

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WASHINGTON]

## REACTION OF SULFUR WITH ALKALI AND ALKALINE EARTH HYDROXIDES IN AQUEOUS SOLUTIONS

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Several years ago, Tartar<sup>1</sup> showed that when sulfur is heated with aqueous solutions of potassium hydroxide and calcium hydroxide, two molecules of polysulfide to one of thiosulfate are produced, a finding which corroborated the suggestion of previous investigators.<sup>2</sup> The results also led to the conclusion that potassium trisulfide is the primary polysulfide formed in the first reaction and calcium tetrasulfide in the second.

A further study has now shown that in this earlier work some factors of importance were overlooked, such as (1) the initial concentration of the hydroxide, (2) the duration of the reaction period, (3) the temperature, and (4) the relative amounts of sulfur and hydroxide. This subsequent work has been devoted to studying the effect of the first two conditions, the others being kept nearly constant.

The hydroxides of barium, potassium and sodium were used so that the conclusions reached are evidently of general application to all strong, soluble hydroxides. The concentration of base was varied from 0.096 to 1.52 *N* and the duration of the reaction period from one-half hour to four and one-half hours. The temperature was kept constant by conducting the reaction in boiling solution. An excess of base was always used.

### Experimental Part

**Materials.**—The sulfur was purified by crystallization of commercial c. p. roll sulfur from carbon disulfide. The crystals were finely ground in a mortar, dried at 50° and preserved in a desiccator over phosphorus pentoxide. The hydroxides were "c. p. Analyzed" from a reliable manufacturer, the sodium and potassium hydroxides being "purified from alcohol." Stock solutions of saturated barium hydroxide and of 6.5 *N* sodium and potassium hydroxides were employed. The latter two hydroxides were almost wholly freed from carbonate by adding a little solid barium hydroxide. After settling, the supernatant liquids contained 0.4% of basicity as sodium carbonate and 0.5% as potassium carbonate, respectively.

**Method of Carrying Out the Reaction.**—Since the technique of causing sulfur to react with an excess of hydroxide in the absence of air has been improved and simplified, compared with that previously employed,<sup>1a</sup> the procedure will be described in detail. The weighed sulfur was wet with a little water and transferred to a half-liter or liter Pyrex flat-bottomed flask. The proper amount of recently boiled distilled water was added and the flask connected to a bulbous reflux condenser. Then commercial hydrogen, freed from oxygen by bubbling through alkaline pyrogallol solution, was passed in through a tube ending about 5 cm. above the liquid in the flask. Any

<sup>1</sup> Tartar, (a) *THIS JOURNAL*, **35**, 1741 (1913); (b) **36**, 495 (1914).

<sup>2</sup> Divers and Schimidzu, *J. Chem. Soc.*, **45**, 270 (1884). Senderens, *Bull. soc. chim.*, [3] **6**, 800 (1894). Haywood, *THIS JOURNAL*, **27**, 244 (1905); Thatcher, *ibid.*, **30**, 63 (1908).

hydrogen sulfide or sulfur dioxide escaping with the hydrogen was absorbed in a sodium hydroxide solution. In the data given below, the sulfur used for the reaction was corrected for that which escaped with the hydrogen.

After the air was out of the flask, the water containing the sulfur was boiled for 15 minutes to remove air which is always unavoidably introduced when dry sulfur is put into water. Then the cork was momentarily removed by an assistant while the appropriate hydroxide was added from a pipet. When the solution had been boiled for the proper length of time, the heating was discontinued and about 20 cc. of kerosene was introduced through the top of the condenser to prevent contact of air with the aqueous solution. The solution was then diluted with boiling distilled water, cooled rapidly and made up to the specially calibrated volume of the reaction flask. After the solution had been carefully stirred it was analyzed.

**Methods of Analysis.**—When sulfur reacts with an excess of hydroxide the resulting solution contains thiosulfate, polysulfide and free hydroxide, as indicated by the following expression:  $6\text{MOH} + (2x + 2)\text{S} + \text{excess MOH} \longrightarrow 2\text{M}_2\text{S} \cdot \text{S}(x - 1) + \text{M}_2\text{S}_2\text{O}_3 + \text{free MOH}$ . In order to express the composition of such a solution from analytical data, it is necessary to use certain terms which need definition. By *free hydroxide* is meant the excess of hydroxide, or that beyond the amount equivalent to polysulfide and thiosulfate. *Thiosulfate hydroxide* and *sulfide hydroxide* mean the hydroxide equivalent to the amount of these salts present, respectively. By *monosulfide sulfur* is meant the  $\text{S}_m$  sulfur in the general formula of a polysulfide which has been expressed as  $\text{M}_2\text{S}_m \cdot \text{S}_p$ . *Polysulfide sulfur* is the  $\text{S}_p$  sulfur represented by this formula.

