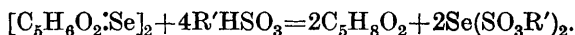


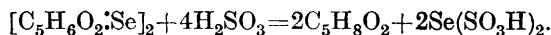
CXVI.—*Researches on Residual Affinity and Coordination. Part VI. Selenodithionic Acid and its Metallic Salts.*

By GILBERT T. MORGAN and J. D. MAIN SMITH.

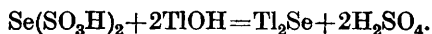
IN an earlier communication (T., 1920, 117, 1461) it was shown that selenium acetylacetone reacted quantitatively with sodium or potassium hydrogen sulphite, giving rise to acetylacetone and the corresponding alkali selenodithionate :



This reaction has been extended to the production of other metallic selenodithionates, and the *lithium*, *rubidium*, *cæsium*, and *ammonium* salts have now been prepared in a state of purity. The isolation of *barium selenodithionate* shows that the reaction is also applicable to the case of the metals of the alkaline earths. With sulphurous acid and selenium acetylacetone a similar double decomposition occurs, with the production of *selenodithionic acid* :



This acid has not been obtained in a concentrated form, for, when its aqueous solution is evaporated at the ordinary temperature under reduced pressure, red selenium separates when a strength of approximately 50 per cent. (or 8*N*-) is reached. At higher concentrations, the aqueous solution deposits selenium and evolves sulphur dioxide, even at 0°. On treatment with aqueous thalious hydroxide, selenodithionic acid yields thalious selenide and sulphuric acid :



EXPERIMENTAL.

By a modification of the method formerly employed (*loc. cit.*) selenium acetylacetone was produced in considerably better yield, with a ready recovery of the by-product, chloroacetylacetone, in the form of its copper derivative.

Acetylacetone (4 mols.), dissolved in its own weight of anhydrous ether, was added slowly to finely divided selenium tetrachloride (2 mols.) suspended in an equal weight of ether. Considerable heat was generated and the mixture was maintained at about 0° by external cooling. The tetrachloride dissolved to an intensely red solution, evolving hydrogen chloride; the ether was then evaporated in a rapid stream of air, which passed through a series of wash bottles charged with an aqueous solution of copper and sodium acetates, from which pale green copper chloroacetylacetone separated (yield 75 per cent. of the calculated quantity). The residue, after removing the volatile solvent, consisted of pale yellow, crude selenium acetylacetone, which was purified by extraction with dry benzene in a Soxhlet apparatus (yield 87 per cent.). In this preparation ether may be replaced by cheaper benzene, but the evaporation takes considerably longer. An attempt to inhibit the formation of chloroacetylacetone as a by-product by the addition of elemental selenium to the tetrachloride was not successful, 94 per cent. of the free element being recovered.

Lithium selenodithionate, $\text{Se}(\text{SO}_3\text{Li})_2 \cdot 3\text{H}_2\text{O}$, an extremely soluble salt, was produced by adding seven grams of finely divided selenium acetylacetone to 5.2 grams of lithium sulphite, $\text{Li}_2\text{SO}_3 \cdot 2\text{H}_2\text{O}$, in 45 c.c. of 2*N*-sulphurous acid. The mixture was shaken mechanically for one hour, selenium acetylacetone disappeared, the liquid was extracted repeatedly with ether to remove acetylacetone, and unaltered lithium sulphite was precipitated by adding absolute alcohol (1 vol.) to the aqueous layer. The filtrate was then concentrated under reduced pressure, a precipitate of red selenium was formed during evaporation, and the final mother-liquor, after being filtered through a layer of French chalk, was evaporated to dryness over sulphuric acid in a vacuum desiccator. This lithium salt separated in colourless, hexagonal plates, which rapidly deliquesced in air and decomposed subsequently with liberation of red selenium (Found: $\text{Se}=25.55$; $\text{Li}=4.56$. $\text{Li}_2\text{S}_2\text{SeO}_6 \cdot 3\text{H}_2\text{O}$ requires $\text{Se}=25.78$; $\text{Li}=4.56$ per cent.).

Sodium selenodithionate tetrahydrate, $\text{Se}(\text{SO}_3\text{Na})_2 \cdot 4\text{H}_2\text{O}$, was prepared by adding 7 grams of selenium acetylacetone to 9 grams of sodium hydrogen sulphite in 30 c.c. of water. The liquid, which became appreciably hot, was cooled externally, and after thirty

seconds the selenium acetylacetone had entirely disappeared, becoming replaced by a heavy, colourless, crystalline precipitate of the sodium salt. This product was dissolved in cold water and the filtered solution treated with alcohol, when the purified salt separated in colourless, prismatic needles (yield 80 per cent.) (Found: Se=21·80; Na=13·1; SO₂=17·7; H₂O=20·5. Na₂S₂SeO₆·4H₂O requires Se=22·1; Na=12·9; SO₂=17·9; H₂O=20·2 per cent.). This hydrated salt, which was extremely soluble in cold water, very readily formed supersaturated solutions; it effloresced rapidly and passed into the anhydrous salt, Se(SO₃Na)₂, when exposed to a dry atmosphere.

Potassium selenodithionate (*loc. cit.*), the least soluble of the alkali selenodithionates, was obtained by neutralising a 2*N*-solution of selenodithionic acid and precipitating with alcohol.

Rubidium Selenodithionate, Se(SO₃Rb)₂.—Selenium acetylacetone (1·8 grams) was shaken mechanically for twenty minutes with 3·6 grams of rubidium hydrogen sulphite (page 1069) in 10 c.c. of water, when the rubidium salt separated in small, colourless needles. This product was dissolved in cold water and reprecipitated by alcohol (yield 76 per cent.) (Found: Se=19·3; Rb=41·8; SO₂=15·4. Rb₂S₂SeO₆ requires Se=19·3; Rb=41·7; SO₂=15·6 per cent.).

