

# HYDROLYSIS OF ELEMENTAL SULPHUR IN A HOMOGENEOUS MEDIUM

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## ABSTRACT

Elemental sulphur dissolved in organic solvents (such as chloroform, carbon tetrachloride and benzene) reacts rapidly and quantitatively, with aqueous alkali at room temperature, when this immiscible liquid mixture is homogenized by the addition of ethyl alcohol. The products of reaction under these experimental conditions are sulphide, thiosulphate and a small quantity of sulphite. A mechanism involving the intermediate formation and decomposition of dihydrogen sulphoxide, HSOH, is suggested for the reaction.

It has been observed that elemental sulphur in an organic solvent (like carbon tetrachloride, chloroform or benzene) becomes extremely reactive and combines at room temperature with sulphite in aqueous solution, in a homogeneous medium rendered by the addition of alcohol.<sup>1, 2</sup> The present communication describes the results of the hydrolysis of sulphur solutions in such organic solvents in alkaline medium under similar experimental conditions when sulphide, thiosulphate and a small quantity of sulphite are formed as the products.

## EXPERIMENTAL

### *Reagents*

Aldehyde-free ethyl alcohol was prepared by refluxing 98% alcohol with silver nitrate and potassium hydroxide for several hours and distilling, as recommended by Weissberger.<sup>3</sup> Benzene was freed from thiophene and purified by the standard methods.<sup>3</sup> AnalaR carbon tetrachloride and chloroform (free from sulphur) were used. Resublimed sulphur (Merck) in the powder form was used. Solutions of sulphur in carbon tetrachloride, chloroform and benzene were prepared and standardized by the method described by Murthy and Rao<sup>1</sup> by reacting with sulphite and estimating as thiosulphate.

*Procedure*

Five ml. of the sulphur solution, containing about 50 mg. of the element, were transferred with the help of a pipetter into a stoppered conical flask. Forty-five ml. of an aqueous solution of carbonate-free sodium hydroxide of different concentrations were added. The immiscible mixture was gradually shaken with small quantities of ethyl alcohol until the liquid phase became homogeneous. Seventy-five ml. of alcohol were usually added for this purpose. Immediately as the medium became homogeneous, it was observed that the solution became intensely yellow and faded off gradually. There was no separation of elemental sulphur under these conditions.

The resulting solution from hydrolysis was treated with a suspension of cadmium hydroxide to remove the sulphide formed. The cadmium sulphide was separated by filtration and estimated iodometrically. The sulphite and thiosulphate in the filtrate were determined by the usual iodometric methods.<sup>4</sup> It may be mentioned that any sulphite produced is not likely to undergo oxidation by atmospheric oxygen since the system contains a high percentage of alcohol which inhibits the atmospheric oxidation of sulphites.<sup>5</sup>

In order to bind the sulphide as soon as it is formed and thereby to minimize the scope of secondary reactions, a second series of hydrolytic experiments was carried out in presence of a suspension of cadmium hydroxide during the process of homogenization. Five ml. of the solution of sulphur in the organic solvent were mixed with 45 ml. of carbonate-free sodium hydroxide solution containing sufficient cadmium hydroxide suspended in it and the liquid phase homogenized as usual.

The analytical results of these experiments are given in Table I.

**RESULTS**

It can be seen from Table I that the amount of sulphite produced in the hydrolytic reaction is comparatively small. Between the range of concentrations of 0.05 N to 1.0 N alkali, the percentage yields of sulphide, sulphite and thiosulphate were nearly the same, although there was a slight increase in the yield of sulphite with increase in alkali strength. Similar results were obtained even when the reaction was carried out in an inert atmosphere of hydrogen or nitrogen. But in presence of cadmium hydroxide at the commencement itself of the hydrolytic reaction, the percentage yields of sulphide and sulphite increased considerably. The yield of thiosulphate was also correspondingly decreased. Therefore, it is reasonable to expect

TABLE I  
*Alkaline hydrolysis of elemental sulphur in homogeneous medium*

Series No.	Expt. No.	Total* Sulphur taken	Solvent for sulphur	Over-all alkali normality	% Sulphide* "a"	% Sulphite* "b"	% Thio-sulphate* "c"	Total sulphur accounted*	$2(\frac{1}{2}c+b)$
A	..	1	19.95 Benzene	0.05	36.69	0.00	59.78	19.25	
	..	2	17.11 Chloroform	0.50	38.85	1.08	58.26	16.81	
		3	19.86 Carbon tetrachloride	1.00	36.29	3.32	57.45	19.28	
B	..	4	19.95 Benzene	0.50	51.05	6.77	41.56	19.83	55.10
		5	17.06 Chloroform	0.50	51.83	7.56	38.98	16.78	54.10
		6	19.86 Carbon tetrachloride	1.00	50.44	4.43	44.21	19.68	53.08

\* Quantities of sulphur and sulphur compounds are all expressed in terms of gm. atoms of sulphur  $\times 10^4$ .

that, in the absence of cadmium hydroxide, additional thiosulphate is produced at the expense of sulphide and sulphite.<sup>6</sup>

