CCCLXIX.—*The Argentothiosulphuric Acids and their Derivatives. Part I. The Preparation of the Sodium Salts and the Isolation of Monoargentomonothiosulphuric Acid.*

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THE preparation of the argentothiosulphuric acids and certain new derivatives was the outcome of an investigation of the mechanism of photographic fixation (*Phot. J.*, 1929, **53**, 314). The complex sodium argentothiosulphates formed by interaction of sodium thiosulphate with silver salts are often assumed to be $Ag_2S_2O_3,Na_2S_2O_3$ and $Ag_2S_2O_3,2Na_2S_2O_3$ (see "Photography as a Scientific Implement," Sheppard *et al.*, 1923, 155; "Photography, its Principles and Practice," Neblette, 1927, 338; "La Technique Photographique," Clerc, 1926, 380; Eder's "Handbuch der Photographie," 1928, iv, I, 75). These formulæ are based upon analyses by Lenz (*Annalen*, 1841, **40**, 98) of compounds first prepared by Herschel (*Edin. Phil. J.*, 1819, **1**, 8, 396).

Sodium Monoargentomonothiosulphate.—The compound

$$Ag_2S_2O_3,Na_2S_2O_3$$

has been isolated by many workers as a sparingly soluble salt. All are agreed as to its composition, but it has been variously described as a monohydrate (Lenz, *loc. cit.*; Richards and Faber, *Amer. Chem. J.*, 1899, **21**, 171), a dihydrate (Schwicker, *Ber.*, 1889, **22**, 1736; Schmidt, *Földtani Köstöny*, 1893, **23**, 100, 38; *Ausz. Z. Kryst.*, **23**, 502; Luther, *Phot. Ind.*, 1928, **26**, 626), a pentahydrate

(Eder, *op. cit.*), and as the anhydrous compound (Rosenheim and Steinhäuser, *Z. anorg. Chem.*, 1900, **25**, 74; Rosenheim and Trewendt, *Ber.*, 1928, **61**, 1731). These discrepancies are probably due to the difficulty of obtaining the compound pure. The two general methods of preparation consist in (1) saturating sodium thiosulphate solution with silver chloride, and (2) adding silver nitrate solution to sodium thiosulphate. Admittedly, impure products are obtained, contaminated in the first method by silver chloride, and in the second by silver sulphide formed by decomposition of normal silver thiosulphate, although, by taking special precautions, Rosenheim and Trewendt (*loc. cit.*) claim to have prepared a pure product by this method. A purer product would probably be yielded by Schwicker's method (*loc. cit.*), *viz.*, addition of ammoniacal silver nitrate solution to sodium thiosulphate solution, and evaporation over sulphuric acid.

The preparation of the compound by addition of an aqueous suspension of silver carbonate to sodium thiosulphate has been described by the author (*Phot. J.*, 1929, **53**, 314). In this way the formation of normal silver thiosulphate was prevented by the prevailing low silver-ion concentration, and the compound was obtained in a high state of purity as a colourless crystalline powder, darkening only very slightly after a week's exposure to bright diffused daylight, whereas it is described by other workers as a dirty white or greyish-white powder, darkening on exposure to light. Since all samples prepared by this method consisted of the dihydrate, and since the probability of two hydrates being formed by crystallisation from cold aqueous solution is somewhat remote, this compound may be assigned the structure $Ag_2S_2O_3,Na_2S_2O_3,2H_2O$ or $Na(AgS_2O_3),H_2O$, for which the name sodium monoargentomonothiosulphate is suggested.

Sodium Triargentotetrathiosulphate.—In the same work, the only soluble complex salt which could be isolated was prepared by alcoholic precipitation from a solution of sodium monoargentomonothiosulphate in excess of sodium thiosulphate, and shown to be the *dihydrate* of sodium triargentotetrathiosulphate,

$$Na_5[Ag_3(S_2O_3)_4],2H_2O.$$

This salt has almost universally been assumed to be

$$Ag_2S_2O_3,2Na_2S_2O_3$$

or $Na_4[Ag_2(S_2O_3)_3]$, although Lumière and Seyewetz (*Phot. J.*, 1907, **31**, 132) give the formula $2Ag_2S_2O_3,3Na_2S_2O_3$ or $Na_6[Ag_4(S_2O_3)_5]$, Lüppo Cramer (Eder, *op. cit.*, 1927, ii, 1, 452; "Jahrbuch für Photographie," 1906, 33) suggests the formation from silver halides of halogen-containing complex salts, and Rosenheim and Trewendt (*loc. cit.*) propose the formula $Na_5[Ag_3(S_2O_3)_4],3H_2O$.

