[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE ACTION OF LIGHT ON ARSENIC TRISULFIDE HYDROSOL[1]

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In connection with an extended study of the electrical conductivity of ferric oxide and arsenic trisulfide hydrosols, to be published later, it was observed that the conductivity of an arsenic trisulfide sol 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. This conclusion was substantiated by the timely appearance of an article by Freundlich and Nathansohn[2] describing experiments on the action of light upon this sol, and offering a theory of the changes which occur.

Preparation and Analysis of the Sol.—The sol used in the experiments was prepared by the addition of an ice-cold, saturated solution of hydrogen sulfide to an equal volume of 0.2% solution of arsenic trioxide. The excess of hydrogen sulfide was removed by bubbling hydrogen through the sol, and then boiling. A portion of the water was evaporated until a sol containing about 4.5 g. of arsenic trisulfide per liter was obtained. The resulting sol was faintly milky by reflected light, but clear by transmitted light. This was taken as the "100% sol." Samples containing 75%, 50%, 25%, 12.5% and 5% of the original sol were prepared by dilution with conductivity water of specific conductivity 1.1×10^{-6}. All samples were allowed to age for 2 weeks before the studies were made.

The following table gives a summary of the analysis of the 100% sol.

	Determined as	G. per liter
As_2S_3	$Mg_2As_2O_7$	4.7737
As_2S_3	As_2S_3	4.7520
Sulfur	H_2S	0.1280
Total S	$BaSO_4$	1.6118
Total S minus S as H_2S		1.4838
As_2S_3 calculated from total S minus S as H_2S		3.7970

It will be observed that the arsenic trisulfide per liter calculated from the total sulfur minus sulfur as hydrogen sulfide is considerably less than that determined directly or as magnesium pyroarsenate. The atomic ratio of arsenic to sulfur, after subtraction of the sulfur present as hydrogen sulfide, is very close to 6:5. It is evident that the sol did not contain a simple compound such, for example, as the molecule As_2S_3. In terms of the complex compound theory of colloids, a compound of arsenic trisulfide or pentasulfide with arsenic trioxide may be considered to exist in the sol. Such formulas as $5As_2S_3.4As_2O_3$ and $As_2S_5.2As_2O_3$ have little significance, however, because of our ignorance of the character of the compounds present.

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[1] This paper constitutes a part of a thesis submitted by R. V. Murphy in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

[2] Freundlich and Nathansohn, *Kolloid-Z.*, **28**, 258 (1921).

Method of Study and Data

Preliminary tests were made by exposing some of the sol in the conductivity cell to the light of a 500watt, nitrogen-filled lamp. A marked increase in the conductivity resulted. The investigation was then extended to a study of the change in the conductivity of the sol when exposed to the light of the lamp under uniform conditions of temperature and intensity of illumination. The lamp was of the condensed filament type, and was placed at a fixed distance of 60 cm. from the cells. The thermostat lamp was painted black and enclosed in black paraffined paper. Exposures to the light were made for definite intervals in a constant-temperature room, the cells transferred to the thermostat, and the conductivities measured after temperature equilibrium had been reached.

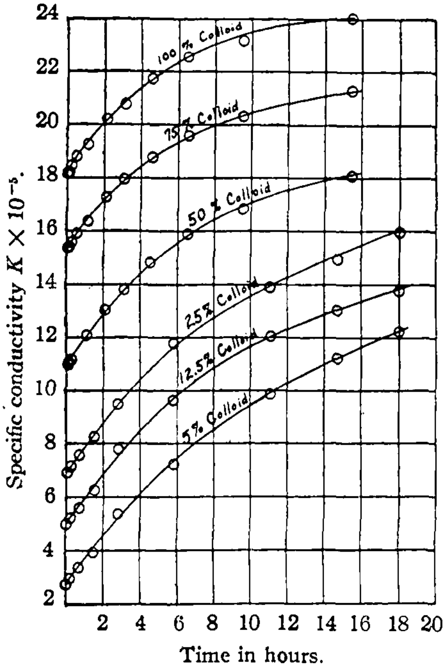
The data for the determinations are given in the accompanying table and curves which were constructed from the data, and indicate the change of conductance with time of exposure to the light. It will be observed on examination of the data and curves that the rate of change of the conductance increases slightly with decreasing concentration of the sol. The slope of the curves gradually becomes less, and all of the curves would

