

XXI.—*Production of Arsenic Subsulphide. Reduction of Certain Arsenic Compounds by Sodium Hypo- sulphite [Hydrosulphite].*

By WALTER FARMER and JAMES BRIERLEY FIRTH.

PRELIMINARY experiments on the reduction of certain arsenic compounds by sodium hyposulphite gave a product which was insoluble in colourless ammonium sulphide and appeared to be a subsulphide of arsenic. In the present investigation the pro-

ducts obtained by reducing various arsenic compounds in acid and in alkaline solution by sodium hyposulphite were examined.

In all the experiments the amounts of the different arsenic compounds taken were equivalent to the quantity of arsenic contained in 1 g. of pure arsenic trioxide, *i.e.*, 0.7575 g. of arsenic.

Filtration and washing of the precipitate at room temperature was a very slow process; if, however, the product was heated to boiling, the precipitate coagulated, and filtration and washing were greatly facilitated; also analysis showed that the composition of the precipitate was not affected by this treatment.

Analysis of the Product.—A solution of the precipitate was obtained by two distinct methods: (a) oxidation by fuming nitric acid, (b) oxidation by sodium peroxide in presence of hydrogen peroxide. Both methods were used for the precipitate obtained in each experiment and the two sets of results obtained showed satisfactory agreement. In each case, the arsenic was estimated as magnesium pyroarsenate (Levol, see Treadwell's "Analytical Chemistry," 1915, Vol. ii, pp. 206—208) and the sulphur as sulphate (Hentz and Weber; *op. cit.*, p. 469). To obtain a further check on the results, the arsenic remaining in the filtrate and washings was also estimated.

Series I. Reduction (a) at 18°, (b) at 0° in Hydrochloric Acid of Definite Concentration by Sodium Hyposulphite in Various Concentrations.—The requisite quantity of the arsenic compound was dissolved, if necessary by heating under reflux, in a mixture of 5 c.c. of concentrated hydrochloric acid and 45 c.c. of water. A solution of the requisite quantity of sodium hyposulphite in 50 c.c. of water was rapidly added, making the total volume 100 c.c. In all cases there was an immediate precipitation of a dark brown product, the quantity of which varied with the concentration of hyposulphite used.

Experiments carried out over periods ranging from 30 minutes to 12 hours showed that the duration of the experiment did not appear to affect the nature of the decomposition product, but only slightly increased the amount of the precipitate. In all subsequent experiments, therefore, the reaction was allowed to proceed for 12 hours, the reaction flask being well stoppered and the contents frequently shaken. After 12 hours, the reaction products were heated just to boiling point, and the precipitate was filtered off, thoroughly washed, dried at 100°, and weighed. In series (b), the solutions were cooled to 0° before mixing and the temperature of the mixed solutions was maintained at 0° for 12 hours. The results are in Table I; *w* = grams of hyposulphite in 100 c.c. of mixed solutions.

TABLE I.

As compd.	w.	(a) Reaction temp. 18°.			(b) Reaction temp. 0°.		
		% As ppted.	% As in ppte.	% S in ppte.	% As ppted.	% As in ppte.	% S in ppte.
As ₂ O ₃	4	64·19	86·69	13·47	61·25	87·50	12·68
	6	68·74	85·63	14·51	65·39	86·38	13·78
	8	73·09	85·92	15·25	69·98	85·80	14·33
	10	79·12	84·03	16·09	75·26	84·87	15·28
As ₂ O ₅	4	36·34	75·79	24·35	35·61	85·87	14·30
	6	37·20	74·87	25·25	36·75	85·13	15·01
	8	38·98	74·02	26·08	37·98	84·50	15·68
	10	40·05	73·41	26·75	39·78	83·81	16·31

Series II. Reduction at 18° in Oxalic Acid Solution of Definite Concentration by Various Amounts of Sodium Hyposulphite.—This series was carried out in order (if possible) to reduce the rate of decomposition of the sodium hyposulphite in the acid solution. The requisite quantity of the arsenic compound (= 0·7575 As) was dissolved in a solution of 4·5 g. of oxalic acid in 75 c.c. of water. The hyposulphite was dissolved in 25 c.c. of water and rapidly added to the oxalic acid solution. Other details were as before. The results are in Table II.

TABLE II.

w.	As ₂ O ₃ .			As ₂ O ₅ .		
	% As ppted.	% As in ppte.	% S in ppte.	% As ppted.	% As in ppte.	% S in ppte.
4	73·20	80·31	19·86	36·19	75·89	24·25
6	87·22	76·91	23·24	37·45	75·12	25·03
8	88·53	76·33	23·86	38·97	74·55	25·56
10	90·89	75·89	24·31	40·11	74·23	25·93

Series III. Reduction at 18° in Hydrochloric Acid of Various Concentrations by Sodium Hyposulphite of Definite Concentration.—In order to ascertain the effect of acid concentration, solutions of 1 g. of arsenic trioxide in 50 c.c. of hydrochloric acid of definite strength were each treated with 25 c.c. of a solution containing 10 g. of sodium hyposulphite. With increasing concentration of acid the colour changed from dark brown to very light brown. The results are in Table IIIa. This series was repeated, a quartz vessel being used. The results are in Table IIIb.

