

## THE ACTION OF LIGHT UPON ARSENIC TRISULFIDE HYDROSOL

RAY V. MURPHY, ILLINOIS WESLEYAN UNIVERSITY

In the course of some experiments upon the conductivity of mixtures of electrolytes and colloids it was observed that the conductivity of a carefully prepared arsenic trisulfide hydrosol was gradually increasing, the increase being most pronounced during those periods when the lamp of the thermostat remained lighted. It was finally decided that the heating lamp was the source of the disturbance, the reaction in the sol being a photochemical one. Tests were made by exposing some of the sol in the conductivity cell to the light of a 500 watt, nitrogen-filled lamp placed about 60 cm. from the cell. A marked increase in the conductivity resulted. The investigation was then extended to a study of the change in the conductivity of the sol of various dilutions when exposed to the light of the lamp under uniform conditions of temperature and intensity of illumination.

## PREPARATION OF THE SOL

One liter of a solution of  $H_2S$ , prepared by saturation of ice-cold freshly boiled distilled water, was added slowly, with constant stirring, to one liter of  $As_2O_3$  solution containing two grams  $As_2O_3$ . The resulting clear sol was then boiled for about six hours to remove excess  $H_2S$ , the boiling being done in a darkened room. A portion of the water was allowed to evaporate until a sol containing about 4.5 grams  $As_2S_3$  per liter was obtained. The resulting sol was faintly milky by reflected light, but clear by transmitted light. It was allowed to stand 48 hours. This is taken as the "100% sol". Samples containing 75%, 50%, 25%, 12.5% and 5% of the original sol were also prepared by dilution of the 100% sol with "conductivity" water of specific conductivity  $1.1 \times 10^{-6}$ . All samples were allowed to stand two weeks to age before the studies were made.

## ANALYSIS OF THE SOL

The analysis of the 100% sol gave the following data:

Arsenic per liter.....	2.9080 g.
As <sub>2</sub> S <sub>3</sub> per liter (calculated from As).....	4.7737 g.
H <sub>2</sub> S per liter.....	.1363 g.

## METHOD

The conductivity cells were of special design, resembling small flat-bottom flasks of about 30cc. capacity, with the electrodes inserted in the sides. The procedures of filling the cells, transferring to the thermostat, etc., were conducted in the dark. The thermostat lamp was painted black and enclosed in black paraffined paper. The samples were exposed to the light of the 500 watt, concentrated filament, nitrogen-filled lamp mentioned above, placed at a fixed distance of about 60 cm. from the cells. Exposures to the light were made for definite intervals at constant temperature, the cells transferred to the thermostat, and the conductivities measured, using a special set-up consisting of a Wheatstone set built up from Curtis coils and a Leeds and Northrup drum-type Kohlrausch slide wire, with air condensers for obtaining proper phase balance. The energizing current was at 1200 frequency and was generated by an audion oscillating circuit, the bridge balance being accurately determined by the use of a DeForest P-200 two-step audion amplifier, using special high-resistance telephones. The point of balance was one of complete silence, the slightest movement of the contact of the 4.7 meter Kohlrausch slide wire to right of left giving a distinctly audible sound. The set-up was built along lines suggested by Hall and Adams.<sup>1)</sup>

## DATA

The data of the determinations are given in the Table. The curves were constructed from the same data.

## DISCUSSION OF THE DATA

It will be observed that the curves for the different concentrations are nearly parallel, thus showing that the

rate of change in the conductance was practically the same for the sols of different initial concentrations. However, on closer examination of the curves for the sols of different concentrations, it will be seen that the slopes at corresponding times increase as the concentration of the sol diminishes. Thus for the eight and sixteen hour periods the slopes are approximately as follows:

Time	Slopes of the curves for					
	100% Sol	75% Sol	50% Sol	25% Sol	12.5% Sol	5% Sol
8 hours	.600	.581	.675	.750	.725	.781
16 hours	.375	.372	.453	.522	.519	.578

These figures indicate that the rate of change of conductance increases with decreasing concentration of the sol. The slope of each of the curves gradually becomes smaller, and all the curves would eventually become parallel to the time axis and further increase in conductivity cease if the runs were continued for a sufficient length of time. It was observed that a finely divided whitish

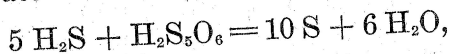
TABLE OF DATA.

