

CCCXLVIII.—*The Formation of the Sulphites of Azo-compounds.*

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THE sodium bisulphite derivatives of azo-compounds, being markedly different in colour from the original azo-compounds, are of great technical interest in relation to commercial azo-dyes. The readiness or otherwise of their formation under various conditions determines the degree of fastness of the dye on wool to stoving (bleaching with sulphur dioxide) and to exposure to town air containing sulphur dioxide.

From preliminary observations that the effect of sulphur dioxide upon azo-compounds is greatly dependent on the conditions under which it is allowed to react, it appeared desirable to examine this reaction further, in relation both to the degree of departure shown, under optimum conditions, from the accepted commercial standards of fastness to stoving and to the influence of constitution and of substituent groups on the ease of sulphite formation.

Spiegel (*Ber.*, 1885, **18**, 1479) prepared a number of these compounds of azo-dyes by reaction of the dyes with warm aqueous or aqueous-alcoholic solutions of sodium hydrogen sulphite, and observed that they were very stable towards dilute acids, but were decomposed by heat and by alkalis into the original dye and alkali sulphite. He regarded them as hydrazo-*N*-derivatives of the general formula $\text{NHX} \cdot \text{NY} \cdot \text{SO}_3\text{Na}$.

Voroschtsov (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 771; 1915, **47**, 1669), on the other hand, regards them as salts of sulphurous esters, *e.g.*, $\text{C}_6\text{H}_5 \cdot \text{N} : \text{N} \cdot \text{C}_{10}\text{H}_6 \cdot \text{O} \cdot \text{SO}_2\text{Na}$. He assumes that sulphurous acid is added to the naphtholic nucleus in the ketonic form, the product losing a molecule of water. He found that the reaction was characteristic of hydroxyazo-compounds, and that the corresponding amino-azo-compounds, on boiling with aqueous-alcoholic bisulphite, formed the sulphite, not of the aminoazo- but of the hydroxyazo-compound. He also found that the reaction was confined to the azo-derivatives of α - and β -naphthols. These reacted readily, whereas *o*- and *p*-hydroxyazobenzenes and benzeneazo-*o*- and -*p*-cresols underwent no change even on prolonged boiling.

He and his collaborators prepared the sulphites of a number of substituted azonaphthols, but did not make anything more than qualitative observations on their relative ease of formation.

A simple method of measuring the rate of formation of the sulphites of soluble azo-compounds is provided by the fact that these derivatives are very stable not only towards dilute mineral acids, but also towards acidified iodine solution. Thus by running the reaction mixture into excess of acidified iodine solution, and titrating back with thiosulphate, the amount of sulphur dioxide which has become inactive by combination with the azo-compound is readily ascertained. The method is free from the difficulties associated with the estimation of ketone bisulphites (Stewart, *J.*, 1905, **87**, 185).

For the series of experiments to be described, the sodium salts of *p*-sulphobenzeneazo- β -naphthol (Orange II), 4-sulpho- α -naphthaleneazo- β -naphthol (Fast Red A), benzeneazo- β -naphthol-6 : 8-disulphonic acid (Acid Orange GG), and α -naphthaleneazo- β -naphthol-6 : 8-disulphonic acid (Crystal Scarlet) were selected, these having different degrees of fastness to stoving * (1—2, 2—3,

