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THE ACTION OF SODIUM THIOSULPHATE SOLUTIONS ON CERTAIN SILVER SALTS.

BY W. M. BARR.

The following work was undertaken at the suggestion of Dr. W. S. Hendrixson, to whom I am indebted for advice and assistance in the work.

The solvent action of the thiosulphates on the halides of silver has long been known, and the fact is almost daily turned to account in the laboratory, and though the reaction has been quantitatively studied to some extent, an examination of the literature shows that no very satisfactory theory of the nature of the reaction and the complexes formed in solution has been established. Rosenheim and Steinhäuser* isolated definite compounds by evaporating saturated solutions of thiosulphates containing all the silver chloride or silver bromide they would dissolve (a compound of definite composition was not obtained with Ag I), but this does not prove that similar salts are formed in more dilute thiosulphate solutions. Barth† has proposed for the reaction which takes place in such dilute solutions $3 \text{Na}_2 \text{S}_2 \text{O}_3 + 2 \text{Ag} (\text{Cl. Br. I}) = (\text{Ag Na S}_2 \text{O}_3)_2 \text{Na}_2 \text{S}_2 \text{O}_3 + 2 \text{Na} (\text{Cl. Br. I})$.

By the solubility determinations of Valenta‡ it is apparent that the results, even in the case of the chloride, do not accord with the above equation, the amount of chloride being too small to satisfy the equation, the same

*Zeit. Anorg. Chem. 25: 72 and 103.

†Zeit. Phys. Chem. 9: 176.

‡Berichte der Wiener Acad. 108; Abt. 11 b.

being true in a more pronounced degree in the case of the bromide and the iodide. The iodide in some cases is but one-twentieth the amount called for.

Cohen * has called in question Valenta's results in two particulars. In the case of the chloride he claims that if the thiosulphate solution is agitated with a large excess of AgCl, a slightly soluble salt $(Ag_2S_2O_3Na)_2$ is formed which separates out. He submits experimental results of his own, supporting his theory and implies that the same is true for the iodide and bromide. He questions whether Valenta obtained saturation in the case of the last two salts. It seemed desirable, therefore, to study the solubility of the iodide, at least, and the effect of temperature upon the solubility of the bromide as well as the iodide. It seemed probable that some light upon the complexes formed might be gained by using some insoluble salt of silver whose acid radical was very different from the closely similar chlorine bromine and iodine, and for this salt silver iodate was chosen, which so far as known to me has not been studied with reference to its action on thiosulphates.

Richards and Faber† made determinations of the solubility of silver Bromide in sodium thiosulphate solutions of varying concentration, also making a few determinations with silver chloride, in all cases working at a temperature of 35°. Valenta's experiments were made apparently at room temperature.

For the determinations of the iodide, pure silver iodide was prepared by precipitating a solution of pure silver nitrate with an excess of pure potassium iodide solution. The precipitate was thoroughly washed and dried at 150°. Solutions of known strength of sodium thiosulphate were made by dissolving weighed amounts of the pure recrystallized salt in recently boiled water, a fresh solution being used in each experiment. An excess of the AgI was placed in the thiosulphate solution in a tightly closed tube and agitated for several hours, the temperature at first being kept several degrees above that at which solubility was to

* Zeit. Phys. Chem. 18: 61.

† Am. Chem. Jo. 21: 167.

be determined, then dropping to the final temperature and running for at least one hour. This was done to insure saturation. Five hours agitation was found to be sufficient time. At the end of this period the precipitates were allowed to settle, a portion of the clear liquid pipetted off and weighed, the Ag precipitated by ammonium sulphide, filtered off, washed, dissolved in hot HNO_3 , precipitated as AgCl with HCl, collected in a Gooch crucible, washed, dried and weighed, the AgI in solution being calculated from the Ag found. The number of c.c. of the thiosulphate solution used was found from the weights by deducting weight of AgI and dividing by sp. gr. of this solution. In the later experiments the Ag was determined in the HNO_3 solution by means of Volhard's method.