Methods for the determination of all these constituents and compounds in a polysulfide solution have been described so often that it will suffice to mention the particular methods which have served for establishing the composition of the solution. Free base was estimated from titration with standard hydrochloric acid by the method used for the determination of calcium hydroxide in lime-sulfur spray.<sup>3</sup> Monosulfide sulfur was determined by titrating with an exactly 0.1 *N* ammoniacal zinc solution prepared from recently ignited zinc oxide in such a manner as to have the composition recommended by Bennett.<sup>4</sup> Roark<sup>5</sup> stated that this solution is satisfactory for the complete precipitation of sulfide. The aliquot for analysis was added to the zinc solution, the mixture allowed to stand for at least 20 minutes, and filtered. Three indicators were satisfactorily used in testing for sulfide ion in the filtrate. These were nickel nitrate, normal lead acetate and 1% cobaltous chloride,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . With the last indicator the dark cobaltous sulfide is, on a spot plate, easily distinguishable from cobalt complexes.

An excess of the zinc solution described above was used to precipitate sulfide sulfur. This precipitate was analyzed for monosulfide plus poly-

<sup>3</sup> Tartar and Bradley, *J. Ind. Eng. Chem.*, **2**, 271 (1910).

<sup>4</sup> Bennett, *J. Am. Leather Chem. Assoc.*, **11**, 112 (1916).

<sup>5</sup> Roark, *J. Assoc. Official Agr. Chem.*, **3**, 352 (1920).

sulfide sulfur. Thiosulfate was determined in the filtrate in the usual way.

Because of greater convenience, sulfur was determined by a rapid precipitation with barium chloride after oxidation with sodium peroxide. Allen and Johnston<sup>6</sup> have reported that a rapid precipitation is likely to give most accurate results for an uncorrected determination.

Since the zinc titration for monosulfide is very tedious, a new method was devised for applying an iodine titration to the determination of monosulfide sulfur in a solution containing free base. Direct titration of such a solution with iodine by the method given in the "Official and Tentative Methods" of the Association of Official and Agricultural Chemists<sup>7</sup> gave entirely different results for monosulfide sulfur than titration with zinc solution. To circumvent the influence of the alkalinity of the solution, direct titration with iodine was attempted after addition to a borax-boric acid buffer. Discordant results were obtained. This was due to the slow decomposition of the polysulfide by the buffer.

The failure of the above procedure suggested the following method which gives very satisfactory results. Fifty cc. of borax-boric acid buffer solution containing 8 g. of crystalline borax and 5.5 g. of boric acid in 100 g. of water is placed in an Erlenmeyer flask; 0.1 *N* iodine, slightly greater in volume than that equivalent to monosulfide sulfur alone, is added from a buret. The aliquot part for analysis is then introduced with stirring. The titration with iodine from the buret is continued until all the thiosulfate has reacted and one drop of iodine gives the iodine color. The volume of iodine equivalent to monosulfide sulfur is obtained by subtracting the volume required for the titration of thiosulfate alone.

The free sulfur liberated by this iodine titration was allowed to settle. The concentration of hydrogen ion in the supernatant liquid was then determined colorimetrically and found to be  $10^{-7.9}$ . Washburn<sup>8</sup> has shown that the lower limit of hydrogen-ion concentration when an accuracy of 0.001% is desired in titration with iodine is  $(H^+) = 10^{-9}$ . The result obtained lies well within the limit. Because the buffer as used here must react with the free hydroxide present, a slightly greater proportion of boric acid was used than that found satisfactory by Chapin<sup>9</sup> for titration of arsenious acid with iodine. It is desirable, however, to use a buffer which is itself slightly alkaline.

A comparison of the new iodine method with the zinc titration of monosulfide sulfur in the presence of free base is embodied in the data of Table II. There the close agreement of the values for monosulfide sulfur as

<sup>6</sup> Allen and Johnston, *THIS JOURNAL*, **32**, 588 (1910).

<sup>7</sup> "Official and Tentative Methods," A. O. A. C., 1920, p. 67.

<sup>8</sup> Washburn, *THIS JOURNAL*, **30**, 35 (1908).

<sup>9</sup> Chapin, *ibid.*, **41**, 351 (1919).

determined by both methods proves the accuracy of the new method for determining monosulfide sulfur in the presence of free base.