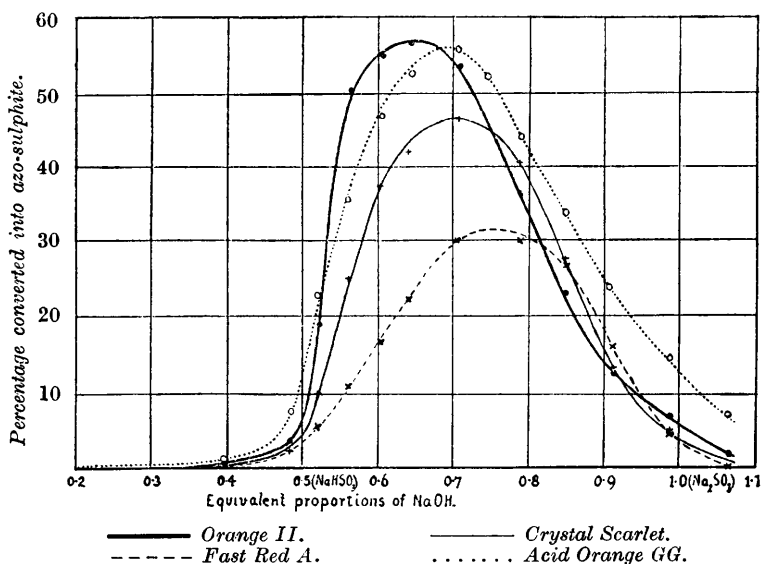
* The standard test for fastness of dyes on wool to stoving is carried out as follows : The dyed sample is soaked in 2% Marseilles soap solution, wrung out, placed in a vessel filled with sulphur dioxide by burning an excess of sulphur, left in for 12 hours, rinsed well in cold water, and dried. The dyes are placed in five classes according to the extent of colour change, class 1 being fast, and 5 the most fugitive.

1, and 2 respectively) and providing some indication of the influence of substitution on the ease of sulphite formation.

The measurements recorded were confined to 2-hour periods of reaction at 25°. Fig. 1 illustrates the percentage converted into sulphite by the equivalent quantity of sulphur dioxide, with various SO_2/NaOH ratios, the reaction mixture corresponding initially to $N/50$ -sulphurous acid.

The most striking variation is shown by Orange II. The reaction is negligible with sulphurous acid alone, and the sharp rise in the

FIG. 1.



percentage of azo-sulphite formed occurs beyond the molecular ratio $\text{SO}_2/\text{NaOH} = 1$ (representing the formula NaHSO_3), the maximum being with about 1.3 mols. of sodium hydroxide. On either side of this maximum the reaction is extremely sensitive to variation of the SO_2/NaOH ratio.

On the assumption that the reaction consists in direct addition of sodium hydrogen sulphite to the dye to give the hydrazo- N -derivative as suggested by Spiegel (*loc. cit.*), $\cdot\text{N}:\text{N}\cdot + \text{NaHSO}_3 \rightarrow \cdot\text{NH}\cdot\text{N}(\text{SO}_3\text{Na})\cdot$, it would be expected that sulphurous acid and caustic soda in equimolecular proportion would effect the most rapid conversion.

Hägglund and Ringborn (*Z. anorg. Chem.*, 1926, **150**, 231) conclude that the addition of bisulphite to ethylenic linkages proceeds according to the similar equation $\text{:C:C:} + \text{NaHSO}_3 \rightarrow \text{:CH}\cdot\text{C}(\text{SO}_3\text{Na})\cdot$.

They found the velocity to depend on the concentration of sodium bisulphite (or the ion HSO_3'), and with normal sulphite there was no action.

Certainly with additional alkali (which readily decomposes azo-sulphites) it would be expected that the reaction would be arrested : $\cdot\text{N}:\text{N}\cdot + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \rightleftharpoons \cdot\text{NH}\cdot\text{N}(\text{SO}_3\text{Na})\cdot + \text{NaOH}$.

With normal sulphite, the reaction is in fact only slight (Fig. 1), although a small excess of sodium hydroxide beyond this proportion is needed to inhibit the reaction completely.

The above optimum ratio of greater than unity accords with the view that the hydroxy-group is participating in the reaction, and that theoretically the most rapid conversion would occur with a further molecular proportion of alkali, but that actually this is balanced by the simultaneous decomposing action of the latter.

It is known (Stewart and Baly, J., 1906, 89, 489) that the bisulphite compounds of ketones are formed much more rapidly in the case of tautomeric compounds like acetoacetic ester, the reactivity being presumed to be inherent, not in the carbonyl group itself, but in its tautomeric character, which is governed by the action of the adjacent groups upon the carbonyl radical.

