

### 868. *The Hydrolysis of Sodium Trithiocarbonate and its Reaction with Ethanol.*

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The hydrolysis of the  $\text{CS}_3^{2-}$  ion has been elucidated by investigating reactions of sodium trithiocarbonate with  $\text{HO}^-$ ,  $\text{H}^+$ ,  $\text{Ag}^+$ ,  $\text{Tl}^+$ , and  $\text{Pb}^{2+}$  ions and with aniline, using chemical, potentiometric, and spectroscopic methods. The analogous process of ethanolysis, which has not previously been described and in which sodium ethyl xanthate is produced, has also been studied. Some properties of silver, lead, and thallos trithiocarbonates are recorded, and the existence of sodium trithiopercarbonate is inferred. Possible mechanisms for basic reactions are discussed, and a comprehensive scheme is presented which shows the relation between sodium trithiocarbonate and sodium ethyl xanthate and also correlates the formation, hydrolysis, and decomposition by hydroxyl ions, of both these compounds.

TRITHIOCARBONIC ACID,  $\text{H}_2\text{CS}_3$ , and some of its salts were first recognized early in the last century, but knowledge of such compounds is still fragmentary.<sup>1</sup> Much of the published literature deals chiefly with the preparation and identification of individual compounds, and systematic investigation of their properties has been hindered by the practical difficulty of isolating and preserving pure specimens, for the trithiocarbonates are prone to decomposition, especially in air. We have obtained ample pure sodium trithiocarbonate by a new method based on classical reactions.

Some properties of silver, lead, and thallos trithiocarbonates are discussed here incidentally, but we shall be concerned mainly with reactions of sodium trithiocarbonate in aqueous and ethanolic solutions and particularly with the hydrolysis and ethanolysis of the  $\text{CS}_3^{2-}$  ion. Our interest in these topics arises from the production of sodium trithiocarbonate in the cellulosic solution from which viscose rayon is manufactured,<sup>2</sup> by a side-reaction between carbon disulphide and sodium hydroxide.

The complex hydrolysis of alkali-metal trithiocarbonates has been studied by Berzelius,<sup>3</sup> Tarugi and Magri,<sup>4</sup> Yeoman,<sup>5</sup> and others, but its mechanism remains obscure, though it is generally thought to depend, like thermal decomposition, on the initial step:  $\text{CS}_3^{2-} \rightarrow \text{CS}_2 + \text{S}^{2-}$ . The present investigation has led to a different and more comprehensive interpretation. We have also discovered production of sodium ethyl xanthate from the  $\text{CS}_3^{2-}$  ion and ethanol and believe we may have detected the trithiopercarbonate ion,  $\text{COS}_3^{2-}$ .

#### EXPERIMENTAL

*Materials.*—Metal salts, alkali hydroxides, mineral acids, carbon disulphide, aniline, and hydrogen peroxide ("100-volume") were of "AnalaR" quality. Sodium hydrogen sulphide was prepared by Rule's method.<sup>6</sup> Ethanol ("absolute" alcohol B.P.), acetone (not less than 95% distilled between 55.5° and 56.5°;  $d_4^{20}$  0.790—0.794), and anhydrous ether (b. range 34.0—35.0°;  $d_4^{20}$  0.713—0.714°) were used, generally without further purification. Hydrogen sulphide

<sup>1</sup> See, e.g., Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green & Co., London, 1947, Vol. VI, p. 119.

<sup>2</sup> Cross, Bevan, and Beadle, *Ber.*, 1893, **26**, 1090, 2524; 1901, **34**, 1513.

<sup>3</sup> Berzelius, *Ann. Chim. Phys.*, 1826, **6**, 450.

<sup>4</sup> Tarugi and Magri, *Gazzetta*, 1909, **39**, I, 405.

<sup>5</sup> Yeoman, *J.*, 1921, **119**, 38.

<sup>6</sup> Rule, *J.*, 1911, **99**, 558.

was generated from ferrous sulphide, washed with sodium sulphide solution, and dried (fused  $\text{CaCl}_2$ ); carbon oxysulphide was obtained by the action of 50% sulphuric acid on saturated aqueous potassium thiocyanate.<sup>7</sup> Distilled water was used throughout.

*Gas Analysis.*—Gaseous products were swept from a reaction mixture by a slow stream of nitrogen which then passed through bubblers containing selectively absorbent liquids. Each absorbent (100 ml.) was distributed between 2 or 3 adjacent bubblers, and groups of bubblers were segregated by suitable traps. (a) Hydrogen sulphide, (b) carbon dioxide, and (c) carbon disulphide vapour were extracted from the carrier gas in that order, (a) by solution of lead acetate (10 g.) in glacial acetic acid (20 g.) and water (80 ml.) (lead sulphide was weighed), (b) by standard sodium hydroxide solution (titration<sup>8</sup>), and (c) by potassium hydroxide (10 g.) in 90–95% ethanol (100 ml.) (potassium ethyl xanthate determined iodometrically<sup>9</sup>).

*Potentiometry.*—Aqueous (and, where possible, ethanolic) solutions of sodium salts (carbonate, hydrogen carbonate, ethyl carbonate, hydroxide, hydrogen sulphide, sulphide, disulphide trithiocarbonate, perthiocarbonate, ethyl xanthate) were titrated potentiometrically against standard aqueous solutions of hydrochloric acid, silver nitrate, and thallos sulphate (and nitrate). The cell systems used are shown in the Table.

| Titrant       | Indicator electrode | Reference electrode   |
|---------------|---------------------|---|
| $\text{H}^+$  | Sb or glass         | Saturated calomel   |
| $\text{Ag}^+$ | Ag                  | Saturated $\text{HgCl}_2$ or Ag-sat. aq. AgCl containing $\text{AgNO}_3$ and $\text{HNO}_3$ . <sup>10</sup> |
| $\text{Tl}^+$ | Sb or Tl            | Sat. $\text{HgCl}_2$  |

Titration were carried out at room temperature, a valve electrometer (Cambridge pH Meter) being used. The solution was stirred continuously, and the free surface (of aqueous solutions) was covered with a layer of toluene.

Equivalent weights were deduced from titrations with standard hydrochloric acid.

