[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Formation of Sodium Thiosulfate from the Oxidation of Sodium Sulfides by Means of an Aromatic Nitro Compound

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The oxidation of sulfide with the subsequent formation of thiosulfate has been recorded as early as 1798 by Berthollet.[1] Since that time many investigators have contributed to knowledge in this field, among whom may be mentioned Gay-Lussac, Vauquelin, Thomas and Rule, Küster and Heberlein, and most recently Pearson and Robinson.[2]

In the field of organic chemistry, especially in the case of aromatic nitro compounds, the use of sulfide ion as a reducing agent has had wide application. This phase of the subject has been studied by Zinin, Beilstein and Kurbatow, Lobry de Bruyn and Blanksma, Brand, Vesely, J. B. Cohen and Flürscheim.[3]

We have restricted our work to the oxidation of sulfide, hydrosulfide, and polysulfide ions by aromatic nitro compounds. We have obtained information concerning the formation of thiosulfate ion.

Previous workers in this field have used nitro compounds that were not appreciably soluble in aqueous solution and have employed higher temperatures and mixed solvents. By the use of sulfonated aromatic nitro compounds—in particular sodium *m*-nitrobenzenesulfonate—we were able to work in aqueous solutions of 0.1 *M* concentration and at room temperature. In this oxidation thiosulfate ion and sodium *m*-amidobenzenesulfonate are the only products formed—sulfite ion was not found in any of our oxidations, see page 236. This enabled us to study the course of the reaction, which is traditionally formulated as follows

$$RNO_2 + Na_2S_2 + H_2O = RNH_2 + Na_2S_2O_3$$

Purification of Materials.—The materials involved could all be obtained in a very pure state or could be purified easily. In the case of sodium hydroxide this was prepared from C. P. sticks made up to a saturated solution with water in a seasoned Pyrex flask. The impurities, chloride, carbonate, and silicate, which may be present settle out on standing quite completely but the small quantities which remained in solution were without effect on the reaction as was proved by a series of blank tests.

Sulfur was purified by recrystallization from carbon disulfide.

Hydrogen sulfide was prepared by heating *p*-toluidine and sulfur together at 200–220°.[4] The resulting gas which is very pure was washed through water to remove any entrained solid.

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(1) Berthollet, *Ann. Chim.*, **25**, 233 (1798).

(2) (a) Gay-Lussac, *ibid.*, **85**, 199 (1813); (b) Vauquelin, *Ann. chim. phys.*, **6**, 5 (1817); (c) Thomas and Rule, *J. Chem. Soc.*, **111**, 1063 (1917); (d) Küster and Heberlein, *Z. anorg. allgem. Chem.*, **43**, 53 (1905); (e) Pearson and Robinson, *J. Chem. Soc.*, 1473 (1930).

(3) Zinin, *J. prakt. Chem.*, **27**, 149 (1842); Beilstein and Kurbatow, *Ber.*, **11**, 2056 (1878); Lobry de Bruyn and Blanksma, *Rec. trav. chim.*, **20**, 115 (1901); Brand, *J. prakt. Chem.*, **74**, 449 (1906); Vesely, *Rec. trav. chim.*, **44**, 352 (1925); J. B. Cohen, *J. Chem. Soc.*, **87**, 1266 (1905); Flürscheim, *J. prakt. Chem.*, **71**, 497 (1905).

(4) Heumann, "Anilinefarben," Vol. III, p. 368.

The nitrobenzenesulfonate was prepared from purified nitrobenzene and the resulting sodium salt recrystallized.

Analytical Methods.—The standard iodine titration was used throughout for the determination of sulfide and thiosulfate ion. In the latter case the sulfide was removed by addition of a freshly prepared suspension of cadmium carbonate. Pure iodine was used as a standard of reference. Weighing burets were employed except in a few instances where time was of more importance than accuracy. Polysulfide sulfur was determined by a method of Küster and Heberlein.[2]

The Synthesis of Sodium Sulfides.—A very complete résumé of the work in this field is found in the paper of Pearson and Robinson already mentioned. We investigated all methods recorded in the literature. For the preparation of monosulfide and polysulfide in aqueous solution the method detailed by Küster and Heberlein was employed with slight variations. By its use with all precautions it was possible to prepare solutions which contained only traces of thiosulfate. In non-aqueous solvents the tetrasulfide was prepared by bringing sodium and sulfur together under boiling toluene. This method has been variously described[2e] but by use of excess sulfur and boiling for twelve hours we obtained the tetrasulfide in a pure state. Pentasulfide was prepared by the method of Hugot.[5]

Another synthesis of sulfide which we employed in this investigation was to heat sulfur in aqueous sodium hydroxide until complete solution was obtained. The resulting solution was then allowed to stand at room temperature for forty-eight hours to attain equilibrium. This solution while it contained large amounts of thiosulfate gave valuable information when oxidized as will be shown later.