TABLE III.

As compd.	C.c. of conc. HCl.	% As ppted.		% As in ppte.		% S in ppte.	
		a.	b.	a.	b.	a.	b.
As ₂ O ₃	5	87·16	82·19	85·69	80·82	14·49	19·46
	10	84·26	78·65	80·96	73·78	19·25	26·47
	20	79·42	76·98	73·48	69·48	26·71	30·83
	30	74·95	71·89	62·77	56·56	37·39	43·73
	40	72·91	70·05	56·22	53·60	43·98	46·76

Series IV. Reduction in Potassium Hydroxide Solution of Definite Concentration by Sodium Hyposulphite in Various Concentrations.—Preliminary experiments showed that no dark brown precipitates were formed at room temperature, even after 3 hours. As the temperature was being raised to the boiling point of the alkaline solution in which the reduction was taking place, there was a continuous darkening of the reaction liquid followed by the formation of a dark brown precipitate, the bulk of which increased after the liquid had reached the boiling point. The escaping vapour contained a gas having a strong garlic odour. This gas was further examined. The flask containing the reaction liquid was fitted with a small reflux condenser, to the top of which a hard glass tube was attached. The reaction liquid was boiled for 30 minutes while one part of the tube was strongly heated. A white, crystalline sublimate of arsenious oxide and a metallic mirror of arsenic formed in the cooler parts of the tube. Further, the gas produced a black deposit of metallic silver in a dilute solution of silver nitrate and reacted with iodine in solution.

The subsequent experiments were carried out at the temperature of the boiling solution. A solution of the arsenic compound in 50 c.c. of 3*N*-potassium hydroxide was treated rapidly with the required amount of sodium hyposulphite dissolved in 50 c.c. of 3*N*-potassium hydroxide. The gas evolved from the boiling mixture was passed into 25 c.c. of *N*/10-iodine solution, the evolution being complete after 20 minutes. In subsequent experiments, therefore, the reaction liquid was maintained at the boiling point for 30 minutes, and was then diluted to 200 c.c. and filtered through a tared filter; the precipitate was thoroughly washed, dried, and analysed. The iodine solution was titrated with *N*/10-thiosulphate. The results are in Table IV.

TABLE IV.

As compd.	w.	% As ppted.	% As in ppte.	% S in ppte.	% As evolved.
As ₂ O ₃	4	77.02	95.84	4.30	0.50
	6	79.75	95.68	4.49	0.50
	8	83.20	93.50	6.65	0.50
	10	86.66	89.02	11.16	0.49
As ₂ O ₅	4	trace	—	—	0.40
	6	trace	—	—	0.40
	8	5.93	92.19	8.06	0.42
	10	8.38	90.09	10.08	0.42

Series V. Reduction at 18°, a Neutralisation Method being used in which the Arsenic Compound dissolved in Hydrochloric Acid of Definite Volume and Concentration is reduced by Various Amounts of Sodium Hyposulphite dissolved in Potassium Hydroxide Solution of the same Volume and Normality as the Hydrochloric Acid.—The

hyposulphite dissolved in 50 c.c. of 1.2*N*-potassium hydroxide was rapidly added to a solution of the arsenic compound in 50 c.c. of 1.2*N*-hydrochloric acid. In all cases, there was an immediate precipitation of a dark brown substance; after 12 hours, this was filtered off, washed, dried, weighed, and analysed. The results are in Table V.

TABLE V.

<i>w.</i>	Arsenic trioxide.			Trisodium arsenite.		
	% As ppted.	% As in ppte.	% S in ppte.	% As ppted.	% As in ppte.	% S in ppte.
4	82.75	93.18	6.96	69.79	88.09	13.12
6	88.37	93.47	6.70	76.02	88.15	13.08
8	94.81	93.62	6.57	80.05	88.21	13.02
10	99.24	93.89	6.24	87.28	88.17	13.06

<i>w.</i>	Arsenic pentoxide.			Trisodium arsenate.		
	% As ppted.	% As in ppte.	% S in ppte.	% As ppted.	% As in ppte.	% S in ppte.
4	50.08	76.89	23.29	40.39	69.31	30.88
6	51.98	76.42	23.72	42.56	69.17	30.97
8	55.13	75.93	24.22	43.97	68.88	31.28
10	57.25	75.73	24.46	45.48	68.77	32.41

With the exception of this series (V), the results obtained with trisodium and tripotassium arsenites and arsenates were similar to those obtained with the trioxide and pentoxide respectively.

Further Examination of the Precipitates.—The precipitates obtained in the foregoing experiments were repeatedly digested with colourless ammonium sulphide until on acidifying the extract no precipitate of arsenic sulphide was obtained.