TABLE I

CHANGE IN CONDUCTANCE OF ARSENIC TRISULFIDE HYDROSOL ON EXPOSURE TO LIGHT

Time	Specific Conductivity, $K \times 10^{-5}$, of		
Hours	100% sol 4.7629 g. of As_2S_3/l.	75% sol 3.5722 g. of As_2S_3/l.	50% sol 2.3815 g. of As_2S_3/l.
0	18.127	15.333	10.943
0.083	18.209	15.413	11.032
0.250	18.444	15.568	11.145
0.583	18.814	15.918	....
1.083	19.265	16.358	12.008
2.083	20.199	17.234	13.004
3.083	20.750	17.911	13.799
4.583	21.746	18.750	14.809
6.583	22.564	19.584	15.867
9.583	23.160	20.294	16.717
15.383	24.069	21.281	18.097
	25% sol 1.1907 g. of As_2S_3/l.	12.5% sol 0.5954 g. of As_2S_3/l.	5% sol 0.2382 g. of As_2S_3/l.
0	6.898	4.983	2.715
0.217	7.129	5.204	2.930
0.650	7.577	5.620	3.333
1.317	8.279	6.281	3.953
2.817	9.445	7.802	5.372
5.817	11.786	9.652	7.250
11.067	13.876	12.036	9.874
14.667	14.934	13.027	11.223
18.000	15.952	13.741	12.220

eventually become parallel to the time axis and further increase in conductivity cease if the runs were continued for a sufficient time. It was observed that a finely divided, whitish precipitate formed on the bottom of the conductivity cells in all cases.



Discussion

In connection with the action of light upon colloids Bancroft[3] summarizes the literature briefly, particularly with reference to the action of ultra-violet light and β-rays. Nordenson[4] has studied the effect of the light of a quartz mercury-vapor lamp on a number of sols both spectroscopically and ultramicroscopically. Both positive and negative colloids were coagulated. Bovie[5] has found that fresh egg-white and ox serum are coagulated into feathery flakes by ultra-violet light, with some decomposition. Tian[6] observed that dry gelatin when exposed to the light of a mercury-vapor lamp was not affected, while the surface of a gelatin gel became liquefied.

Of more direct interest to the case at hand is the work of Freundlich and Nathansohn,[2] who have pointed out that the gradual clouding and final precipitation of sulfur from a carefully prepared, clear arsenic trisulfide hydrosol may be explained upon the following grounds. Arsenic trisulfide hydrosol sensitizes the photochemical oxidation of such dyestuffs as eosin and malachite green. Due to this photo-sensitizing action of the arsenic trisulfide micelle, hydrogen sulfide, produced by the hydrolysis of arsenic trisulfide, is oxidized to colloidal sulfur which is stabilized by adsorbed pentathionic acid. That pentathionic acid is the stabilizing electrolyte for sulfur hydrosols of the Odén type, has been shown by Freundlich and Scholz.[2] This acid is unstable in the presence of hydrogen sulfide, with which it reacts to form free sulfur and water: $5H_2S + H_2S_6O_6 = 10S + 6H_2O$; this reaction explains the great sensitiveness of the

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[3] "Applied Colloid Chemistry," McGraw-Hill Book Co., **1921**, p. 223.

[4] Nordenson, *Z. physik. Chem.*, **90**, 603 (1915).

[5] Bovie, *Science*, **37**, 24 (1913).

[6] Tian, *Compt. rend.*, **151**, 219 (1910).