Evidence has been advanced, principally by Goldschmidt and Löw Beer (*Ber.*, 1905, 38, 1908), refuting the quinonoid structure of *p*-hydroxyazo-compounds, but there is still a conflict of opinion on this point (compare Puxeddu and Germain, *Gazzetta*, 1922, 52, i, 216) and Voroschtsov's view can be supported, even accepting the azophenolic structure, by assuming a similarly tautomeric hydroxyl group. This may also be the determining factor in the velocity of reaction, as Stewart and Baly maintain in the case of ketones. In the tautomerism of the latter, however, alkali favours the enol form, and the precise rôle of the excess of alkali above mentioned in accelerating the formation of azo-sulphites is not at present clear.

So far as is indicated by the four azo- β -naphthols examined, the sulphonaphthalene group obviously has a retarding effect compared with the benzene derivative, and the benzenazonaphtholdisulphonate also is more reactive than the corresponding naphthalene-azonaphtholdisulphonate, but any generalisation must be deferred pending results over a wider range of azo-derivatives.

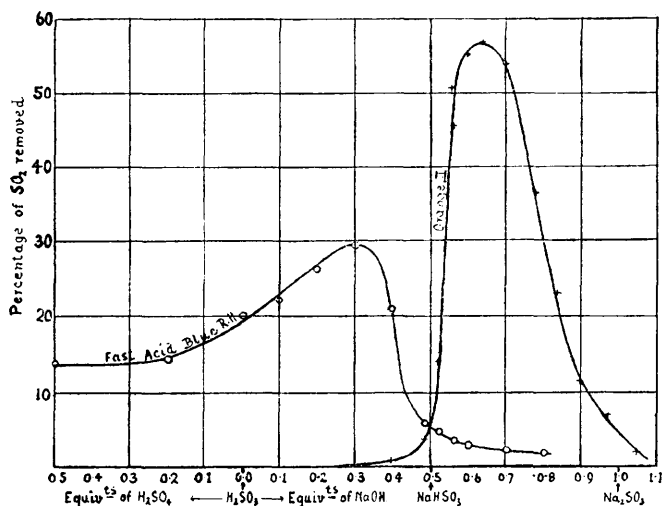
This preliminary series is, however, sufficient to illustrate both the varying reactivity of azo-compounds to sulphur dioxide under different conditions and also the anomalous behaviour at times encountered with dyes scheduled as of good fastness to sulphur dioxide under the special conditions of the stoving test, owing to their unsuspected sensitiveness to this reagent under favourable

conditions which can in various ways be fortuitously realised in practice.

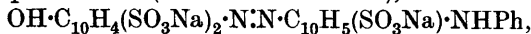
As previously mentioned, the formation of azo-sulphites is not general with azo-dyes. The examples above were selected on account of their observed susceptibility and are all β -naphthol derivatives. The α -naphthol derivatives would appear to be generally less sensitive, and similar work on these is projected.

In addition, a third type, principally aminoazo-compounds, does not, according to Voroschtsov, give bisulphite derivatives, but either through fission or other form of decomposition is destroyed by bisulphite and is thus not regenerated by subsequent treatment

FIG. 2.



with caustic soda. As an example of such compounds, the sodium salt of 3:6-disulpho-8-hydroxy- α -naphthaleneazo- α -naphthylphenylamine-8-sulphonic acid (Fast Acid Blue RH),



was investigated. This is very fugitive to stoving, turning eventually yellow, and is entirely different in behaviour towards sulphur dioxide from the sulphite-forming azo-compounds (Fig. 2). The extent of reaction in the 2-hour period employed is most marked with about 0.3 equivalent of alkali, and under the optimum sulphite-forming conditions the dye scarcely reacts at all.

Thus the foregoing results indicate that more precise information on the reactivity of sulphur dioxide towards the various types of azo-dyes is desirable from both the theoretical and the practical aspect, and further work is in progress with this end in view.

EXPERIMENTAL.