The salt is most conveniently prepared by alcoholic precipitation from a solution of silver carbonate in sodium thiosulphate. Considerable excess of the latter must be used, owing to the tendency of the triargentotetrathiosulphates to break down into monoargentomonothiosulphates.

Sodium Monoargentodithiosulphate.—In addition to the two salts which have been isolated, there is strong evidence for the existence in solution of a third complex salt of the formula $Na_3[Ag(S_2O_3)_2]$. Bodländer (*Centr.*, 1901, II, 1109) concluded from *E.M.F.* measurements that the ions $(AgS_2O_3)^{I}$, $Ag(S_2O_3)_2^{III}$, and $Ag(S_2O_3)_3^{V}$ are present in solutions of silver salts in sodium thiosulphate solution; and Slator (J., 1905, **87**, 489) deduced the formation of the ion $Ag(S_2O_3)_2^{III}$ from consideration of the velocity of formation of alkyl thiosulphates from sodium thiosulphate containing dissolved silver salts.

Since the silver-kation concentration of such solutions is extremely minute (Bodländer, *Ber*, 1903, **36**, 3933), the ions must be formed from the salts $Na(AgS_2O_3)$, $Na_3[Ag(S_2O_3)_2]$, and $Na_5[Ag(S_2O_3)_3]$, respectively. The existence of the first salt is well known, and the isolation of a potassium salt of the formula $K_3[Ag(S_2O_3)_2]$, in conjunction with the evidence of Bodländer and Slator (*locc. cit.*), renders the existence in solution of the sodium analogue very probable. Moreover, if to a moderately concentrated solution of sodium triargentotetrathiosulphate, acidified with a slight excess of nitric acid, excess of alcohol be added, *monoargentomonothiosulphuric acid* (see later) is precipitated; now, this partial decomposition of triargentotetrathiosulphuric acid into monoargentomonothiosulphuric acid must be accompanied by the formation either of free thiosulphuric acid or of an argentothiosulphuric acid richer in thiosulphate than triargentotetrathiosulphuric acid, but since the supernatant liquid is quite stable, probably no free thiosulphuric acid is formed, and hence we have further evidence for the existence in solution of a highly thiosulphated complex.

No confirmation has been found of the existence of the quinquevalent ion $Ag(S_2O_3)_3^{V}$, but sodium triargentotetrathiosulphate probably exists as such in solution, forming the quinquevalent ion $Ag_3(S_2O_3)_4^{V}$, as is shown by the following observation. Although very concentrated solutions of sodium triargentotetrathiosulphate tend to deposit a precipitate of sodium monoargentomonothiosulphate, yet it is possible to obtain stable concentrated solutions of the former salt. If the ion $Ag_3(S_2O_3)_4^{V}$ did not exist, such solutions would have to undergo complete readjustment in the sense

$$Na_5[Ag_3(S_2O_3)_4] \longrightarrow 2Na(AgS_2O_3) + Na_3[Ag(S_2O_3)_2],$$

or

$$Na_5[Ag_3(S_2O_3)_4] \longrightarrow 3Na(AgS_2O_3) + Na_2S_2O_3,$$

but the sparing solubility of sodium monoargentomonothiosulphate renders it certain that such readjustment could not have taken place.

Alternative Method of Preparation of Sodium Monoargentomonothiosulphate.—Since acid sulphites when added to sodium thiosulphate give a more stable photographic fixing bath than the latter salt alone, their action upon argentothiosulphates was investigated. No precipitate was formed in a solution of sodium triargentotetrathiosulphate by treatment with either sodium sulphite or sulphur dioxide. Treatment with both sodium sulphite and excess of sulphur dioxide, however, gave a dense white precipitate of sodium monoargentomonothiosulphate, $Na(AgS_2O_3),H_2O$. The gradual deposition of the compound by saturation of a dilute solution of silver carbonate and sodium sulphite in sodium thiosulphate with sulphur dioxide results in the formation of sodium monoargentomonothiosulphate in comparatively large crystals, which are superior in crystalline form and stability even to those obtained by the silver carbonate method.