Rubidium selenodithionate, which was obtained in well-defined, colourless prisms, was more soluble in water than the potassium salt, but less so than the sodium and caesium salts.

Caesium selenodithionate, Se(SO₃Cs)₂, prepared by the interaction of selenium acetylacetone and caesium hydrogen sulphite as in the preceding preparation, crystallised from hot, dilute alcohol in colourless, filamentous needles (yield 87 per cent.) and from water in transparent, tabular prisms [Found: Se=15·9; Cs=52·6; SO₂=12·4; SO₄ (from residue on heating)=19·0. Cs₂S₂SeO₆ requires Se=15·6; Cs=52·7; SO₂=12·7; SO₄=19·0 per cent.]. This caesium salt has greater capacity for crystallising than any other alkali selenodithionate.

Ammonium selenodithionate, Se(SO₃NH₄)₂, prepared by double decomposition between selenium acetylacetone and ammonium hydrogen sulphite, was a somewhat unstable salt; it separated at first as a mass of colourless needles (yield 84 per cent.), which rapidly reddened on exposure to air (Found: Se=28·4; NH₄=12·7. (NH₄)₂S₂SeO₆ requires Se=28·8; NH₄=13·1 per cent.). On reprecipitating dissolved ammonium selenodithionate with alcohol-ether, colourless needles were obtained, which soon assumed a fawn colour.

Barium Selenodithionate, Se(SO₃)₂Ba·2H₂O.—Selenium acetyl-

acetone (7 grams) was shaken mechanically with 9 grams of barium sulphite suspended in 26 c.c. of 3·3*N*-sulphurous acid. After seven hours, the organic compound was replaced by a heavy, colourless, crystalline precipitate of the barium salt. When redissolved in water and precipitated by alcohol, barium selenodithionate separated in colourless needles, which reddened on prolonged exposure (yield 70 per cent.) (Found: Se=19·1; Ba=33·1; SO₂=15·7; SO₄ (from residue)=23·2; H₂O=8·9. BaS₂SeO₆·2H₂O requires Se=19·2; Ba=33·3; SO₂=15·5; SO₄=23·3; H₂O=8·7 per cent.).

Attempts to prepare the corresponding calcium salt showed that this compound was extremely soluble in water or alcohol and was not precipitated by ether from either of these solutions.

In the course of the foregoing preparations the following salts were characterised.

Rubidium hydrogen sulphite, RbHSO₃, obtained by passing sulphur dioxide into a solution of rubidium carbonate until a pale green tint was assumed, was precipitated by alcohol as a voluminous, white precipitate, which separated in colourless prisms (yield 80 per cent.). This salt, which was readily soluble in water, gave acid reactions with litmus and phenolphthalein, but was neutral to methyl-orange (Found: Rb=51·5; SO₃H=48·5. RbHSO₃ requires Rb=51·4; SO₃H=48·7 per cent.). When gradually heated to redness, dry rubidium hydrogen sulphite evolved water, sulphur, and sulphur dioxide, leaving a residue of rubidium sulphate.

Rubidium Sulphite.—(a) *Alcoholate*. A solution of rubidium carbonate was divided into two equal portions; one portion was treated with sulphur dioxide and the hydrogen sulphite precipitated by alcohol. The hydrogen sulphite was added to the other portion of rubidium carbonate solution, carbon dioxide was eliminated by heating, and a large excess of absolute alcohol added to the cooled solution. A heavy, oily, milky liquid was precipitated, which in a freezing mixture slowly set to a colourless, crystalline mass. The product was washed with a mixture of alcohol and ether and dried over calcium chloride (Found: Rb=62·0; C₂H₅·OH=8·7. 2Rb₂SO₃·C₂H₅·OH requires Rb=62·4; C₂H₅·OH=8·4 per cent.). The alcoholate readily gave up its alcohol on heating, and was freely soluble in water.

(b) *Anhydrous Salt*.—The alcoholate was dissolved in just sufficient water for solution, and evaporated by boiling under reduced pressure until a white, crystalline powder was deposited (Found: after drying on porous tile over sulphuric acid, Rb=68·3; SO₂=25·9. Rb₂SO₃ requires Rb=68·1; SO₂=25·5 per cent.).

Anhydrous *rubidium sulphite* consisted of small, colourless,

prismatic tablets, extremely soluble in water and aqueous alcohol, reacted strongly alkaline to litmus, evolved sulphur dioxide with dilute mineral acids, and on ignition gave a residue of rubidium sulphate and sulphide.

Reactions of Selenodithionates.

Solutions of	Silver nitrate	Brownish-black precipitate.
	Mercurous nitrate	Greenish-black precipitate.
	Mercuric chloride	Yellow precipitate, becoming orange, then buff, and turning black on boiling.
	Stannous chloride	Becomes slowly milky, then pale yellow precipitate formed, becoming orange-yellow and turning orange-red on boiling.
	Hydrogen peroxide	Red selenium precipitated on boiling.
	Sodium hyposulphite	Red selenium precipitated in the cold.
	$\text{KMnO}_4 + 2N\text{-H}_2\text{SO}_4$	Decolorised, then turns yellow, then green, and bronze-green precipitate formed.
	Hydrogen sulphide	Yellow precipitate, turning orange-red on boiling.
	$2N\text{-HCl}$ and $2N\text{-HNO}_3$	Red selenium separates on boiling.
	$4N\text{-H}_2\text{SO}_4$ or weaker	No reaction even on boiling.

The authors desire to express their thanks to the Department of Scientific and Industrial Research for grants which have partly defrayed the expense of this investigation.

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[Received, June 1st, 1921.]