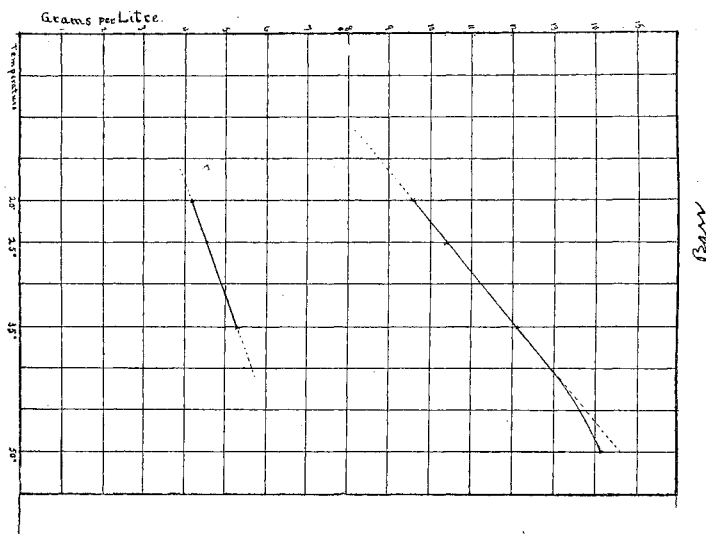
The agitator used was similar to that used by Richards and Faber based upon the Noyes' Apparatus, consisting of a wooden roller rotating in a large bath regulated by an Ostwald thermostat. The rubber stoppered tubes were strapped to the roller by means of rubber bands, the roller being driven by a small hot air engine.

The solubility of the silver iodide is shown by the following tabular statement, N and N/2 solutions being used.

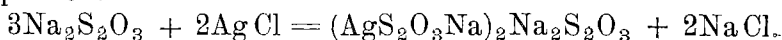
Temp.	Time of Agitation.	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ to 100 c.c. sol.	AgI dissolved to 100 c.c. sol.	Ratio AgI in mol's to 1 mol. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.
20°	7 hours	24.83	.9613	.040945
25°	8 hours	24.83	1.0380	.044211
35°	8 hours	24.83	1.1870	.050558
50°	6 hours	24.83	1.4115	.060129
20°	6 hours	12.415	.4173	.035549
25°	6 hours	12.415	.4564	.038865
35°	7 hours	12.415	.5277	.044953

From the accompanying diagram the effect of temperature upon solubility is clearly seen, the amount of AgI dissolved increasing quite rapidly with the increase of temperature, and the solubility curve being practically a straight line. After standing some time the AgI in the tubes begins to blacken, probably caused by a slight decom-

position of the thiosulphate. This is noticeable at as low a temperature as 25°, and at 50° becomes very marked, which probably accounts for the failure of this point in the diagram to fall upon the straight line. Above 50° the decomposition is too great to permit the further determination of solubilities. That light does not affect the solubility of the AgI was shown by using, in two experiments, AgI made by red light, the agitation being carried out under the same condition.



A few experiments were tried to determine the effect of temperature on the solubility of Ag Br in thiosulphate solutions, and it was found that as much Ag Br was dissolved at 20° as at 35°. Thus it is seen that the solubility of the bromide does not increase with the temperature as is so markedly true in the case of the iodide. Cohen states, in the case of the chloride that the full amount of Ag Cl will be found in solution only when an excess of the Ag Cl is avoided and there is just enough present to satisfy the equation.



This method was tried with both the AgI and Ag Br, the agitation being continued for several hours, but in neither case was as much silver found in the solution as when the

silver salt was in excess, showing that in these cases saturation was not obtained, and that the bromide and iodide did not unite with sodium thiosulphate in these experiments, in the proportion corresponding to the equations of Cohen.

In attempting to determine the solubility of silver iodate in sodium thiosulphate solution it was found that with strong thiosulphate solution and an excess of AgIO_3 a rather violent reaction occurred and much heat was evolved. It was found necessary then, to use a more dilute thiosulphate solution, so a N/10 solution was employed. By shaking this with a small excess of AgIO_3 until the first signs of reaction appeared, requiring 20 to 30 minutes, then by filtering off and weighing a portion of the solution and determining the silver an approximation at the amount of AgIO_3 dissolved was obtained.

100c.c. N/10 THIO. DIS- SOLVED AgIO_3 GRAMS.	GRAMS AgIO_3 PER GRAMS THIO.
4.26	1.176
4.97	2.002

Upon the molecular basis of iodide and iodate the AgIO_3 is about 16 times as soluble as the AgI .

The reaction just described between the AgIO_3 and $\text{Na}_2\text{S}_2\text{O}_3$ has not, so far as known to me, been described in the literature, and the nearest approach to it is that described by Landholdt* on the action of sulphur dioxide on iodic acid.

A preliminary experiment showed that with 1.5 molecules of thiosulphate to one molecule AgIO_3 there was no very apparent reaction, but when molecule for molecule was used practically all the AgIO_3 went into solution, that which remained blackened showing the formation of Ag_2S , then began the precipitation of AgI which continued until there was no more silver in solution. It was deemed best to study the reaction when the substances were put together in equal molecules. After shaking and allowing to stand for about forty-eight hours the solution was found to be acid, neither silver nor thiosulphate was found in the

* Berichte 19: 1317.

solution, no hydriodic acid was present, but a small quantity of iodic acid was found. A determination of the sulphuric acid in the solution and the amount of sulphur combined with the silver and in the free state accounted for all the S in the $\text{Na}_2\text{S}_2\text{O}_3$ used, showing complete decomposition of the thiosulphate. In a similar experiment, in which the substances were allowed to stand for about a week, the residue contained no silver sulphide, showing that the formation of Ag_2S is an intermediate reaction and that the reaction of the first experiment did not complete itself in the time allowed it.