Another comparison of the new iodine titration under different conditions was made by analyzing a sodium polysulfide solution prepared from an excess of sulfur with sodium hydroxide and consequently containing

TABLE I  
COMPARISON OF METHODS FOR MONOSULFIDE SULFUR

Method	Cc. of 0.1 N solution
Hydrochloric acid and methyl orange.....	35.69
Zinc titration.....	35.90
Iodine, old method.....	35.75
Iodine, new method in Erlenmeyer flask.....	35.83
Iodine, new method in open beaker.....	36.20

no free base. The titrations were made in triplicate and the average results in terms of 0.1 N solution are given below. The values for the iodine have been corrected for the amounts necessary to react with the thiosulfate present.

TABLE II  
COMPOSITIONS OF SOLUTIONS PREPARED BY BOILING SULFUR WITH AN EXCESS OF DIFFERENT HYDROXIDES IN AQUEOUS SOLUTION

Expt.	1	2	3	4	5	6	7	8	9	10
Base.....	NaOH	NaOH	Ba(OH) <sub>2</sub>	NaOH	NaOH	NaOH	NaOH	NaOH	Ba(OH) <sub>2</sub>	KOH
Normality of base during reaction, N.....	1.0	1.0	0.11	1.31	1.61	1.52	1.32	0.096	0.40	1.5
Time of boiling, hours...	0.5	0.5	1.00	2.00	4.25	4.75	0.50	4.25	4.25	4.5
Free hydroxide plus sulfide hydroxide, g.....	7.59	7.64	3.52	9.40	11.71	12.31	10.02	2.01	9.68	16.04
Thiosulfate hydroxide, g.	2.41	2.49	1.33	3.77	4.43	3.50	3.18	0.98	....	5.98
Free hydroxide, g.....	3.81	2.77	0.96	2.00	3.20	5.46	3.72	0.29	2.05	4.40
Total hydroxide	From analysis, g.....									
	9.99	10.13	4.85	13.17	16.14	15.81	13.20	2.99	....	22.02
Mono-sulfide sulfur	Taken for reaction, g.....									
	....	....	....	13.17	15.80	15.80	13.17	2.90	14.15	22.00
Mono-sulfide sulfur	Zinc method (S <sub>m</sub> ), g.....									
	1.710	1.950	0.480	2.96	3.43	2.72	2.47	0.639	1.445	3.33
Mono-sulfide sulfur	Iodine method (S <sub>m</sub> ), g.....									
	....	....	....	2.97	3.41	2.74	2.52	0.691	1.428	3.33
Monosulfide plus polysulfide sulfur (S <sub>m</sub> + S <sub>p</sub> ), g.....	5.55	6.42	1.776	7.67	7.12	5.03	8.05	2.224	3.48	6.41
Thiosulfate sulfur, g.....	1.93	2.00	0.498	3.02	3.55	2.80	2.55	0.785	0.33	3.42
Total sulfur	Monosulfide plus polysulfide plus thiosulfate, g...									
	7.48	8.42	2.274	10.69	10.66	7.84	10.59	3.009	3.81	9.83
	7.45	8.39	2.284	10.63	10.73	7.86	10.49	2.955	3.85	9.77
Total sulfur	Taken for reaction, corrected, g.									
	7.5	8.5	2.25	10.72	10.70	7.97	10.72	2.988	4.7	9.97
Ratio monosulfide to thiosulfate sulfur....	0.885	0.980	0.964	0.982	0.961	0.979	0.992	0.880	....	0.973
Ratio monosulfide plus polysulfide to monosulfide sulfur, $\frac{S_m + S_p}{S_m}$ .	3.24	3.29	3.70	2.586	2.088	1.834	3.188	3.105	2.438	1.929

The data of Table I show that for polysulfide solutions containing no free base the method gives the same results, practically, as the common iodine titration. There is the disadvantage, however, that slight loss of iodine occurs, causing high results.

For all analytical work, calibrated burets, pipets and flasks were employed. Polysulfide samples were delivered with the tip of the pipet below the surface of the receiving liquid.

The data given in Table II are quite complete in order to show that all of the hydroxide and sulfur used for the reaction are accounted for in the analyses. The data are arranged for quick comparison of certain values arrived at in different ways.

### Discussion of Results

The ratio of monosulfide plus polysulfide sulfur to monosulfide sulfur indicates the average number of atoms of sulfur contained in the polysulfide molecules present in the solution. When sulfur is dissolved in approximately normal aqueous solutions of sodium hydroxide the average polysulfide formed with short boiling is slightly higher than the trisulfide. The results from Expts. 1, 2 and 7 gave 3.24, 3.29 and 3.188 atoms of sulfur in the polysulfides, respectively.