Time in Hours	Specific Conductivity, $K \times 10^{-5}$		
	100% Sol	75% Sol	50% Sol
0	18.127	15.333	10.943
.0833	18.209	15.413	11.032
.2500	18.444	15.568	11.145
.5833	18.814	15.918	.....
1.0833	19.265	16.358	12.008
2.0833	20.199	17.234	13.004
3.0833	20.750	17.911	13.799
4.5833	21.746	18.750	14.809
6.5833	22.564	19.584	15.867
9.5833	23.160	20.294	16.717
15.3833	24.069	21.281	18.097
0	25% Sol	12.5% Sol	5% Sol
.2167	6.898	4.983	2.715
.6500	7.129	5.204	2.930
1.3167	7.577	5.620	3.333
2.8167	8.279	6.281	3.953
5.8167	9.445	7.802	5.372
11.0667	11.786	9.652	7.250
14.6670	13.876	12.036	9.874
18.0000	14.934	13.027	11.223
	15.952	13.741	12.220

precipitate formed on the bottom of the conductivity cells in all cases.

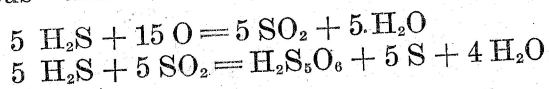
Freundlich and Nathansohn<sup>2)</sup> have pointed out that the gradual clouding and final precipitation of sulfur followed by coagulation of arsenic trisulfide from a care-

fully prepared, clear arsenic trisulfide hydrosol may be explained upon the following grounds: Arsenic trisulfide hydrosol sensitizes the photochemical oxidation of dye-stuffs like eosin and malachite green. Due to this photosensitizing action of the arsenic trisulfide micelles, hydrogen sulfide produced by the hydrolysis of arsenic trisulfide is oxydized to colloidal sulfur which is stabilized by absorbed pentathionic acid. That pentathionic acid is the stabilizing electrolyte for sulfur hydrosols of the Odén type, has been shown by Freundlich and Scholz<sup>3)</sup>. This acid is quite stable in the presence of hydrogen sulfide, with which it reacts to form free sulfur and water:



this reaction explaining the great sensitiveness of the Odén S-hydrosols toward  $\text{H}_2\text{S}$ . It is the reaction between the stabilizing pentathionic acid of the S-micelles and the stabilizing  $\text{H}_2\text{S}$  of the arsenic trisulfide-micelles according to the above equation which deprives the micelles of both sols of their stabilizing electrolyte and results in the coagulation of a mixture of the two sols.

In their presentation of the above explanation of the action of light upon arsenic trisulfide hydrosol, Freundlich and Nathansohn do not discuss the mechanism of the formation of pentathionic acid. It is probable, however, that the photochemical oxidation of  $\text{H}_2\text{S}$  which results in the formation of colloidal sulfur may also account for the formation of the pentathionic acid, presumably by the photochemical oxidation of  $\text{H}_2\text{S}$  to  $\text{SO}_2$  which reacts with  $\text{H}_2\text{S}$  to form the acid, a reaction which is probably one of many taking place in the formation of Wackendorfer's solution, and which has been investigated by Debus<sup>4)</sup> and others:



Assuming that a condition of equilibrium exists in an arsenic trisulfide hydrosol with respect to adsorbed hydrogen sulfide and pentathionic acid on the one hand, and intermicellular hydrogen sulfide and acid on the



other, the action of light would be merely to maintain the equilibrium by the formation of pentathionic acid and colloidal sulfur as the reaction between  $H_2S$  and the acid proceeds.

With certain assumptions regarding the mechanism of the above process the explanation offered by Freundlich and Nathansohn can be reconciled with the fact that the conductivity of the sol increases upon exposure to light. If the process resulted in the reaction between the first traces of pentathionic acid formed and  $H_2S$ , the conductivity of the sol could not increase, since no substance of sufficiently high conductivity is formed to account for the changes produced. On the other hand, if the formation of S-hydrosol, whether by the photochemical oxidation of  $H_2S$  or by the  $H_2S$ -pentathionic acid reaction, is assumed, a gradual increase in conductivity can be more readily explained. Colloidal sulfur produced by either or both of these reactions will adsorb pentathionic acid as stabilizing electrolyte, the S-micelles, with their adsorbed acid, serving to augment the conductivity of the solution, and maintaining at the same time a certain concentration of free acid in the intermicellular liquid by virtue of the adsorption equilibrium set up. Both of these factors serve to increase the conductance. Eventually the concentration of the intermicellular pentathionic acid will reach such a value that the rather slow reaction of the acid with intermicellular  $H_2S$ , which has been increasing in speed with continued increase in the concentration of the acid, will proceed unhampered, an equilibrium having thus been set up between the various components of the system. The attainment of this equilibrium marks the end of the increase in the conductivity of the sol.