Odén sulfur hydrosols toward hydrogen sulfide. It is the reaction between the stabilizing pentathionic acid of the sulfur micelles and the stabilizing hydrogen sulfide 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 discuss briefly the mechanism of the formation of pentathionic acid. They suggest that the photochemical oxidation of hydrogen sulfide which results in the formation of colloidal sulfur may also account for the formation of the pentathionic acid. We may consider that this is brought about by the photochemical oxidation of hydrogen sulfide to sulfur dioxide which reacts with more hydrogen sulfide to form the acid, a reaction which is probably one of several taking place in the production of Wackenroder's solution, and which has been investigated by Debus[7] and others: $5H_2S + 15O = 5SO_2 + 5H_2O$; $5H_2S + 5SO_2 = H_2S_5O_6 + 5S + 4H_2O$. 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 *intermicellar* hydrogen sulfide and acid on the other, the action of light upon the system would consist in accelerating the slow reaction and thus forcing it to completion by the photochemical oxidation of hydrogen sulfide to pentathionic acid, colloidal sulfur and water, the equilibrium between the various components of the system being maintained.

A much simpler explanation of the changes which occur in the sol upon exposure to light may be obtained by assuming that hydrogen sulfide formed by the hydrolysis of arsenic trisulfide according to the equation, $As_2S_3 + 3H_2O \rightleftarrows 3H_2S + As_2O_3$, is photochemically oxidized owing to the sensitizing action of arsenic trisulfide micelles. The oxidation of hydrogen sulfide to free sulfur and water would drive the reaction to the right, with formation of arsenic trioxide. Sulfur would be precipitated in a finely divided state. The removal of adsorbed stabilizing hydrogen sulfide would produce destabilization of arsenic trisulfide micelles and consequent gradual precipitation of the sol.

When we attempt to reconcile this simple picture of the changes occurring in the sol with the fact that the conductance increases upon exposure to light, we conclude that such a change can take place only when the conductance of the reaction products is greater than that of the reactants. The removal of hydrogen sulfide by photochemical oxidation to sulfur and water would tend to diminish the conductance of the sol, and the formation of arsenic trisulfide to increase it. Neglecting the probably very small changes in conductance due to the removal of micelles of

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[7] Debus, *J. Chem. Soc.*, **53**, 278 (1888).

arsenic trisulfide and the formation of micelles of sulfur, whatever change occurs in the conductivity must be due to the removal of hydrogen sulfide and the formation of arsenic trioxide. Since the hydrolytic equilibrium is maintained, the direction of any change in conductance must depend upon the relative conductivities of hydrogen sulfide and arsenic trisulfide solutions. In making this comparison the data of Walker and Cormack[8] for hydrogen sulfide and of Wood[9] for arsenic trioxide may be taken. For 0.04 N hydrogen sulfide (H.HS) at 18°, $\mu = 0.426$, from which $K = 1.7 \times 10^{-5}$. For 0.04 N metarsenious acid at 25°, $\mu = 0.0817$ (by extrapolation), from which $K = 3.26 \times 10^{-6}$. The conductance of 0.04 N hydrogen sulfide is thus about 5 times greater than that of 0.04 N metarsenious acid.

It is evident from the above discussion that the change in conductance which occurs upon exposure of the sol to light cannot be ascribed to the formation of arsenic trioxide, for the decrease in conductance which must accompany the removal of the more active electrolyte, hydrogen sulfide, greatly overbalances any increase due to the production of the weaker metarsenious acid. We are thus forced to the conclusion that the increase in the conductivity of the sol must be due to the formation of a substance whose conductance is appreciably greater than that of hydrogen sulfide. This statement is based upon the consideration that, if none of the hydrogen sulfide were removed by oxidation and the hydrolytic reaction were to go to completion, the total change in the conductivity of the sol studied could not be greater than $K = 2 \times 10^{-5}$, whereas differences as large as 8×10^{-5} were noted after a period during which only a small fraction of the arsenic trisulfide could have been hydrolyzed. If we agree with Freundlich and Nathansohn that a thionic acid is formed, we can readily account for the marked increase in conductance which takes place, because data for the conductance of the thionic acids show that they are active electrolytes. The value of μ for 0.03125 N tetrathionic acid[10] at 25° is 773.