For the determination of the products of the reaction the following methods were pursued. The residue was filtered off, washed, and the filtrate and washings made up to 100 c.c., portions of 20 c.c. being taken for analysis. The sulphates were precipitated by means of barium chloride and weighed as barium sulphate. To determine the iodic acid the solution was digested for several hours with 10 c.c. conc. HCl and KI in a closed bottle, the free iodine being then titrated with N/10 thiosulphate and the iodine found as HIO_3 calculated. The residue was dried at 110° , the free sulphur extracted by repeated treatment with hot chloroform, the chloroform evaporated and the sulphur weighed. The following results were obtained from the analysis of the completed reaction:

Weight of AgIO_3 taken.....	.4046g.
c.c. N/10 thiosulphate 14.31= $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$..	.3553g.
Weight of BaSO_4 .1124g., total S as sulphate07718g.
Free S in residue.....	.0178g.
<hr/>	
Total sulphur found... ..	.09498g.
Sulphur in thiosulphate taken09158g.
Total iodine in HIO_3 in filtrate.....	.03530g.
Iodine as HI.....	None.
Total iodine in AgIO_3 used1815g.
Hence iodine in residue.....	.1462g.

The iodine in the residue is in combination with silver as AgI , excepting the possibility of a very small quantity of AgIO_3 undecomposed in the reaction. There being no Ag in the solution, there must be more Ag in the residue

than will combine with the iodine, and which probably, then, exists as Ag_2O .

The starting of this reaction requires an excess of AgIO_3 and seems to be due to the formation of Ag_2S setting free acid. It might be accounted for by the occurrence of such a reaction as the following: $2\text{AgIO}_3 + \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} = \text{Ag}_2\text{S} + 2\text{HIO}_3 + \text{Na}_2\text{SO}_4$. When the thiosulphate is in excess no reaction takes place, but on the addition of the slightest amount of free acid the reaction begins.

It is practically impossible to obtain even a close approximation of the solubility of silver bromate in thiosulphate because of the fact that the substances begin to react within ten minutes after they are put together, hence saturation could not be obtained. In a trial at this 100 c.c. N/10 thiosulphate solution dissolved 1.835g. AgBrO_3 .

For studying this reaction the AgBrO_3 and the $\text{Na}_2\text{S}_2\text{O}_3$ were put together molecule for molecule and after thorough shaking for several hours were allowed to stand for a week. Qualitative tests show that the solution contained no thiosulphate, no silver, a little bromic acid, sulphuric acid either free or as sulphate, and hydrobromic acid; the residue contains silver bromide, free sulphur, but no silver sulphide.

On analysis the following results were obtained, using the same methods as in the iodate reaction:

Weight of AgBrO_3 taken.....	6491g.
N/10 thiosulphate taken.....	27.52c.c.

Filtrate was made to 150 c.c. and 40 c.c. taken for each determination.

Weight BaSO_4 .3162g. Total S as sulphate....	16283g
Weight of free S in residue.....	0130g

Total sulphur found.....	17583g
Total sulphur in $\text{Na}_2\text{S}_2\text{O}_3$ used.....	17610g

Dried residue was treated with hot HNO_3 washed, dried and weighed as AgBr .

Weight of AgBr .3883g., weight Ag found....	22305g
Weight Br found.....	16525g

The Ag found in the filtrate from the AgBr was precipitated as AgCl by HCl and weighed in a Gooch crucible.

Weight of AgCl .0976g., weight of Ag found07347g.
Total silver found.....	.29652g.
Total silver in AgBr used29700g.
Weight of AgBr in 40 c. c., original filtrate.....	.0280g.
Weight of Br found as HBr.....	.04468g.
Weight of Br found as HBrO ₃0091g.
Weight of total bromine found.....	.21903g.
Weight of bromine in AgBrO ₃ taken.....	.2200g.

From the above analysis there seems to be silver in the residue which cannot be in combination with either Br or S, and hence probably exists as Ag₂O, being undissolved by the very weak acid solution formed in the reaction.

There seems to be in general a similarity between the reactions of AgIO₃ and AgBrO₃ with sodium thiosulphate solutions. In both reactions the Ag₂S, which is at first formed, entirely disappears if the reaction be allowed to go to completion. The essential difference in the reactions seems to be the presence of HBr in the bromate reaction, while HI is absent from the iodate reaction, though a larger amount of HIO₃ is found in the latter than HBrO₃ in the former.

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