The fact that the rate of change of conductance increases with decrease in the concentration of the sol is readily explained in view of the work of several investigators who have pointed out that dilution of a sol results in increased dispersion, i. e., diminution of the size of the particles. Increased dispersion of the colloid particles will favor the speed of the reaction due to the increased photochemical activity of the micelles per unit

mass of  $\text{As}_2\text{S}_3$  owing to the relatively greater active surface.

In the above discussion of the mechanism of the reaction it is assumed that the  $\text{H}_2\text{S}$ -pentathionic acid reaction proceeds only in the intermicellular liquid, and not in the adsorbed layer enveloping the  $\text{As}_2\text{S}_3$  particles, since it is taken for granted that  $\text{As}_2\text{S}_3$  and S-micelles, respectively, retain the  $\text{H}_2\text{S}$  and pentathionic acid adsorbed as stabilizing electrolyte, out of the sphere of reaction with each other. The photochemical formation of colloidal sulfur and pentathionic acid takes place only in the adsorbed layer.

It is noteworthy to remark that the photochemical reaction is not reversible, samples of the sol which had been exposed to light suffering only a very slight decrease in conductance on being kept in the dark for periods as long as several days. This slight decrease in conductance is explained as being due to the fact that the slow  $\text{H}_2\text{S}$ -pentathionic acid reaction, which in itself tends to lower the conductance by formation of  $\text{H}_2\text{O}$  and S from the active electrolyte, pentathionic acid, continues for some time after the action of light ceases, the resultant effect being a slight diminution of the concentration of the intermicellular pentathionic acid.

There may be some question as to the nature of the electrolyte formed in the photochemical process. The fact that Freundlich and Scholz have demonstrated the existence of pentathionic acid in colloidal sulfur is not to be taken as *a priori* evidence of the existence of the same stabilizing acid for the colloidal sulfur formed in  $\text{As}_2\text{S}_3$  hydrosol. Whether the acid formed is pentathionic, tetrathionic or another of the thionic acids known to exist in Wackenroder's solution, or a mixture of two or more members of the family, is conjectural. It would seem more plausible, possibly, to assume the formation of tetrathionic acid, since this is undoubtedly the first product formed in the preparation of Wackenroder's solution.

## SUMMARY

1. The electrical conductivity of arsenic trisulfide hydrosol increases upon exposure to light, the rate of increase being practically independent of the initial concentration of the sol, although increasing somewhat with decreasing concentration of the colloid. Studies were made upon a very pure arsenic trisulfide hydrosol (one containing very little excess hydrogen sulfide), following the conductivity during exposure to the light of a 500 watt nitrogen-filled lamp under constant conditions of temperature and intensity of illumination.

2. The reaction is explained, after the suggestion of Freundlich and Nathansohn, as one of a two-stage photochemical oxidation of  $H_2S$  adsorbed on the  $As_2S_3$ -micelles to colloidal sulfur and pentathionic acid (or tetrathionic), followed by the reaction between  $H_2S$  and the thionic acid in the intermicellular liquid with liberation of free sulfur, and with final precipitation of  $As_2S_3$  upon removal of the stabilizing  $H_2S$ . The increase in conductivity is to be explained as due to the building up of a concentration of the thionic acid more than sufficient to serve as the stabilizing electrolyte for the colloidal sulfur, the reaction with  $H_2S$  then proceeding at such a rate that the equilibrium is maintained between the several components of the system, further change in conductance thus being prevented. The increase of the rate of change of the conductance with decreasing concentration of the sol is explained as due to the increased photochemical activity per unit mass of  $As_2S_3$ , brought about by the greater dispersity of the more dilute colloid.

The author wishes to acknowledge the kind assistance of Dr. J. H. Mathews of the Department of Chemistry at the University of Wisconsin, under whose direction the work described in this paper was done.

## REFERENCES.

- 1) Jour. Am. Chem. Soc. 41, 1515, (1919).
- 2) Koll. Zeit., 28, 258, (1921).
- 3) cf. Freundlich and Nathansohn, loc. cit.
- 4) Jour. Chem. Soc. 53, 278, (1888).