Elemental sulphur itself, when left in contact with aqueous alkali (0.5 N or even 2 N) at room temperature for 24 hours suffers practically no reaction. In the absence of the homogenizing liquid, the reaction between elemental sulphur in carbon tetrachloride and aqueous alkali (0.5 N) is negligibly small even after 24 hours. In the case of chloroform, however, a small percentage of sulphur is converted into sulphide under similar conditions. This may be attributed to the greater miscibility of chloroform with water. In presence of the homogenizing liquid, the reaction is complete in 5–10 minutes at higher alkali concentrations and in about 30 minutes in dilute alkali. Almost the entire quantity of sulphur is consumed and nearly 99% of the total sulphur originally taken can be accounted for in terms of the products in most of the experiments. The small discrepancy observed in a few experiments is to be attributed to the probable formation of a small amount of polysulphide which, on the addition of cadmium hydroxide, is decomposed into cadmium sulphide and sulphur and removed; this polysulphide sulphur is thus likely to be unaccounted. The yellow colour of the homogenized reaction mixture may be due to the presence of polysulphide. Polysulphides are known to be formed during the alkaline hydrolysis of sulphur.<sup>7, 8</sup>

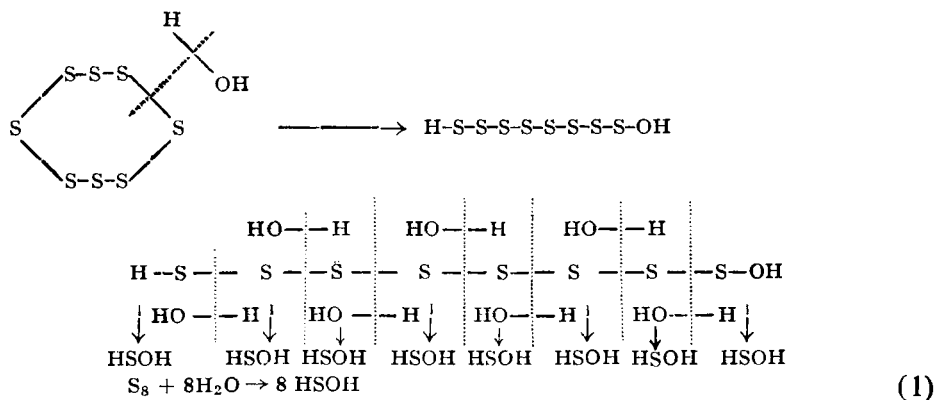
No reaction was observed between elemental sulphur in organic solvents and aqueous solutions of acids (hydrochloric or acetic) even after being homogenized and allowed to stand for 24 hours. The silver acetate taken along with acetic acid in a few experiments remained unaffected confirming the absence of reaction under these conditions.

#### DISCUSSION

It is known that elemental sulphur reacts with strong alkali solutions, slowly in the cold and rapidly at elevated temperatures, to form sulphide and thiosulphate with a small quantity of sulphite.<sup>9</sup> In the present investigation, the rapid conversion of elemental sulphur into sulphide, thiosulphate and traces of sulphite has been effected at considerably lower alkali concentrations in homogeneous medium at room temperature.

The rapid reactivity of elemental sulphur may be attributed to the rupture of the S-S linkage in the sulphur molecule  $S_8$ . The  $OH^-$  ion, which is a strong nucleophile, can rupture the  $S_8$  ring in homogeneous medium and

thereby bring about the hydrolytic reaction, like the  $\text{SO}_3^-$  and  $\text{CN}^-$  ions.<sup>9</sup> The breaking of the  $\text{S}_8$  ring may be pictured as follows:—



During the hydrolysis of sulphur, one may thus expect dihydrogen sulphoxide,  $\text{HSOH}$  (or sulphur hydrate  $\text{S} \cdot \text{H}_2\text{O}$ ), as an intermediate product. This intermediate species has been postulated to explain several other reactions of sulphur and sulphur compounds, and is expected to be highly reactive.<sup>10, 11</sup> It has been supposed to decompose as follows:—

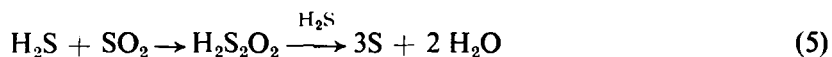


The elemental sulphur or its hydrate ( $\text{HSOH}$ ) can then react with the sulphite in homogeneous medium to give thiosulphate:<sup>1, 11</sup>



This mechanism explains the formation of sulphide, sulphite and thio-sulphate during the alkaline hydrolysis of elemental sulphur. Assuming that these are the only reactions taking place, and that thiosulphate is formed by the thionization of sulphite according to equations (3) or (4), it is possible to evaluate the analytical results quantitatively. If  $a$ ,  $b$  and  $c$  represent the sulphide sulphur, sulphite sulphur and thiosulphate sulphur respectively, then  $(\frac{1}{2}c + b)$  would represent the total sulphite sulphur produced immediately on hydrolysis, the major part of which combines with elemental sulphur to form thiosulphate. This amount of sulphite sulphur may be expected to be half the sulphide sulphur, according to equation (2); *i.e.*,  $2(\frac{1}{2}c + b) = a$ . Nearly 50% of the elemental sulphur taken would be converted into sulphide and the remaining 50% would be found as thiosulphate and sulphite. This relationship is found to hold good approximately for the experiments carried out in presence of cadmium hydroxide.

The hydrolytic reaction of elemental sulphur, however, is not to be interpreted as so simple. Elemental sulphur in a finely dispersed state has been reported to be in the form of a polymeric diradical.<sup>12</sup> Radical mechanisms might therefore play a prominent part in these complicated reactions. In the reaction between hydrogen sulphide and sulphur dioxide, thiosulphurous acid has been supposed to be an intermediate product,<sup>10</sup> which would react with a further molecule of hydrogen sulphide giving elemental sulphur and water.



The hydrolytic reaction of elemental sulphur may be looked upon as the reverse of this reaction, namely, elemental sulphur and water giving hydrogen sulphide and sulphur dioxide *via* thiosulphurous acid. This sulphite produced further reacts with elemental sulphur in the homogeneous medium forming thiosulphate.

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