*Absorption Spectroscopy.*—Optical densities in the 200–600  $\mu$  wavelength region were measured, at room temperature, by means of a photoelectric quartz spectrophotometer (Unicam Model SP. 500). The solutions were contained in quartz cells (width, 1 cm.; thickness, 0.2 or 1 cm.) fitted with lids.

*Elementary Analysis.*—The sulphur contents of metal trithiocarbonates could not be determined accurately by a rapid micro-combustion method<sup>11</sup> because the carbon disulphide released ( $\text{MCS}_2 \rightarrow \text{MS} + \text{CS}_2$ ) was not completely oxidized in the (empty) combustion tube. However, in the corresponding method for estimating carbon and hydrogen,<sup>12</sup> the carbon disulphide was completely oxidized on reaction with the hot silver packing of the combustion tube.

The sulphur content of sodium trithiocarbonate was estimated by dissolving the sample (0.5 g.) in 25N-sodium hydroxide (100 ml.) and adding an excess of hydrogen peroxide (20 ml.). The solution was then heated to promote decomposition ( $\text{CS}_3^{2-} + 6\text{HO}^- \rightarrow 3\text{S}^{2-} + \text{CO}_3^{2-} + 3\text{H}_2\text{O}$ ), and the sulphate produced was weighed as the barium salt.

Sodium was determined by igniting a specimen with 50% sulphuric acid and weighing the residual sodium sulphate.

*Preparation of Sodium Trithiocarbonate.*—(a) *From sodium sulphide.* Sodium sulphide ( $9\text{H}_2\text{O}$ ; 30 g.), water (60 ml.), and carbon disulphide (10 ml.) were shaken in a glass-stoppered flask (100 ml. capacity; air-space small) at room temperature for 36–48 hr. The resulting red solution (ca. 85 ml.) and residual carbon disulphide (2–3 ml.) were poured into acetone (750 ml.) and the whole was shaken. The red, oily, lower layer (ca. 30 ml.) was run into acetone (250 ml.). The upper layer was discarded; it exhibited striking changes of colour (yellow  $\rightarrow$  dark green  $\rightarrow$  colourless) as dissolved sodium hydrogen sulphide was oxidized:  $2\text{HS}^- \rightarrow \text{S}_2^{2-} \rightarrow \text{S}_2\text{O}_3^{2-}$  ( $\text{S}_2^{2-}$  gives a green colour with acetone). The red oil and acetone were stirred together for a few minutes and then the acetone was decanted.

The red oil (now ca. 25 ml.) was extracted, at room temperature, with ethanol ( $4 \times 250$  ml.). Each extraction took about 3 min. and was effected by vigorous stirring; as extraction proceeded,

<sup>7</sup> Klason, *J. prakt. Chem.*, 1887, **36**, 66.

<sup>8</sup> Martin and Green, *Ind. Eng. Chem. Analyt.*, 1933, **5**, 114.

<sup>9</sup> Jacobs, "Analytical Chemistry of Industrial Poisons, Hazards, and Solvents," Interscience Publ. Inc., New York, 1944, p. 265.

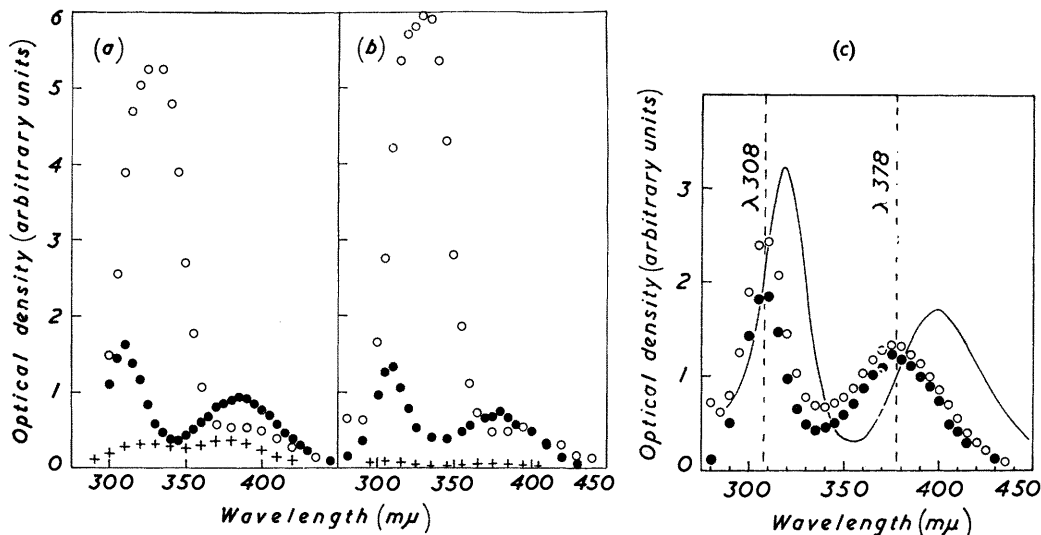
<sup>10</sup> Ingram, *Mikrochim. Acta*, 1956, 877.

<sup>11</sup> Belcher and Ingram, *Analyt. Chim. Acta*, 1952, **7**, 319.

<sup>12</sup> *Idem, ibid.*, 1950, **4**, 118.

the oil solidified. The combined extracts were filtered through sintered glass (porosity 3), and residual solid was discarded. The entire orange filtrate was then stirred vigorously while ether (1 l.) was added as quickly as possible. Crystallization, which began after a few seconds, was allowed to continue, with intermittent stirring, for about 15 min. The yellow rectangular plates were filtered off, drained free from mother-liquor (which contained sodium ethyl xanthate), and washed with ether. When the ether had been removed, the crystals were stored *in vacuo*, or in dry nitrogen, or under liquid carbon disulphide in a well-stoppered bottle. (These operations were carried out as rapidly as possible so as to minimize exposure of the crystals to the atmosphere from which they very quickly absorbed moisture and carbon dioxide. Rapid working also reduced the loss of sodium trithiocarbonate caused by its reaction with ethanol.)

FIG. 1.