Experimental

The first part of the work was to determine the course of the oxidation. As has already been stated only thiosulfate results from the oxidation of sulfide ion by means of an aromatic nitro compound. Further in the case of mononitro compounds only amine is formed. One of us had established this point. The system that we were to study would contain, then, only sulfide, thiosulfate, and hydroxyl ions together with amine and the nitro compound. These latter had no effect on the analytical methods.

In the preliminary work we employed the solution obtained by the use of sodium hydroxide and sulfur. This solution is in equilibrium when $OH^-/S_x^=$ is 2.4 and polysulfide $S/S_x^=$ is 3.4. The thiosulfate ion does not enter into the equilibrium but is always formed according to reaction (4) page 236.

The reactions were carried out in a liter round-bottomed flask provided with a mechanical agitator. The flask was swept free of air by means of nitrogen and the solution introduced. Temperature was maintained within 0.1° by immersion in a thermostat of the usual type. Samples were withdrawn by means of a pipet, added directly to weighing bottles which contained weighed quantities of standard iodine or cadmium carbonate suspension as the case might be and the weight of the sample determined. A slow stream of nitrogen was passed into the reaction flask throughout the experiment. Blanks in this apparatus showed no air oxidation during six hours.

(5) Hugot, *Compt. rend.*, **128**, 338 (1899).

During the course of the investigation nearly a hundred oxidations were made. Table I shows results obtained from typical oxidations.

TABLE I

DISULFIDE OXIDIZED BY SODIUM NITROBENZENESULFONATE

Temp., 25.0°; concentration of oxidizing agent, 0.1 *M*; time in minutes; data, moles per 1000 g. of solution

Time	Total iodine	$S_2O_3^=$	S^-	Time	Total iodine	$S_2O_3^-$	S^-
	No. 52				No. 54		
0	0.2424	0.0000	0.1212	0	0.2037	0.0067	0.0986
15	.1048	.0293	.0377	15	.0990	.0326*	.0299
30	.0998	.0372	.0313	30	.0939	.0384*	.0245
45	.0945	.0453	.0256	45	.0976	.0427*	.0242
60	.0955	.0489	.0233	60	.0955	.0489*	.0226
	No. 51				No. 53		
0	0.2520	0.0000	0.1260	0	0.0980	0.0255	0.0420
15	.1129	.0288	.0420	15	.0976	.0175*	.0228
30	.1055	.0392	.0331	30	.0931	.0268*	.0219
45	.1071	.0456	.0307	45	.0940	.0333*	.0191
60	.1020	.0505	.0258	60	.0947	.0373*	.0171
	Composite						
0	0.2000	0.0000	0.1000				
1	.1637	.0074	.0781				
2	.1399	.0113	.0643				
3	.1326	.0146	.0590				
5	.1234	.0196	.0519				
7	.1205	.0222	.0492				
10	.1180	.0248	.0471				

* Represents increase over amount initially present. No. 52 solvent molal sodium chloride. No. 54 0.15 molal sodium hydroxide. No. 51 sodium sulfate, ionic concentration equal to unity. No. 53 polysulfide from solution of sulfur in sodium hydroxide.

It will be noted that in every case the sulfide concentration diminishes rapidly at first while the thiosulfate-ion concentration does not increase at a proportional rate. The color of the reaction mixture is intensified and frequently there is a definite precipitation of sulfur. If a test of an early stage of the oxidation which has been treated with cadmium carbonate to remove sulfide ions is titrated with standard acid it is found that there is a large increase in the hydroxyl-ion concentration which is equal to the loss of anions containing sulfur, $S_x^=$ and $S_2O_3^=$. This would indicate that thiosulfate is not a direct product of the reaction as the stoichiometric equation shows but that the first products of the reaction are hydroxyl ion and sulfur—this is established in a quantitative way on page 236 reaction (2a). The sulfur as it is formed is taken up by the sulfide ion to saturation. However, when the hydroxyl-ion concentration has increased to the value given on page 233 for the $OH'/S_x^=$ ratio then the thiosulfate formation progresses uniformly (Table I, No. 53). Further oxidation is then conditioned by the thiosulfate formation since by equation (4), page 236, two sulfide ions are regenerated for each thiosulfate ion formed.