The effect of long boiling with a considerable excess of hydroxide is shown by Expts. 5 and 6 in which the average polysulfide has been reduced approximately to the disulfide. With low concentration of base the change to lower polysulfides is not so rapid. In Expt. 8 with 0.096 *N* sodium hydroxide, even with long boiling, the average polysulfide formed was higher than the trisulfide.

These findings afford an explanation for the results obtained for the reaction on sulfur with calcium hydroxide.<sup>1b</sup> A saturated solution of this base is even more dilute than 0.096 *N*; consequently, the reaction with sulfur near boiling temperature for a brief period gave a higher polysulfide containing on the average approximately, 4 atoms of sulfur.

Expt. 10 using potassium hydroxide shows that long boiling with excess of base results in the formation of lower potassium polysulfides. In this case the average polysulfide contained less than 2 atoms of sulfur. The earlier work by Tartar<sup>1a</sup> was done under conditions such that the trisulfide was obtained. The results reported above show that his conclusion, that potassium trisulfide is stable in the presence of excess of hydroxide, is erroneous.

To test further the general application of the principles enunciated here, two experiments were tried using barium hydroxide (Expts. 3 and 9). The results show that the greater the initial concentration of base and the longer the boiling, the lower are the polysulfides produced.

On the whole, the experimental data show that the complexity of the polysulfides formed when sulfur reacts with an excess of an alkali or alkaline earth hydroxide in boiling aqueous solution is not dependent upon the particular hydroxide employed. Rather, the average number of atoms of sulfur in the polysulfides finally obtained under these conditions is dependent primarily upon (1) the initial concentration of the hydroxide and (2) the duration of the reaction period.

It is apparent from the data that after the polysulfides have been reduced to the disulfide by boiling in the presence of free hydroxide the rate of further reduction decreases. In other words, the disulfides seem to be more stable toward reduction by excess of base than the higher polysulfides. This stability of the disulfides in aqueous solution conforms with their stability in the dry state. Rule and Thomas<sup>10</sup> reported that sodium tetrasulfide and potassium pentasulfide lose sulfur when heated in a stream of hydrogen but that the disulfides in both cases are extremely stable compounds from which sulfur can be removed only with difficulty. Tartar and Bradley<sup>8</sup> found that in the dry state the disulfide is the most stable polysulfide of calcium. Later Auld<sup>11</sup> reported that from aqueous solution of calcium polysulfides, it is the disulfide which is most stable toward extraction of sulfur with solvents.

Table II offers evidence which indicates that the change from higher polysulfides to lower by boiling with excess of base may possibly continue, although at a slower rate, from the disulfide to the monosulfide. In Expt. 6 with sodium hydroxide and in Expt. 10 with potassium hydroxide, the final average polysulfides, after boiling for at least four and a half hours, contained 1.834 and 1.929 atoms of sulfur, respectively.

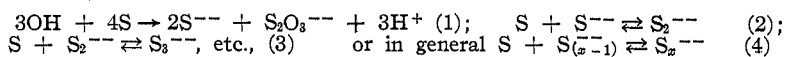
The ratio of monosulfide sulfur to thiosulfate sulfur is in all cases a little less than unity. The variation from unity is evidently due to slight oxidation of polysulfide to thiosulfate which could not be avoided under the experimental conditions employed. Considerable oxidation occurred in Expt. 1 because the technique had not then been fully perfected. The proportion of oxidation was evidently greater in Expt. 8 because of the degree of dilution of the solution. The results show that even with the change of higher polysulfides to lower this constant ratio of monosulfide to thiosulfate is maintained.

If the conclusion is valid that the average number of atoms of sulfur in the polysulfides formed in heated aqueous solution is dependent only upon the concentration of the base, when all other conditions are the same, and not upon the particular hydroxide employed, then the mechanism of the solution of sulfur in an aqueous hydroxide should be written in ionic form. The following expressions are offered as a possible explanation of the

<sup>10</sup> Rule and Thomas, *J. Chem. Soc.*, **111**, 1063 (1917).

<sup>11</sup> Auld, *J. Chem. Soc.*, **107**, 480 (1915).

formation of polysulfide and thiosulfate from the reaction of sulfur with hydroxide ions.