- (a) Absorption spectrum of a solution of sodium trithiocarbonate in water when freshly prepared (○) and after 3.5 (●) and 21 hours (+) at room temperature.
- (b) Absorption spectrum of a solution of sodium trithiocarbonate in 2N-sodium hydroxide when freshly prepared (○) and after 15 (●) and 25 days (+) at 25°.
- (c) Absorption spectra of an old solution of sodium trithiocarbonate in 2N-sodium hydroxide (●) and of a solution of sodium sulphide which had been treated with carbon oxysulphide and then oxidized (○). The curve represents the absorption spectrum of a solution of sodium tetrathiopercarbonate.

The crystals consisted of sodium trithiocarbonate dihydrate (A) (10–15 g., 40–60%) (Found: C, 6.3, 6.3; H, 2.0, 2.1; S, —, 48.8; Na, 23.9, 23.9%; equiv., 95.0.  $\text{Na}_2\text{CS}_3 \cdot 2\text{H}_2\text{O}$  requires C, 6.3; H, 2.1; S, 50.5; Na, 24.2%; equiv., 95.1).

Apricot-coloured needles of trihydrate and salmon-pink needles of tetrahydrate were obtained by using less acetone in the initial treatment of the reaction mixture or by adding water to the filtered ethanolic solution, but the conditions for producing these higher hydrates appeared to be critical. Attempts to prepare a monohydrate were unsuccessful, but anhydrous sodium trithiocarbonate (B) was obtained as a pink powder by drying the di-, tri-, or tetrahydrate for 24–48 hr. in a vacuum at 40–50° (Found: S, 59.4; Na, 29.8%; equiv., 77.1. Calc. for  $\text{Na}_2\text{CS}_3$ : S, 62.4; Na, 29.9%; equiv., 77.0).

(b) *From sodium hydroxide.* Sodium hydroxide (16 g.), water (80 ml.), and carbon disulphide (12 ml.) were shaken in a glass-stoppered 100-ml. flask at room temperature for 72–120 hr. Treatment as described in (a) gave yellow needles (10–15 g., 40–60%) of  $\text{Na}_2\text{CS}_3 \cdot 2\text{H}_2\text{O}$  or  $\text{Na}_2\text{H}_2\text{COS}_3 \cdot \text{H}_2\text{O}$  (Found: C, 6.1, 6.6; H, 3.1, 2.2; S, —, 50.2; Na, 23.8, 24.1%; equiv., 95.0). Recrystallization from ethanol-ether gave rectangular plates which were indistinguishable from those of (A), but this change of habit could not be reversed.

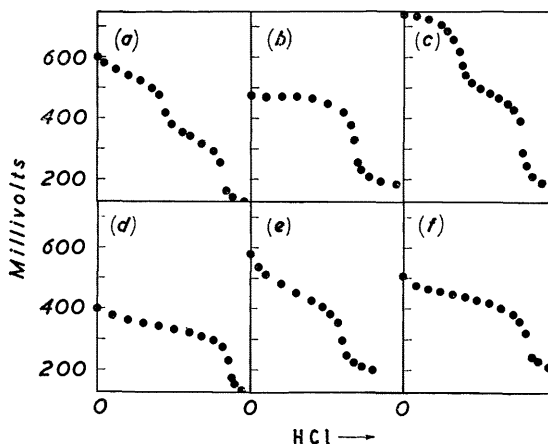
*Reactions of Sodium Trithiocarbonate in Aqueous Solution.*—(a) *With water.* (i) A solution of the dihydrate (A) (0.21 g.;  $1.1 \times 10^{-3}$  mole) in boiled distilled water (50 ml.) was kept under

nitrogen for 72 hr. at room temperature. Hydrolysis produced  $<0.1 \times 10^{-3}$  mole of each of hydrogen sulphide, carbon disulphide, and sodium carbonate (or hydrogen carbonate).

(ii) A solution of dihydrate (A) ( $0.19$  g.;  $1.0 \times 10^{-3}$  mole) in boiled distilled water ( $50$  ml.) was heated in a stoppered flask (*ca.*  $50$  ml. capacity; air-space small) on a water-bath at about  $90^\circ$  (internal), its colour changing from orange to green. After  $2.5$  hr. the solution was cooled and treated with  $5N$ -hydrochloric acid ( $15$  ml.): hydrogen sulphide ( $1.7 \times 10^{-3}$  moles) and carbon dioxide ( $0.47 \times 10^{-3}$  mole) were released.

(iii) The absorption spectrum of sodium trithiocarbonate in aqueous solution was observed at wavelengths between  $250$  and  $450$   $m\mu$  for solutions containing about  $5 \times 10^{-4}$  mole/l., and at wavelengths between  $400$  and  $600$   $m\mu$  for those containing about  $5 \times 10^{-2}$  mole/l. In agreement with previous work,<sup>13</sup> three absorption bands were found. Two of these, with peaks at  $325$ – $330$  and at  $500$   $m\mu$ , respectively, were well defined; in a freshly-made solution, the third band appeared as a "shoulder" extending from  $375$  to  $400$   $m\mu$ , approximately. The absorption at wavelengths greater than  $300$   $m\mu$  gradually disappeared (Fig. 1a). The absorption band with its peak at  $325$ – $330$   $m\mu$  disappeared rapidly and was replaced, after  $3$ – $4$  hr., by a well-defined band with its peak at  $308$ – $310$   $m\mu$ , whilst absorption in the  $375$ – $400$   $m\mu$  region increased until a well-defined band with its peak at about  $385$   $m\mu$  had been formed. Later, both of the "new" absorption bands disappeared.

FIG. 2. Potentiometric titration curves obtained by adding  $0.1N$ -hydrochloric acid to aqueous solutions containing (a)  $\text{Na}_2\text{CO}_3$ , (b)  $\text{Na}_2\text{CS}_3$ , (c)  $\text{Na}_2\text{S}$ , (d)  $\text{NaHCO}_3$ , (e)  $\text{NaHCO}_3$  and  $\text{NaSH}$  in equimolar proportion, (f)  $\text{NaSH}$ .



For comparison, samples of sodium tetrathio-percarbonate were prepared by reaction between carbon disulphide and sodium disulphide and by adding sulphur to a solution of sodium trithiocarbonate, as described by Yeoman.<sup>5</sup> The absorption spectrum of this compound ( $0.01$  g.) in water ( $100$  ml.) contained well-defined bands<sup>13</sup> with peaks at  $320$  and  $400$   $m\mu$  (see Fig. 1c).