The data set forth in Table I can be utilized to give evidence of what has been briefly outlined above. In the case of disulfide oxidations at 25° there is no appreciable precipitation of sulfur and so from these few data the complete condition of the system is easily calculated.

The equation

$$S_2^{=} + RNO_2 + H_2O = S_2O_3^{=} + RNH_2 \qquad (1)$$

it is shown is made up of several, the first of which may be written

$$3S^{=} + RNO_2 + 4H_2O = 6OH^- + 3S + RNH_2 \qquad (2)$$

and the second

$$S^{=} + xS = S^{=}_{x+1} \qquad (3)$$

The cases of monosulfide and hydrosulfide were next investigated and it was found in both cases that there was an induction period of about thirty minutes before any appreciable oxidation began. Since the reaction was autocatalytic in character we investigated the effect of each of the known products of the reaction, RNH_2, OH^-, $S_2O_3^{=}$ and polysulfide S.

Table II shows this effect during the first minute of the oxidation.

TABLE II

Polysulfide sulfur	Fraction oxidized	Polysulfide sulfur	Fraction oxidized
0.00	0.0007	1.00	0.0295
.25	.0098	1.20	.0285
.50	.0225	1.50	.0260
.75	.0262	2.00	.0220
.83	.0263	3.00	.0160
		Satd.	.0146

Oxidations of saturated polysulfide were carried out in neutral salt solution and a good velocity constant obtained, using the bimolecular formula for different concentrations of (a) the oxidizing agent and (b) the total sulfide ion, both in moles per 1000 g. of solution.

TABLE III

Time	Total iodine	$S_2O_{3x}^{=}$	$S_x^{=}$	k^a
0	0.1621	0.0020	0.0801	..
15	.1230	.0195	.0517	0.308
30	.1030	.0266	.0382	.292
60	.0840	.0410	.0215	.308
90	.0750	.0485	.0132	.320
120	.0715	.0535	.0090	.318

[a] $k = \frac{1}{t(a - b)} \ln \frac{a(b - x)}{b(a - x)}$

Using concentrations greater than 0.11 molal of either sulfide or nitro compound the reaction ran too fast to measure with the requisite accuracy.

According to reaction (2) there should be a definite *P*H which would allow the oxidation to progress without favoring the formation of thiosulfate. This was found to be close to *P*H 8. By the use of a borax-boric acid buffer oxidations were carried out which contained only a small amount of thiosulfate ion. Substituting boric acid in reaction (2) we obtain

$$3S^{=} + 12H_3BO_3 + RNO_2 = 3B_4O_7^{=} + 3xS + 17H_2O + RNH_2 \qquad (2a)$$

In an oxidation using this buffer the sulfur was filtered, thoroughly washed and dried. It was then dissolved in carbon disulfide, filtered, the solvent evaporated and the sulfur dried and weighed: calcd., 3.65 g.; found, 3.62 g.

The Formation of Thiosulfate.—As has been shown the oxidation of sulfide ion leads to the formation of hydroxyl ion and free sulfur. The formation of thiosulfate ion then takes place by a subsequent reaction which may be written as

$$6OH^- + 12S = S_2O_3^{=} + 2S^{=} + 3H_2O \qquad (4)$$

With regard to the formation of sulfite ions which are sometimes considered as intermediate in the formation of thiosulfate, we have shown that when a buffer is used only hydroxyl ion and sulfur result. All investigators agree that from the reaction between hydroxyl ion and sulfur only thiosulfate and polysulfide ions result. But if it were assumed that without a buffer the oxidation were carried further and sulfite were formed, then our analyses would show it. For it is well known and we have checked the fact in our work that sulfite and sulfide ions do not react rapidly or completely in alkaline solution. The behavior of solutions containing sulfite and hydrosulfide ions has been studied extensively by Foerster and his co-workers.[6] Their work shows that only under conditions of very careful adjustment of hydrogen-ion concentration is sulfite ion ever completely converted into thiosulfate. We employed the same method of analysis to determine sulfite as did Foerster and were not able to obtain a positive test in a single case.

Reaction (4) takes place rather rapidly at elevated temperature even with ordinary rhombic sulfur but at 25° the reaction is slow unless the sulfur is in an "active" state—set free by an oxidation of sulfide or in some similar way. We spent much time trying to prepare "active" sulfur but without success.