Reaction 1 indicates a reaction of the seventh order. Very likely this equation is simply a summation of two or more reactions of lower order. The formation of high polysulfides may take place in steps with the addition of one sulfur atom at a time as indicated in Reactions 2, 3 and 4. Since the experimental data show that the higher polysulfides may be reduced to lower by long boiling with excess of hydroxide, Reactions 2, 3 and 4 should be represented as being reversible.

Reaction 4 is not to be regarded as showing that only the polysulfide ion may gain or lose an atom of sulfur; the molecular and hydrolytic products which are in equilibrium, such as  $\text{M}_2\text{S}_x$ ,  $\text{H}_2\text{S}_x$ , and  $\text{HS}_x^-$ , may function in this manner.

The initial formation of higher polysulfides when sulfur is boiled with a solution of a hydroxide can easily be explained. It is well known that at room temperature sulfur reacts readily with alkali hydrosulfides in aqueous solution and more slowly with an hydroxide even at an elevated temperature. These facts, considered with the experimental results reported herein, justify the conclusion that the addition of sulfur to the sulfide, hydrosulfide, or various polysulfide radicals takes place with greater ease than the reaction of sulfur with the hydroxide ion.

### Summary

1. A simple and accurate method has been devised for an iodine titration of the monosulfide equivalent of polysulfide solutions containing free hydroxide.

2. When sulfur reacts with an aqueous solution of an alkali or alkaline earth hydroxide the average complexity of the polysulfide obtained does not depend upon the particular hydroxide employed but depends, rather, upon the following conditions: (1) the initial concentration of the hydroxide, (2) the duration of the reaction period, (3) the temperature and (4) the relative amounts of sulfur and hydroxide.

3. Former conclusions that potassium trisulfide is necessarily one of the primary products of the reaction of sulfur and potassium hydroxide in heated aqueous solution and that this trisulfide is stable toward boiling in the presence of free hydroxide are erroneous.

4. When sulfur dissolves in boiling aqueous sodium, potassium and barium hydroxides the solution first contains higher polysulfides. These, upon prolonged boiling in the presence of free base, are reduced at least to disulfides. Evidence is offered which indicates that the disulfides may even be reduced to monosulfides in this manner.

5. Equations written in ionic form are offered in explanation of the facts observed in the reaction of sulfur with alkali and alkaline earth hydroxides in aqueous solution.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]  
**THE DETERMINATION OF HYDROGEN-ION CONCENTRATION  
BY A SPECTROPHOTOMETRIC METHOD AND THE  
ABSORPTION SPECTRA OF CERTAIN INDICATORS<sup>1</sup>**

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In the study of the absorption spectra of dyes and other colored organic substances in aqueous solutions, knowledge of the hydrogen-ion concentration of the solutions is quite essential, due to the variation of the absorption band in shape and intensity with various hydrogen-ion concentrations. Several methods have been suggested for the colorimetric determination of hydrogen-ion concentration of colored solutions, but all of them are more or less complicated and in most cases give only approximate results.<sup>2</sup>

All of these methods require the use of a colorimeter or other special apparatus, whereas the suggested spectrophotometric method employs no apparatus in addition to that necessary for the determination of the absorption band of the colored solution, and may be made in a comparatively short time after the completion of the determination of the absorption band.

It was observed in the spectrophotometric study of certain dyes at various hydrogen-ion concentrations,<sup>3</sup> that on the change of the hydrogen-ion concentration of the dye solution the absorption band did not shift gradually in wave length but merely changed in height. In the same manner the absorption bands of the indicators studied did not shift in wave length with a change in hydrogen-ion concentration but varied in intensity while, in most of the cases observed, another band proceeded in the opposite direction at the same time. By using the same concen-

<sup>1</sup> This paper is the result of suggestions derived from a paper given by Buswell and Smith on "Color Standards in Water Analysis," at the 1923 Spring Meeting of the American Chemical Society, in which the absorption spectra curves of phenol red for various hydrogen-ion concentrations were determined in a manner somewhat similar to the method used in this paper, and a paper by Baker and Davidson (see Ref. 4d) on "Spectroscopic Measurements of the Hydrogen-ion Concentration Color Changes in Recent Indicators."

<sup>2</sup> (a) Gillespie, *J. Bact.*, **6**, 399 (1921). (b) Meyers, *J. Biol. Chem.*, **50** [Proc.] 22 (1922). (c) Everz, *Analyst*, **46**, 393 (1921). Other references as given in (d) Clark's "The Determination of Hydrogen Ions," Williams and Wilkins Co., 1922, pp. 66-73.

<sup>3</sup> Brode with Adams, Forthcoming article in *THIS JOURNAL*, **46** (1924).