The mechanism of the reaction underlying this preparation is obscure.

Isolation of Monoargentomonothiosulphuric Acid, $H(AgS_2O_3),H_2O$.—The observation that solutions of the pure complex salts are much more stable towards mineral acids than is a solution of sodium thiosulphate, indicated that the argentothiosulphuric acids from which the sodium salts are derived are comparatively stable. As the free acids appeared not to be known, attempts were made to isolate and examine them. Addition of nitric acid to an aqueous suspension of sodium monoargentomonothiosulphate produced, after a few minutes, a fine crystalline suspension in the supernatant liquid. As conversion of the sparingly soluble salt into an acid by this means might be incomplete, an ammoniacal solution of the sodium salt was strongly acidified with concentrated nitric acid. The resulting silky-white precipitate had the composition $H(AgS_2O_3),H_2O$, and resembled the sodium salt in solubility and appearance, but was less stable. The dry white powder darkened after several hours, becoming black in a few days.

Attempts to isolate Triargentotetrathiosulphuric Acid.—The addition of mineral acids to dilute solutions of sodium triargentotetrathiosulphate produced no visible change. In concentrated solutions, decomposition occurred. Triargentotetrathiosulphuric acid therefore appears to be stable in dilute solution, but unstable in concentrated solution. The pure aqueous solution of the acid has been obtained by the treatment with sulphuric acid of barium triargentotetrathiosulphate, $Ba_5[Ag_3(S_2O_3)_4]_2,10H_2O$. Addition of alcohol to acidified solutions of sodium triargentotetrathiosulphate resulted in the precipitation of monoargentomonothiosulphuric acid. Attempts to isolate this acid are being continued.

EXPERIMENTAL.

Methods of Analysis.—1. *Determination of* S_2O_3 *groups.* 0·4—1·0 G. of the argentothiosulphate is suspended or dissolved in 30 c.c. of water, and titrated with *N*/10-iodine, starch being used as indicator.

2. *Determination of silver.* 0·4—1·0 G. of the substance is boiled with 20 c.c. of water and 5 c.c. of concentrated nitric acid until the solution becomes clear (a slight residue of coagulated sulphur does not adversely affect the determination). It is then diluted to 50 c.c. and titrated with *N*/10-alkali thiocyanate according to Volhard's method.

3. *Determination of sodium.* 0·4—1·0 G. in 50 c.c. of water is boiled until the precipitate of silver sulphide is coagulated. A few c.c. of concentrated ammonium sulphide solution are added to ensure complete precipitation, and the precipitate is filtered off and well washed. (This precipitate may be dissolved in nitric acid, and the silver determined as above.) The filtrate and washings are evaporated almost to dryness, 1 c.c. of concentrated sulphuric acid is added, and the residue evaporated, ignited, and weighed as sodium sulphate.

The more elaborate procedure recommended by Rosenheim and Trewendt (*loc. cit.*) was found to be quite unnecessary in the case of those compounds analysed.

Preparation of Sodium Monoargentomonothiosulphate.—Washed silver carbonate, precipitated by addition of excess of sodium carbonate to 75 c.c. of *N*-silver nitrate, is added as an aqueous suspension to 100 c.c. of *N*-sodium thiosulphate, and the volume of the mixture adjusted to about 250 c.c. About 10 g. of anhydrous sodium sulphite are added, and the solution is saturated by a slow current of sulphur dioxide and kept over-night. The granular crystals are well washed with 50% aqueous alcohol, and dried in a vacuum desiccator; yield, 13 g. (calc., 19 g.) [Found: Ag, 41·2; S_2O_3, 42·95; Na, 8·9; Ag : S_2O_3 : Na = 1 : 1·004 : 1·01. Calc. for $Na(AgS_2O_3),H_2O$: Ag, 41·4; S_2O_3, 42·9; Na, 8·82%]. A further quantity of the salt in a more finely divided condition may be obtained by adding more alcohol or silver carbonate.

The following crystallographic data were kindly provided by Professor A. Hutchinson, F.R.S.