(b) *With hydrogen ions.* (i) The dihydrate (A) ( $0.11$  g.;  $0.58 \times 10^{-3}$  mole) in water ( $75$  ml.) was decomposed, at room temperature, by adding  $0.1N$ -hydrochloric acid ( $30$  ml.): hydrogen sulphide ( $0.56 \times 10^{-3}$  mole) and carbon disulphide ( $0.56 \times 10^{-3}$  mole) were released, but not carbon oxy-sulphide.

When this reaction was observed potentiometrically at room temperature and at  $0^\circ$ , both the antimony and the glass electrode gave one-step titration curves, the former showing the equivalence point at about  $300$  mv, and the latter at about  $165$  mv. These titration curves, and particularly the curve obtained with the antimony electrode at room temperature (Fig. 2b), were compared with curves obtained by titrating various model aqueous solutions under the same conditions. There was a striking resemblance between the trithiocarbonate curve and those given by sodium hydrogen sulphide solution (Fig. 2f) and by a freshly-made solution containing sodium hydrogen sulphide and sodium hydrogen carbonate in equimolar proportion (Fig. 2e). In contrast, the curves given by sodium sulphide (Fig. 2c) and sodium carbonate (Fig. 2a) each had two steps (corresponding to  $\text{HO}^-$  and  $\text{HS}^-$  in the case of sulphide, and to  $\text{HO}^-$  and  $\text{HCO}_3^-$  in the case of carbonate), while sodium hydrogen carbonate gave a distinctive one-step curve with the equivalence point at about  $200$  mv (Fig. 2d).

<sup>13</sup> Halban, Mackert, and Ott, *Z. Elektrochem.*, 1923, **29**, 445; Atsuki and Takata, *J. Soc. Chem. Ind., Japan*, 1940, **43**, 394B; Schauenstein and Treiber, *Melliand Textilber.*, 1951, **32**, 43.

(ii) When carbon dioxide was bubbled through a solution of dihydrate (A) ( $0.49 \text{ g.}$ ;  $2.6 \times 10^{-3}$  mole) in water (50 ml.) for 1 hr. at room temperature, hydrogen sulphide ( $2.4 \times 10^{-3}$  mole) and carbon disulphide were released. After nitrogen had been bubbled through it for 30 min., the residual solution contained sodium hydrogen carbonate only ( $5.1 \times 10^{-3}$  mole).

(iii) Hydrogen sulphide was bubbled through a solution of dihydrate (A) ( $0.13 \text{ g.}$ ;  $0.69 \times 10^{-3}$  mole) in water (75 ml.) for about 20 min. The solution became green, carbon disulphide appeared, and it was evident that the trithiocarbonate had been decomposed. The excess of hydrogen sulphide was removed by bubbling nitrogen through the solution for about 60 min., and then the solution was made up to 100 ml. with water. The solution contained sodium hydrogen sulphide, the amount of which ( $1.4 \times 10^{-3}$  mole) was determined by bubbling carbon dioxide through a sample (50 ml.) and collecting the hydrogen sulphide released (the amount of sodium hydrogen carbonate in the residual solution was also determined); another sample of the hydrogen sulphide solution was titrated with 0.1*N*-iodine solution. (Consistent results were obtained by the different methods.)

(c) *With hydroxyl ions.* (i) A solution of dihydrate (A) ( $0.19 \text{ g.}$ ;  $1.0 \times 10^{-3}$  mole) in aqueous 0.1*N*-sodium hydroxide (50 ml.) was kept under nitrogen for 72 hr. at room temperature, then

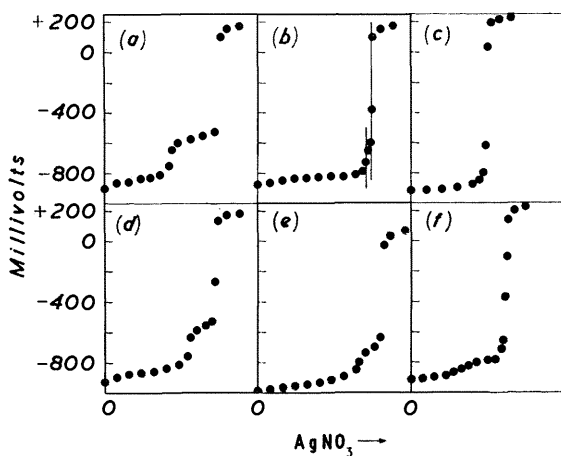


FIG. 3. Potentiometric titration curves obtained by adding 0.1*N*-silver nitrate to aqueous solutions containing (a) NaSH, (b)  $\text{Na}_2\text{CS}_3$ , (c)  $\text{Na}_2\text{S}$ , (d)  $\text{Na}_2\text{CS}_3$  and NaSH in equimolar proportion, (e) NaSH and  $\text{NaHCO}_3$  in the molar proportion 2 : 1, (f)  $\text{Na}_2\text{CS}_3$  and  $\text{Na}_2\text{S}$  in equimolar proportion.

treated with 5*N*-hydrochloric acid (15 ml.) which released hydrogen sulphide ( $0.95 \times 10^{-3}$  mole), carbon disulphide, and carbon dioxide ( $0.17 \times 10^{-3}$  mole). Combined sulphur (polysulphides?) in the residual solution was oxidized and collected as barium sulphate ( $0.10 \times 10^{-3}$  mole).

(ii) A solution of dihydrate (A) ( $1.0 \times 10^{-3}$  mole) in aqueous 0.1*N*-sodium hydroxide (50 ml.) was heated, under reflux, for 3 hr. at about  $90^\circ$ , then cooled and treated with 5*N*-hydrochloric acid (15 ml.): hydrogen sulphide ( $2.8 \times 10^{-3}$  mole), carbon disulphide (a trace), and carbon dioxide ( $0.94 \times 10^{-3}$  mole) were released. The residual solution contained combined sulphur ( $0.15 \times 10^{-3}$  mole).