If one treats a pentasulfide ion with an excess of hydroxyl ion some of the sulfur in the polysulfide is available for this reaction and the solution on analysis shows an increase in sulfide and thiosulfate. Such a solution which tested 4.15 polysulfide sulfur, 0.675 sulfide and 0.207 thiosulfate after dilution with an equal weight of water was diluted with an equal weight of 0.1 *M* hydroxide and allowed to stand for two days. It then gave on analysis 0.748 sulfide and 0.243 thiosulfate. The sulfide increase is 0.073, that for thiosulfate 0.036—almost exactly two to one as shown by

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[6] Foerster, *Z. anorg. allgem. Chem.*, **177**, 61 (1928).

equation (4). This ratio holds for all temperatures. The value of the polysulfide sulfur/$S_x^=$ ratio is a function of the temperature, the hydroxyl-ion concentration and the ionic strength of the solution where neutral salt is employed.

In a series of experiments where neutral salt was employed—sodium sulfate in ionic strength equal to unity—together with hydroxyl ion of varying concentration, we obtained for variation of hydroxyl ion from 2.4–5.7, polysulfide sulfur 3.4–1.0 correspondingly. Küster and Heberlein, in a paper already cited, obtained in pure monosulfide solution the value 4.24 for polysulfide sulfur.

The Use of Other Aromatic Nitro Compounds.—While the greater part of the work was carried out with *m*-nitrobenzenesulfonate we prepared a set of other nitro compounds and measured their oxidizing rate against the one just mentioned. These results are set forth in Table IV. The compounds were synthesized with great care and were recrystallized from aqueous solution and dried to constant weight as sodium salts.

TABLE IV

Name	Relative speed of oxidation of disulfide
1-Nitro-4-carboxybenzene	1.263
1-Nitro-3-sulfobenzene	1.000
1-Nitro-3,5-disulfobenzene	0.962
1-Nitro-5-sulfonaphthalene	.95 app.
1-Nitro-4-methyl-3-sulfobenzene	.935
1-Nitro-3-carboxybenzene	.918
1-Nitro-2-oxy-3-carboxy-5-sulfobenzene	.425
1-Nitro-2-methyl-5-sulfobenzene	.417
1-Nitro-8-sulfonaphthalene	.4 app.
1-Nitro-2-carboxybenzene	.089

The chloro derivatives were abnormal, giving very rapid oxidation analogous to dinitro compounds.

From the data in Table IV it is seen that the para substituted compound oxidizes most rapidly. The meta substituted compounds all react at about the same rate while the ortho substituted compounds have very little oxidizing power.

The Effect of Temperature.—While reduced temperature slows down the rate of oxidation—reaction (2)—the effect is much more pronounced in thiosulfate formation—reaction (4). Below 25° the solution of sulfur is so slow that the greater part of it is precipitated in an unreactive form even in excess of hydroxyl ions. Thus the oxidizing power of sulfide ion is diminished, for it will be noted by reference to reaction (4) that two sulfide ions are formed for each thiosulfate ion produced.

If an oxidation of disulfide is carried out slowly no appreciable amount of thiosulfate is formed until the system is saturated with sulfur. On the other hand, in the normal case where equal concentrations of sulfide ion and nitro compound are added together at the start, about 30% of the initial sulfide is oxidized in the first minute—Table II. Under these conditions there is a large amount of sulfur present in the "active" state at any particular time during the first few minutes. This sulfur would normally be dissolved by the sulfide ion still present but the large concentration of hydroxyl ion also present slows down this process and forms thiosulfate and regenerates polysulfide from the "active" sulfur. In the presence of other anions, as when neutral salt is employed, some of the sulfur is precipitated in solid form. This redissolves, in part at least, unless temperatures lower than 25° prevail. At higher temperatures the sulfur held in the polysulfide ion is more reactive and thiosulfate is formed at a much lower value of the ratio $xS/S_x^=$. Tartar and Draves[7] have shown that this ratio may be less than one with excess hydroxyl ion at 100°.

Summary

The oxidation of sulfide ion by means of an aromatic nitro compound progresses only as far as free sulfur. This sulfur is then removed from the system either by the formation of thiosulfate ion with regeneration of polysulfide ion or the sulfur is precipitated in solid form.

Thiosulfate ion is formed from free sulfur in the presence of hydroxyl ion with the simultaneous formation of two polysulfide ions. This reaction progresses slowly at room temperature unless the sulfur is in an active form.

Various ortho, meta and para substituted mononitro compounds were used as oxidizing agents and their rates of oxidation compared.

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[7] Tartar and Draves, THIS JOURNAL, **46**, 574 (1924).