With the exception of those obtained in the experiments in alkaline solution, the precipitates contained 6, 12, 25, or 32% of sulphur. A few contained 40% or more, and some were of intermediate composition.

Products of similar composition gave similar results when digested with colourless ammonium sulphide. The following are typical examples. In the fifth experiment there was, after digestion, a very small, dark brown residue containing arsenic and sulphur.

TABLE VI.

Original As compd.	Exptl. condition as in series.	Comp. before digestion.		Comp. after digestion.		Time of digestion (days).
		% As.	% S.	% As.	% S.	
As ₂ O ₃	I (a)	85.63	14.51	77.38	12.69	5
As ₂ O ₅	I (b)	83.81	16.31	77.33	12.71	5
As ₂ O ₃	II	80.31	19.86	77.35	12.68	7
As ₂ O ₅	II	74.23	25.93	77.31	12.75	7
As ₂ O ₃	III	56.22	43.98	—	—	10
As ₂ O ₃	IV	95.84	4.30	96.11	3.92	7
As ₂ O ₅	V	90.19	9.98	94.87	5.22	7
Na ₃ AsO ₄	V	68.81	31.41	71.17	25.89	3
				77.41	12.81	10

The average sulphur content of the residues after extraction was 12.69% in the case of the precipitates containing initially 12.5 to 32.5% of sulphur. As As_3S requires S, 12.45%, the final product would appear to be this subsulphide, the slightly high value for sulphur being due to retention of a little arsenious sulphide, the removal of the last traces of which is very difficult. For those precipitates containing less than 12% of sulphur, the results were not so consistent; *e.g.*, for the final product from arsenic trioxide treated by the neutralisation method the mean sulphur content after extraction was 4.8%, whilst the precipitates from alkaline solutions gave final products containing 2.5 to 5.35% of sulphur.

Discussion and Conclusions.

One of the products of reduction of the arsenic compounds used is a sulphide of arsenic which contains about 12.7% of sulphur and is insoluble in colourless ammonium sulphide. It agrees in composition with the subsulphide of arsenic As_3S and appears to be identical with the substance obtained by Scott (J., 1900, **77**, 651) by treating an aqueous solution of an alkali arsenate with phosphorus trichloride and saturating the mixture with sulphur dioxide. Products containing from 2.5 to 5.35% of sulphur have also been isolated.

In moderately acid solutions trivalent arsenic compounds yield precipitates of arsenic subsulphide, As_3S , containing comparatively small quantities of arsenic trisulphide, whilst quinquevalent arsenic compounds yield precipitates which approximate in composition to the formula $\text{As}_2\text{S}_3, \text{As}_3\text{S}$ (25.42% S). The total arsenic precipitated from the latter compounds is approximately half that from the former.

Similar results are obtained by the neutralisation method, except that the precipitates from arsenic trioxide contain 6—7%, and those from alkali arsenates 30—32%, of sulphur ($2\text{As}_2\text{S}_3, \text{As}_3\text{S}$ requires S, 29.89%).

Increase in acid concentration increases the amount of arsenic precipitated as trisulphide, and in strongly acid solutions the precipitate is mainly the trisulphide.

In alkaline solution, precipitation occurs not at room temperature but at the boiling point of the mixed solutions. In the case of arsenic trioxide the products contain 4—11% of sulphur. Arsenic pentoxide gives a comparatively small precipitate. A small amount of arsenic is volatilised at the boiling point of the mixture, mainly as trioxide associated with the hydride. The total arsenic precipitated increases, but not proportionally, with the concentration of the hyposulphite.

It would appear from the results that the subsulphide is formed by reaction between the trivalent arsenic compound and the hyposulphite, whilst the trisulphide is produced by the interaction of the arsenic compounds with thiosulphate and other thio-decomposition products of the hyposulphite. A yellow precipitate of arsenic sulphide is obtained when a solution of sodium thiosulphate containing alkali arsenite is acidified with hydrochloric acid and warmed. Hence increased concentration of hydrochloric acid increases the rate of decomposition of the hyposulphite, and the quantity of subsulphide produced is diminished and that of the trisulphide increased.

In the case of quinquevalent arsenic compounds, reduction to the trivalent compound first takes place with the production of thio-decomposition products; the arsenic is subsequently precipitated, partly as subsulphide by the hyposulphite and partly as trisulphide by the thiosulphate, etc.

At 0° (Series *Ib*), the sulphur content is diminished owing to the diminution in the rate of decomposition of the hyposulphite.

In no case was the arsenic completely precipitated from solution, but in neutral solution, with 10 g. of hyposulphite for 1 g. of arsenic trioxide, 99.24% (Series V) was precipitated. The maximum precipitation of arsenic from quinquevalent compounds was 57.25%, obtained in the same series under similar conditions.

UNIVERSITY COLLEGE, NOTTINGHAM.

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