(iii) When dissolved in aqueous 0.1—3*N*-sodium hydroxide, sodium trithiocarbonate gave the same absorption spectrum as in aqueous solution (see p. 4331). The spectrum changed with time, but more slowly than in aqueous solution, and the rate of change varied inversely with the concentration of sodium hydroxide. Fig. 1*b* indicates how absorption in the 250—450  $m\mu$  region altered when a solution of dihydrate (A) (0.01 g.) in 2*N*-sodium hydroxide (100 ml.) was kept at  $25^\circ$ : two well-defined bands, with peaks at 308 and 378  $m\mu$ , developed after about 2 weeks, persisted for more than a week, but eventually disappeared.

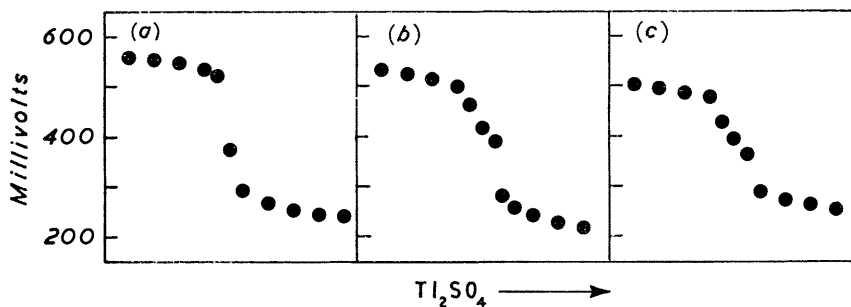
A solution of dihydrate (A) (0.4 g.) in *N*-sodium hydroxide (100 ml.) was heated on a boiling-water bath; a sample (3 ml.) was withdrawn hourly, diluted with *N*-sodium hydroxide (97 ml.), and examined spectrophotometrically (250—450  $m\mu$  region only). The original absorption bands, with peaks at 325—330 and 375—400  $m\mu$ , gradually disappeared and had almost vanished after 7 hours' heating; but the appearance of "new" bands was not observed. However, when the several (diluted) samples were kept at room temperature, two bands with peaks at 308 and 378  $m\mu$  developed eventually in every case. It seemed reasonable to conclude that these bands should be assigned to thermolabile ion(s) produced by oxidation.

A solution of sodium tetrathio-percarbonate in 0.1N-sodium hydroxide gave the same absorption spectrum as an aqueous solution of that salt (see p. 4331).

(d) *With silver nitrate.* (i) A trace of silver nitrate gave a dark red colour with a fresh aqueous solution of dihydrate (A). Further addition of silver nitrate produced hydrogen sulphide and a precipitate of silver sulphide (Found: Ag, 86.6. Calc. for  $\text{Ag}_2\text{S}$ : Ag, 87.2%). When an excess of silver nitrate was present, the amount of silver sulphide increased on storage, probably owing to reaction between silver nitrate and carbon disulphide:  $4\text{Ag}^+ + \text{CS}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{Ag}_2\text{S} + 4\text{H}^+ + \text{CO}_2$ .

(ii) When dihydrate (A) (0.092 g.;  $0.48 \times 10^{-3}$  mole) in water (100 ml.) was titrated carefully with 0.1N-silver nitrate, a two-step curve, with one equivalence point at about -700 mv and the other at about -250 mv, was obtained (Fig. 3b). This curve was compared with curves obtained by titrating various model aqueous solutions under the same conditions. A solution of sodium hydrogen sulphide gave a two-step curve (Fig. 3a) with one equivalence point at about -700 mv (corresponding to completion of the reaction:  $2\text{HS}^- + 2\text{Ag}^+ \longrightarrow [2\text{AgSH}] \longrightarrow \text{Ag}_2\text{S} + \text{H}_2\text{S}$ ) and the other at about -200 mv (corresponding to completion of the reaction  $\text{H}_2\text{S} + 2\text{Ag}^+ \longrightarrow \text{Ag}_2\text{S} + 2\text{H}^+$ ); a similar curve (Fig. 3d) was obtained by titrating a solution containing sodium hydrogen sulphide and sodium trithiocarbonate in equimolar proportion. In contrast, a solution of sodium sulphide gave a one-step curve with the equivalence point at

FIG. 4. Potentiometric titration curves obtained by adding 0.1N-thallos sulphate to aqueous solutions of (a) freshly crystallized  $\text{Na}_2\text{CS}_3 \cdot 2\text{H}_2\text{O}$ , (b) old crystals of  $\text{Na}_2\text{CS}_3 \cdot 2\text{H}_2\text{O}$ , (c) pure  $\text{Na}_2\text{CS}_3 \cdot 2\text{H}_2\text{O}$  and a trace of NaSH.



about -300 mv (Fig. 3c), while a solution containing sodium sulphide and sodium trithiocarbonate in equimolar proportion gave a two-step curve (Fig. 3f), with one equivalence point at about -850 mv (corresponding to completion of the reaction:  $\text{S}^{2-} + 2\text{Ag}^+ \longrightarrow \text{Ag}_2\text{S}$ ) and the other at about -250 mv (corresponding to completion of the reaction:  $\text{CS}_3^{2-} + 2\text{Ag}^+ \longrightarrow \text{Ag}_2\text{S} + \text{CS}_2$ ).

A titration curve of very similar form to that given by sodium trithiocarbonate, but with both equivalence-point potentials reduced by about 90 mv, was obtained with a fresh solution containing sodium hydrogen sulphide and sodium hydrogen carbonate in the molar proportion 2:1 (Fig. 3e); when, however, the molar ratio  $\text{HS}^- : \text{HCO}_3^-$  was 1:1 or 1:2, the titration curve had only one step owing to elimination of  $\text{HS}^-$  ions ( $\text{HS}^- + \text{HCO}_3^- \longrightarrow \text{CO}_3^{2-} + \text{H}_2\text{S}$ ).

(e) *With lead nitrate.* When dilute aqueous solutions of dihydrate (A) and of lead nitrate were mixed, a characteristic crimson-red precipitate of lead trithiocarbonate was produced;<sup>14</sup> this darkened as it decomposed to lead sulphide and carbon disulphide and became black overnight.

