potential activity of the second hydroxy-

group, rather than caused by a simple splitting off of the bisulphite molecule originally added.

This failure to observe any disulphite formation is additional evidence in support of the view previously expressed (see above ref.) that the azo-sulphites are definitely of hydrazone- and not azo-structure. The much greater rate of fading of the azo-sulphites compared with the original dyes (King, *J. Soc. Dyers & Cols.*, August, 1928) also supports a difference in structure.

On the other hand, the formation of disulphites is usually realisable with dis-azo-compounds containing two β -naphthol nuclei.

Thus with sodium diphenyldisazobis- β -naphthol-8-sulphonate (Bordeaux extra, Bayer) each hydroxy-group can ketonise independently of the other, and a *disulphite* is obtained :



Sodium 2 : 5 : 2' : 5'-tetramethyltriphenylmethane-4 : 4'-disazobis- β -naphthol-3 : 6-disulphonate (Brilliant Carmine L., B.D.C.) similarly yields a *disulphite*. These show marked stability towards further action of bisulphite, and even hydrosulphite, though the latter readily reduces the parent colours. Attempts to isolate the monosulphite failed. Sodium 2 : 2'-disulphodiphenyldisazobis- β -naphthol (Coomassic Milling, Scarlet, G, B.D.C.), on the other hand, gives a well-defined *monosulphite*, but the disulphite was not isolated. In this case the sulpho-groups are adjacent, but one would scarcely be expected to interfere more than the other.

The observation that where both the nitrogen linkages are "protected" the fission effect found with the sulphites of the dis-azo-compounds previously described (preceding paper), ascribed to the azo-linkage being reduced, but not the hydrazone linkage, does not

occur, is a further contribution to these studies of constitutional influences on the action of sulphur dioxide upon azo-dyes.

Eriochrome Blue Black R.C. has the additional interest of illustrating how the same azo-linking can be sulphite-forming or reducible, with bisulphite, under appropriate conditions.

As already stated, this azo-sulphite reverts to the original dye when the temperature of the solution is raised, and after some hours' heating of the diluted solution complete reduction of the nitrogen link results. That this reduction is not detected with azo-dyes which readily form azo-sulphites is accounted for by the fact that usually azo-sulphite formation proceeds far more rapidly than reduction.

This is supported by the behaviour of Ponceau 2 R.E., which, as previously pointed out (J., 1929, 608), forms an azo-sulphite only with difficulty. After some hours' heating on the water-bath with bisulphite, in addition to formation of azo-sulphite, the fission products were found to be present in appreciable quantity. In this connexion it is noteworthy that on wool fabric dyed with this dye, "spotting" with the "active range" bisulphite reagent (King, *J. Soc. Dyers and Cols.*, 1928, 44, 14) produces in the cold no sign of the off-shade effect through azo-sulphite formation characteristic of β -naphtholic azo-dyes in general. When placed in the steam-oven, however, the dye is rapidly bleached from the fabric at the spot where the reagent was applied.

EXPERIMENTAL.

Sodium 4-sulpho-2-hydroxy- α -naphthaleneazo- β -naphthyl sulphite was obtained by maintaining the bisulphite-pyridine reaction mixture at not above 50° for an hour or so and isolating the product as previously described. It may also be crystallised direct from the filtered bisulphite-pyridine liquor, and forms an orange-red crystalline powder, tending to cake in the air (Found : S as sulphite, 6.25. $C_{20}H_{14}O_8N_2S_2Na_2$ requires S, 6.2%).

Sodium 4-sulpho-5-nitro-2-hydroxy- α -naphthaleneazo- β -naphthyl sulphite was obtained in similar manner to, but less readily than, the foregoing, as a full-brown crystalline powder (Found : S as sulphite, 5.8. $C_{20}H_{13}O_{10}N_3S_2Na_2$ requires S, 5.7%).

Sodium 5-sulpho-2-hydroxybenzeneazo- β -naphthyl sulphite readily salts out from the reaction mixture as a buff crystalline powder, stable to bisulphite solution at 100° (Found : S as sulphite, 7.1. $C_{16}H_{12}O_8N_2S_2Na_2$ required S, 6.8%).

Sodium diphenyldisazobis-8-sulpho- β -naphthyl disulphite salts out readily as an orange-red crystalline powder (Found : S as sulphite, 7.0. $C_{32}H_{22}O_{14}N_4S_4Na_4$ requires S, 7.1%).

Sodium 2 : 5 : 2' : 5'-tetramethyltriphenylmethane-4 : 4'-disazobis-

3 : 6-*disulpho-β-naphthyl disulphite* was easily formed from aqueous bisulphite solution, on cooling, as a bright orange-red crystalline powder (Found : S as sulphite, 5.1. $C_{43}H_{34}O_{20}N_4S_6Na_6$ requires S, 5.1%).

Sodium 2 : 2'-disulphodiphenyldisazobis-β-naphthyl sulphite was formed readily in the aqueous reaction mixture and salted out as a bright orange crystalline powder (Found : S, 3.9. $C_{32}H_{21}O_{11}N_4S_3Na_3$ requires S, 4.0%). Further treatment with bisulphite gave a product somewhat paler in colour than the monosulphite, with S, 4.6%, but the pure disulphite (S as sulphite, 7.1%) was not isolated.

WOOL INDUSTRIES RESEARCH ASSOCIATION,
HEADINGLEY, LEEDS.

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