Symmetry : monoclinic domatic.
Habit : tabular parallel to (010) or prismatic in the zone [100, 010].
Forms developed : *b*(010), *a*(100), *m*(110), *p*($\bar{1}$10), *q*(011).

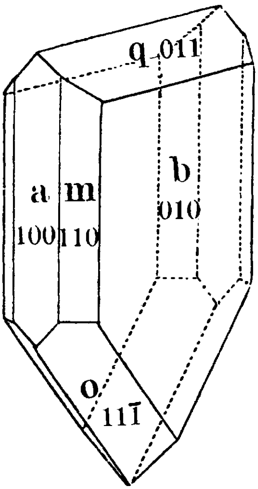
A few very small crystals showed faces in the zone [010, 101] but were not sufficiently good for accurate determination; the figure shows such a form taken to be *o*(111).

Axial ratios: $a : b : c = 0{\cdot}853 : 1 : 0{\cdot}868$. $\beta = 97° 32'$.

Table of angles.

Faces.	Angles.	No. of measurements.
100—110	40° 14′	16
010—011	49 17	4
100—011	84 18	3

FIG. 1.



Crystal of $Na(AgS_2O_3),H_2O$.

Piezo-electric properties. The substance was examined by the method of Giebe and Scheibe (*Z. Physik.*, 1925, **33**, 760) for crystal grains in an oscillating valve circuit and found to be strongly piezo-electric in accord with the domatic symmetry.

Optical properties. Refractive indices (by immersion)

$$\gamma = 1{\cdot}74,\ \alpha = 1{\cdot}69.$$

The optic axial plane is perpendicular to (010) and inclined at 12° to the *c* axis in the obtuse axial angle, the bisectrix γ being perpendicular to (010). Optic axial angle 2V is approximately 90°.

Preparation of Sodium Triargentotetrathiosulphate.—Silver carbonate precipitated from 40 c.c. of *N*-silver nitrate is washed, drained, suspended in 60 c.c. of water, and dissolved in 80 c.c. of *N*-sodium thiosulphate. Alcohol (140 c.c.) is added, and the precipitate kept for about 30 minutes until it becomes crystalline. It is filtered off, washed with 50% aqueous alcohol, and dried in a vacuum desiccator. (By use of these quantities, there is no fear of contamination of the product by sodium thiosulphate or sodium carbonate. If an aqueous layer separates on the first addition of alcohol, more water and correspondingly more alcohol must be added.) There were thus obtained 8 g. of colourless crystals quite stable towards light and exposure, easily soluble in water, insoluble in alcohol and acetone [Found: Ag, 35·3; S_2O_3, 48·7; Na, 12·5; Ag : S_2O_3 : Na = 3 : 3·99 : 5·00. $Na_5Ag_3(S_2O_3)_4,2H_2O$ requires Ag, 35·1; S_2O_3, 48·5; Na, 12·45%. Calc. for $Na_5Ag_3(S_2O_3)_4,3H_2O$ (*vide* Rosenheim and Trewendt, *loc. cit.*): Ag, 34·4; S_2O_3, 47·7; Na, 12·2%]. Very concentrated solutions deposit a white precipitate of sodium monoargentomonothiosulphate.

Crystallographic data. Needle-like crystals showing straight extinction in parallel polarised light, the slow vibration direction being parallel to the length. High double refraction, as estimated by polarisation colours. Mean refractive index about 1·67.

Preparation of Monoargentomonothiosulphuric Acid.—10 G. of sodium monoargentomonothiosulphate are suspended in 200 c.c. of water, and ammonia is added until the suspension is dissolved. If the solution is not clear and colourless, it is filtered. Concentrated nitric acid is added until the solution (which must be kept cool throughout the preparation) is neutral to litmus paper; a further 10 c.c. are then added, and the white precipitate is rapidly collected, well washed with 50% aqueous alcohol, and dried in a vacuum desiccator. The *acid* is an unstable, colourless, crystalline solid, insoluble in water, alcohol, and acetone, but soluble in excess of ammonia [Found : Ag, 45·6; S_2O_3, 46·2; Na, 0·3; Ag : S_2O_3 : Na = 1 : 0·98 : 0·04. $H(AgS_2O_3),H_2O$ requires Ag, 45·2; S_2O_3, 46·8; Na, 0·0%].

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