The dyes in question readily lend themselves to purification. Orange II, already practically pure in commercial form, was recrystallised twice from 90% ethyl alcohol. Acid Orange GG, Crystal Scarlet, and Fast Red A were first separated from inorganic salts by solution in pyridine and reprecipitation with ether; the Fast Red A was then recrystallised from amyl alcohol, and the other two from 90% ethyl alcohol. Their purity was checked by evaluation with titanous chloride, which gave Orange II 99.93%, Acid Orange GG 100.3%, Crystal Scarlet 99.0%, and Fast Red A 99.1%.

Preparation of Azo-sulphites.—The sulphites of the above-mentioned azo-compounds were obtained by stirring the powdered dye into excess of concentrated sodium bisulphite solution, gently warming the liquid, and keeping it over-night. The bisulphite solution is conveniently made by adding 10% sodium hydroxide solution to commercial bisulphite solution (20% SO_2) until the latter reacts only faintly acid to litmus paper. The ease of isolating the azo-sulphite varies with the azo-compound employed.

Sodium 4-Sulpho- α -naphthaleneazo- β -naphthyl Sulphite (Bisulphite Compound of Fast Red A).—The reaction mixture was filtered, and the solution saturated with sodium chloride. The precipitate thus obtained was twice again salted out from aqueous solution and was then deposited from aqueous-alcoholic solution, by gradual addition to ether, as a reddish-orange, crystalline, hygroscopic powder (Found: S as sulphite, 6.65. Calc. for $\text{C}_{20}\text{H}_{12}\text{O}_6\text{N}_2\text{S}_2\text{Na}_2$: S as sulphite, 6.6%).

The sulphite sulphur was estimated by adding the substance, dissolved in excess of air-free aqueous sodium hydroxide, to excess of acidified iodine solution and titrating the residual iodine with thiosulphate. Estimations of total sulphur by the Carius method gave low results, presumably through incomplete breaking down of the sulphonic group.

Sodium p-Sulphobenzeneazo- β -naphthyl Sulphite (Bisulphite Compound of Orange II, commercial name "Narceine").—The reaction mixture deposited a portion of the azo-sulphite on cooling. The bulk was separated by adding a little sodium chloride. It was again salted out and then recrystallised by cooling a warm concentrated aqueous solution, being thus obtained in buff-yellow crystals (Found: S as sulphite, 7.3. Calc. for $\text{C}_{16}\text{H}_{10}\text{O}_6\text{N}_2\text{S}_2\text{Na}_2$: S, 7.3%).

Sodium Benzeneazo-6:8-disulpho- β -naphthyl Sulphite (Bisulphite Compound of Acid Orange GG).—This substance, which is not precipitated from its aqueous solution by sodium chloride, was

isolated by adding to the reaction mixture twice its volume of alcohol, which left it in solution together with some sodium bisulphite. The solution was evaporated to small bulk at a low temperature and fractionally precipitated by careful addition of alcohol. The inorganic salt was precipitated first, and the azo-sulphite was obtained, by pouring the filtrate slowly into alcohol-ether, in fairly pure condition as a canary-yellow, hygroscopic powder.

Sodium α -naphthaleneazo-6:8-disulpho- β -naphthyl sulphite (bisulphite compound of Crystal Scarlet) was isolated by the method described under Acid Orange GG and obtained as a reddish-orange powder deliquescent in air.

Stability of Azo-sulphites towards Acidified Iodine Solution.—The azo-sulphite (0.5 g.) was added to 25 c.c. of acidified iodine solution and kept for 24 hours. The blank required 21.9 c.c. of thiosulphate, and the azo-sulphites required: Fast Red A (A) 21.9 c.c., Acid Orange GG (B) 21.9 c.c., Orange II (C) 20.9 c.c., Crystal Scarlet (D) 19.6 c.c. The low results for (C) and (D) were mainly due to contamination with inorganic sulphite, since it was found that by adding iodine to the azo-sulphite in solution until the latter reacted to starch paper, and then pouring the mixture into 25 c.c. of acidified iodine, the thiosulphate figures were 21.54 and 21.4 c.c. respectively. The reaction, if any, after 24 hours' contact with iodine is thus so small as to warrant the accuracy of the method described below of estimating mixtures of alkali- and azo-sulphites.