(f) *With thallos salts.* (i) Addition of an aqueous solution of thallos sulphate or nitrate to a solution of dihydrate (A) gave a characteristic orange-red precipitate of thallos trithiocarbonate<sup>15</sup> (Found: Tl, 79.0. Calc. for  $\text{Tl}_2\text{CS}_3$ : Tl, 79.1%). This compound was stable at room temperature, but decomposed to carbon disulphide and thallos sulphide when warmed.

(ii) Solutions of dihydrate (A) (ca. 0.1 g.) in water (100 ml.) were titrated potentiometrically (antimony electrode) with 0.1N-thallos sulphate; some of the results were checked by using a thallium electrode, but this was prone to corrosion. Whenever a newly-crystallized specimen of dihydrate was used, the titration curve had one step only, with the equivalence point at

<sup>14</sup> O'Donoghue and Kahan, *J.*, 1906, **89**, 1812.

<sup>15</sup> Picon, *Compt. rend.*, 1932, **195**, 1274.

about 400 mv (Fig. 4a); but if the trithiocarbonate had been kept for 48 hr. or more in a vacuum-desiccator, which was opened and re-evacuated occasionally, the titration curve had one equivalence point at about 450 and another at about 350 mv (Fig. 4b): a similar curve was obtained by adding a trace of sodium hydrogen sulphide to a solution of newly-crystallized (A) just before the titration (Fig. 4c).

Quantitative experiments showed that the amount of sodium trithiocarbonate in an aqueous solution could not be estimated reliably either by titrating the solution with standard thallos sulphate solution or by adding an excess of that reagent and then collecting and weighing the precipitated thallos trithiocarbonate. It always appeared that some loss of trithiocarbonate had occurred, and this was attributed to decomposition caused by hydrogen ions released from thallos hydrogen sulphide ( $2\text{TlSH} \longrightarrow \text{Tl}_2\text{S} + \text{H}_2\text{S}$ ;  $\text{TlSH} + \text{H}_2\text{O} \longrightarrow \text{TlOH} + \text{H}_2\text{S}$ ).

(g) *With aniline.* The dihydrate (A) (5 g.;  $2.6 \times 10^{-2}$  mole), aniline (5 ml.;  $5.5 \times 10^{-2}$  mole), carbon disulphide (2 drops; about  $0.15 \times 10^{-2}$  mole), and water (50 ml.) were shaken in a stoppered flask, at room temperature, for 48 hr. The resulting yellow solution and residual aniline were shaken with acetone (500 ml.). The lower layer, a red oil which contained sodium trithiocarbonate (0.3 g.) and sulphide, was discarded; the upper (acetone) layer was evaporated at reduced pressure. The solid residue was extracted with acetone ( $3 \times 20$  ml.): undissolved solid (1.9 g.), which contained sulphide, was filtered off. When the filtrate was evaporated to dryness, a white residue (4.7 g.) remained: this was dissolved in acetone (40 ml.). On addition of ether (500 ml.) to the acetone solution, colourless hygroscopic crystals (2.8 g.) were obtained: these were recrystallized from acetone-ether, dried *in vacuo* ( $\text{P}_2\text{O}_5$ ) (final yield, 1 g.), and identified as sodium phenyldithiocarbamate (Found: C, 43.9; H, 3.3; N, 7.0; S, 33.1; Na, 12.1. Calc. for  $\text{C}_8\text{H}_6\text{NS}_2\text{Na}$ : C, 44.0; H, 3.1; N, 7.3; S, 33.5; Na, 12.0%). Addition of thallos sulphate solution to an aqueous solution of this compound produced a characteristic yellow precipitate.

When this experiment was repeated with the same quantities of sodium trithiocarbonate, aniline, and water but without the carbon disulphide, no sodium phenyldithiocarbamate was found, and most of the trithiocarbonate (3.3 g.) was recovered.

*Reactions of Sodium Trithiocarbonate in Ethanolic Solution.*—(a) *With ethanol.* (i) When a solution of the salt (A) (1 g.) in ethanol (100 ml.) was kept in a stoppered flask at room temperature, its colour changed gradually from orange to yellow-green, a faint turbidity developed, and hydrogen sulphide was slowly evolved. Samples were tested periodically with aqueous 0.1M-thallos sulphate and with ethanolic thallos nitrate. At first, red thallos trithiocarbonate only was thrown down, but after 30–60 min. a brown precipitate, which became red on storage, was obtained. The latter was an intimate mixture of red and black particles, and its colour changed as the black component (thallos hydrogen sulphide and/or sulphide) disappeared. In later tests, the red component was absent, and the precipitate, which appeared black or dark grey, then consisted of a mixture of thallos sulphide and white flocculent thallos ethyl xanthate. After about 5 hr. a portion (5 ml.) of the remaining trithiocarbonate solution was treated with a large excess of ether (150 ml.): sodium hydrogen sulphide and trithiocarbonate (a trace) were precipitated and filtered off. The filtrate was then extracted with water (15 ml.). The presence of sodium ethyl xanthate in the aqueous extract was denoted by the formation of a yellow precipitate with aqueous cupric sulphate.<sup>16</sup>

(ii) A solution of salt (A) (5 g.;  $2.6 \times 10^{-2}$  mole) in ethanol (250 ml.) was kept in a stoppered flask at room temperature for 120 hr. Carbon dioxide was then bubbled through the solution for 30 min. A bulky precipitate of sodium ethyl carbonate was produced (2.5 g.;  $2.2 \times 10^{-2}$  mole). From the filtrate most of the ethanol was distilled off at reduced pressure on a water-bath. Addition of ether (75 ml.) to the residual solution (*ca.* 25 ml.) gave a white precipitate, which contained sodium ethyl carbonate; this was filtered off and washed with ether-ethanol (3 : 1 by vol.). The combined filtrate and washings were evaporated on a water-bath at reduced pressure: the residual solid (3.2 g.) consisted almost entirely of sodium ethyl xanthate (*ca.*  $2.2 \times 10^{-2}$  mole). The crude product was crystallized by dissolving it in ethanol (25 ml.) and adding ether (1000 ml.). The crystals (rectangular plates; 1 g., 30%) were hygroscopic (Found: C, 24.6; H, 4.4; S, 43.9; Na, 15.8. Calc. for  $\text{C}_3\text{H}_5\text{OS}_2\text{Na}$ : C, 25.0; H, 3.5; S, 44.4; Na, 16.0%).