The mechanism of the formation of a thionic acid in the sol may be assumed to be substantially that suggested by Freundlich and Nathansohn. A portion of the hydrogen sulfide is photochemically oxidized to free colloidal sulfur and water, and another portion to the thionic acid. Hydrogen sulfide reacts with the thionic acid to form water and colloidal sulfur. Colloidal sulfur adsorbs pentathionic acid as stabilizing electrolyte, the sulfur micelles with their adsorbed acid serving to augment the conductivity of the sol and maintaining at the same time a certain concentration of free acid in the intermicellar liquid by virtue of the adsorption equi-

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[8] Walker and Cormack, *J. Chem. Soc.*, **77**, 5 (1900).

[9] Wood, *ibid.*, 93, 411 (1908).

[10] Landolt-Börnstein, "Tabellen," **1912**, p. **1112**.

librium set up. Both of these factors serve to increase the conductance. Eventually the concentration of the intermicellar thionic acid will reach such a value that the rather slow reaction of the acid with hydrogen sulfide, 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 decreasing concentration of the sol is readily explained in view of the work of several investigators[11] who have pointed out that dilution of a sol results in increased dispersion. Increased dispersion of the colloid will favor the speed of the reaction, owing to the increased photochemical activity of the micelles per unit mass of arsenic trisulfide because of the greater active surface.

It is noteworthy 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 several days. This slight decrease is explained as being due to the fact that the slow reaction between hydrogen sulfide and pentathionic acid, which in itself tends to lower the conductance by formation of water and sulfur from the active electrolyte, continues for some time after the action of light ceases, the resulting effect being a slight diminution of the concentration of the intermicellar thionic acid.

There may be some question as to the nature of the electrolyte formed in the photochemical process. The fact that Freundlich and Scholz[2] 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 electrolyte for the colloidal sulfur in arsenic trisulfide 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, as 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 change increasing somewhat with decreasing concentration of the colloid. This is explained as being due to the increased photochemical activity of the colloid per unit mass of arsenic trisulfide, brought about by the greater dispersity of the more dilute sol.

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[11] Compare Coward, *Trans. Faraday Soc.*, 9, 142 (1913). Svedberg, *Z. physik. Chem.*, **65**, 624 (1909).

2. The reaction is explained, after the suggestion of Freundlich and Nathansohn, as one of a 2-stage photochemical oxidation of hydrogen sulfide to colloidal sulfur and a thionic acid, accompanied by reaction between hydrogen sulfide and the thionic acid which serve as stabilizing electrolytes for micelles of arsenic trisulfide and sulfur, respectively. Removal of the stabilizing electrolytes produces destabilization of the 2 colloids which are consequently precipitated. The increase in conductivity is explained as due to the building up of a concentration of the thionic acid sufficient to serve as the stabilizing electrolyte for the colloidal sulfur, the reaction between hydrogen sulfide and the thionic acid then proceeding at such a rate that the equilibrium is maintained between the several components of the system, further change in the conductance thus being prevented.

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THE CRYSTAL STRUCTURE OF HEXAMETHYLENE-TETRAMINE

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Introduction

The successful determination of crystal structures by means of X-rays has for the most part been confined to elements and polar inorganic compounds. The structures found in these cases have been of such a character that it has been natural to regard the crystals as built up of atoms or ions rather than of molecules. It is to be expected, however, that the molecule retains its identity as such in crystals of organic compounds not possessing the character of salts.

The investigation of such compounds presents difficulties which less frequently arise with inorganic compounds. Most organic substances which crystallize readily are relatively complicated in composition, and most of them crystallize in the triclinic, monoclinic, or rhombic system. The determination of the unit of structure is more difficult in these systems than in those possessing greater symmetry, and the positions of the atoms within the unit are much less fully fixed by symmetry alone. In order to avoid these difficulties as far as possible, hexamethylene-tetramine, $C_6H_{12}N_4$, was chosen for the investigation since it is one of the few known organic compounds without salt character which have cubic symmetry.

The commonest method of preparation of hexamethylene-tetramine is by the action of aqueous ammonia on aqueous formaldehyde according to the equation, $4\ NH_3 + 6\ CH_2O = C_6H_{12}N_4 + 6\ H_2O$. The product, which is obtained by evaporation in a vacuum, is soluble in water and in

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[1] National Research Fellow in Chemistry.