Determination of Azo-sulphite Formation.—The purified anhydrous azo-compounds were dissolved in boiled-out water and made up to $M/40$ -solutions, 20 c.c. thus being equivalent to 10 c.c. of $N/10$ -sulphurous acid. To 20 c.c. of each dye solution were added first the desired volume of $N/10$ -sodium hydroxide, then water (to make up eventually to 50 c.c.), and finally the sulphurous acid, the solution thus being $N/50$ as regards both azo-compound and sulphite. The reaction mixtures were contained in stoppered tubes of slightly greater capacity, to reduce air-oxidation of the sulphur dioxide to the minimum. After remaining 2 hours in a water-bath at 25° , the contents of the tube were washed out into excess of acidified iodine solution, which was thereafter titrated with thiosulphate. The highly coloured solutions necessitated the use of starch as indicator. The end-point was very sharp.

Preparation of the Sulphurous Acid Solution.—In the initial experiments concordant results could not be obtained owing to the changing strength of the sulphurous acid and simultaneous formation of free sulphuric acid, each of which changed the SO_2/NaOH ratio and thus greatly affected the rate of reaction. To obviate this, a Winchester filled with boiled-out water was allowed to cool

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with wash-bottles of alkaline pyrogallol attached, and sulphur dioxide from a syphon was passed in to give an approximately $N/10$ -solution. A self-filling burette was fitted so that air entering by displacement was deprived of oxygen by alkaline pyrogallol; the absorption bottles were cut off except during the running off from the burette, to avoid any loss of sulphur dioxide from the inside atmosphere by absorption in the pyrogallol. This solution remained practically constant in strength throughout the whole series of analyses. It gave a normality of 0.1423 as sulphurous acid, and 0.1444 as total sulphur, estimated as barium sulphate, the free sulphuric acid present thus involving the small correction of 0.15 c.c. to the calculated volumes of $N/10$ -sodium hydroxide added.

Tabulated Results.

C.c. of 0.103N-NaOH added (expressed as c.c. of $N/10$ -NaOH and corrected).	SO ₂ combined (c.c. of $N/10$ -soln.).			
	A.	B.	C.	D.
—	(-0.05)	(-0.03)	0.05	0.10
3.97	(-0.15)	0	0.07	0.13
4.86	0.35	0.78	0.37	0.16
5.21	0.55	1.81	1.90	1.0
5.62	1.10	3.58	5.05	2.5
6.03	1.65	4.68	5.50	3.79
6.44	2.20	5.38	5.65	4.20
7.06	3.00	5.60	5.35	4.65
7.47	—	5.24	—	—
7.88	3.00	4.43	3.65	4.05
8.50	2.70	3.43	2.30	2.75
9.12	1.60	2.43	1.25	1.30
9.86	0.45	1.46	0.70	0.45
10.66	0	0.73	0.20	0.2

The percentage of sulphur dioxide combined is obtained by multiplying the number of c.c. of $N/10$ -solution by 10.

The curves plotted from these values are shown in Fig. 1. The values for sulphurous acid have been disregarded, since even after 24 hours no reaction could be detected with certainty; also no correction has been made for any loss of sulphurous acid by oxidation, blank determinations having shown that the loss during 2 hours, although increasing slightly with alkalinity, involved no serious error.

Reaction with Fast Acid Blue RH.—In this case, the deep blue colour obscures the colour change of starch in the solution, but by using starch as external indicator the end-point can be determined with fair precision.

The following results were obtained, the same quantities of dye and sulphurous acid being used as before, for a 2 hours' period of reaction (see Fig. 2) :

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N/10-H ₂ SO ₄ added (c.c.).	% SO ₂ combined.	N/10-NaOH added (c.c.).	% SO ₂ combined.
5	14.2	3	29.5
2	14.5	3.98	21.0
		4.86	6.0
H ₂ SO ₃ alone.	20.0	5.21	5.0
N/10-NaOH added (c.c.).		5.62	3.5
1	22.0	6.03	3.0
2	26.5	7.06	2.3
		8.1	2.3

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