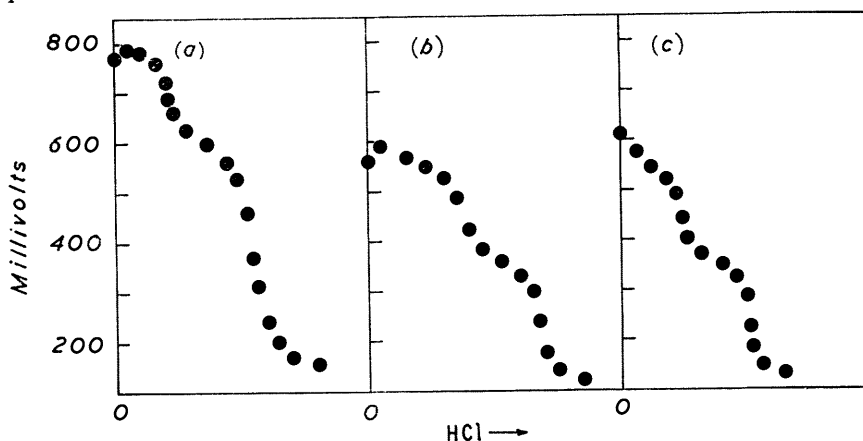
(iii) The anhydrous salt (B) (0.95 g.;  $6.2 \times 10^{-3}$  mole) was evacuated in a round flask at  $10^{-4}$  mm. Hg, at room temperature, for 3–4 hr., then cooled below  $-70^\circ$ , and ethanol (*ca.* 50 ml.), which had previously been redistilled, dried, and degassed, was distilled on to it under

<sup>16</sup> Johnson, *J. Amer. Chem. Soc.*, 1906, **28**, 1211.

vacuum. The flask was sealed and allowed to warm to room temperature. The pink solid became yellow on contact with cold ethanol, but did not dissolve until the temperature had risen considerably. The fresh solution was orange and slightly cloudy; it was kept under vacuum at room temperature for about 24 hr. and then filtered; 0.05 g. of sodium carbonate was collected. On addition of ether (1500 ml.) to the greenish-yellow filtrate, a white precipitate was produced: this was filtered off and proved to be almost pure sodium hydrogen sulphide (0.35 g.;  $6.2 \times 10^{-3}$  mole). The ethereal filtrate was then extracted with water ( $4 \times 25$  ml.). Addition of cupric sulphate solution to a portion of the aqueous extract gave a yellow precipitate. A specimen (0.4 g.) of pure sodium ethyl xanthate was isolated by evaporating the aqueous solution to dryness, extracting the residue with acetone, and treating the filtered acetone solution (*ca.* 20 ml.) with ether (1250 ml.).

(iv) Ethanolic solutions of salts (B) (0.06 mole/l.) and (A) (0.05 mole/l.) were kept at 20° in stoppered flasks. From time to time, a sample (25 ml.) of each solution was treated with carbon dioxide for 30 min. (to remove sodium hydrogen sulphide and residual trithiocarbonate), and then titrated with 0.1N-iodine (to determine the amount of sodium ethyl xanthate). This

FIG. 5. Potentiometric titration curves obtained by adding 0.1N-hydrochloric acid (aqueous) to (a) a freshly-prepared solution of sodium trithiocarbonate in ethanol, (b) the same solution when it was 4 hours old, (c) an ethanolic solution containing sodium ethyl xanthate and sodium hydrogen sulphide in equimolar proportion.



analytical method was not suitable for studying the initial stage of the reaction, but when the conversion of trithiocarbonate exceeded 25% (after about 30 min.) the reactivities of the anhydrous salt and the dihydrate did not differ significantly. The yield of xanthate amounted to 0.75 mol. after 3 hr. and 0.90 mol. after 6 hr.; after 24 hr. it was 1 mol., and the reaction had ended.

(v) Attempts to map the absorption spectrum of sodium trithiocarbonate in ethanol were unsuccessful owing to the rapidity of the reaction between solute and solvent.

(b) *With hydrogen ions.* (i) A solution of dihydrate (A) (1 g.) in ethanol (100 ml.) was kept at room temperature. From time to time, a sample (2.5 ml.) was diluted with ethanol (50 ml.) and titrated potentiometrically (antimony electrode) with aqueous 0.1N-hydrochloric acid. The titration curve had two steps with equivalence points at potentials which depended upon the age of the ethanolic solution. Initially, the equivalence points occurred at approx. 700 and 400 mv (Fig. 5a), but after 4 hr. were at about 450 and 250 mv, respectively, and the titration curve (Fig. 5b) then resembled that obtained by titrating ethanolic sodium ethyl xanthate and sodium hydrogen sulphide in equimolar proportion under the same conditions (Fig. 5c).

(ii) When carbon dioxide was bubbled through a fresh solution of salt (A) (1 g.;  $5.3 \times 10^{-3}$  mole) in ethanol (50 ml.), sodium ethyl carbonate was precipitated and after about 30 min. was collected (0.95 g.;  $8.5 \times 10^{-3}$  mole) (Found: OEt, 37.0; Na, 20.9%; equiv., 111. Calc. for  $C_3H_5O_3Na$ : OEt, 40.2; Na, 20.6%; equiv., 112). The filtrate contained small amounts of sodium ethyl xanthate, sodium sulphide (? hydrogen sulphide), and sodium thiosulphate.

In another experiment, carbon dioxide was bubbled through a fresh solution of salt (A)



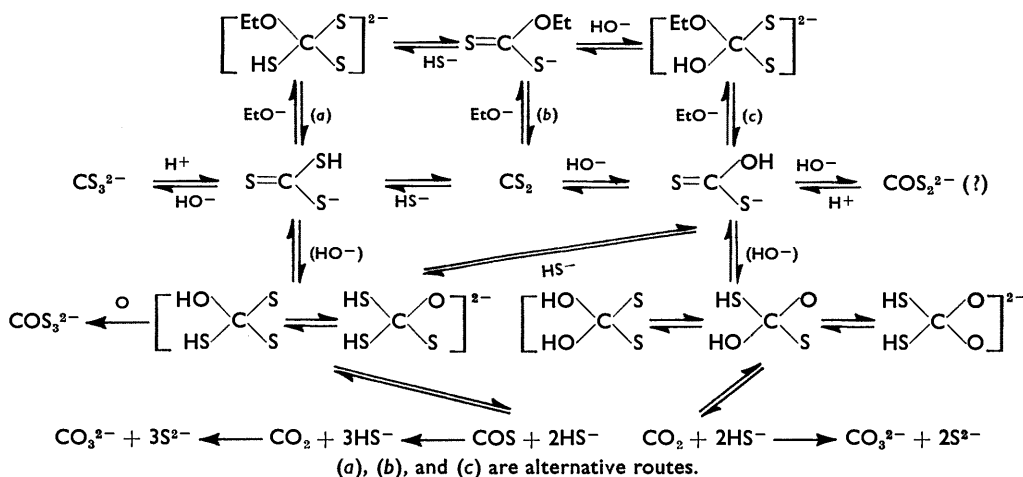
(0.09 g.;  $0.47 \times 10^{-3}$  mole) in ethanol (60 ml.) for about 30 min. Hydrogen sulphide ( $0.47 \times 10^{-3}$  mole) was evolved; the amount of sodium ethyl carbonate ( $0.93 \times 10^{-3}$  mole) in the residual ethanolic solution was determined by titration with 0.1*N*-hydrochloric acid.

(iii) Hydrogen sulphide was bubbled through a fresh solution of salt (A) (0.13 g.;  $0.69 \times 10^{-3}$  mole) in ethanol (75 ml.) for about 5 min. The solution rapidly became greenish-yellow, and it was evident that the trithiocarbonate had been decomposed. The excess of hydrogen sulphide was removed by bubbling nitrogen through the solution for 90 min., and then the solution was made up to 100 ml. with ethanol. The solution contained sodium hydrogen sulphide ( $1.3 \times 10^{-3}$  mole, determined by independent methods which gave consistent results). (One sample of the ethanolic solution was treated with carbon dioxide, and the amounts of hydrogen sulphide and sodium ethyl carbonate produced were determined; another sample was titrated with 0.1*N*-iodine.)

### DISCUSSION

Sodium trithiocarbonate in water gives carbon disulphide and sodium sulphide, but our spectrophotometric and potentiometric results show that the hydrolysis is not adequately represented by the simple equilibrium  $\text{CS}_3^{2-} \rightleftharpoons \text{CS}_2 + \text{S}^{2-}$ . It is not possible, for instance, to account for the observed variation with time of the absorption spectrum of a dilute solution of sodium trithiocarbonate (Fig. 1*a*), or to explain how the reaction between  $\text{CS}_3^{2-}$  and hydrogen ions (Fig. 2*b*) differs from that between  $\text{H}^+$  and  $\text{CO}_3^{2-}$  (Fig. 2*a*) or  $\text{S}^{2-}$  (Fig. 2*c*), without postulating some intermediate reactions.

In formulating a satisfactory scheme we have assumed that  $\text{HS}^-$ ,  $\text{HO}^-$ , and  $\text{EtO}^-$  can add to the  $>\text{C}=\text{S}$  link and that proton rearrangement can occur in (hypothetical) dihydrogen salts of di- and tri-thio-orthocarbonic acid. The susceptibility of the carbon-sulphur double bond to anionic attack is well known, but the existence of salts of thio-orthocarbonic acids has not been proved, though esters are known,<sup>17</sup> and the occurrence of sodium salts in certain aqueous solutions has previously been surmised.<sup>18</sup> We have introduced reactions of  $\text{HCOS}_2^-$ ,  $\text{HCS}_3^-$ ,  $(\text{CH}_2\text{O}_2\text{S}_2)^{2-}$ , and  $(\text{CH}_2\text{OS}_3)^{2-}$  in the present context primarily because they are convenient and plausible, but we think we may have isolated the ortho-salt  $\text{Na}_2\text{H}_2\text{COS}_3 \cdot \text{H}_2\text{O}$  and detected the trithiopercarbonate ion,  $\text{COS}_3^{2-}$ , in solution. A scheme, which we believe comprehensive for formation, hydrolysis, and reactions in aqueous ethanol of sodium trithiocarbonate, is annexed.

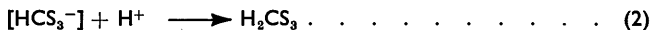


*Reactions in Aqueous Solutions.*—It has previously been observed,<sup>3,14</sup> and we have confirmed, that when a trithiocarbonate is decomposed by a mineral acid, the products vary with the temperature and composition of the mixture and depend particularly on

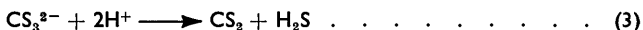
<sup>17</sup> Arndt, *Annalen*, 1911, **384**, 322; 1913, **396**, 1.

<sup>18</sup> Herrent and Jnof, *J. Polymer Sci.*, 1948, **3**, 487; Treiber, Porod, and Lang, *Oesterr. Chem.-Ztg.*, 1952, **53**, 162.

the concentration of hydrogen ions. Thus, if the solid salt is mixed with an excess of concentrated hydrochloric acid at room temperature, trithiocarbonic acid is produced:<sup>19</sup>



but if dilute hydrochloric acid is used, or if the concentrated acid is added slowly to a dilute aqueous solution of sodium trithiocarbonate, carbon disulphide and hydrogen sulphide are obtained:



This reaction (3) cannot be explained by assuming that (1) and (2) are followed by the decomposition of  $\text{H}_2\text{CS}_3$  unless chemical and spectroscopic evidence, which proves that sodium trithiocarbonate is extensively hydrolysed in (dilute) solution, is ignored. But before we discuss the mechanism of (3) further it is necessary to review some of our potentiometric results.

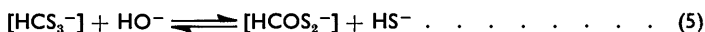
When the reaction between  $\text{CS}_3^{2-}$  and  $\text{H}^+$  ions in aqueous solution is followed potentiometrically, a titration curve with *one* step is obtained (Fig. 2*b*), provided the sodium trithiocarbonate is pure. This characteristic curve is easily distinguished from the corresponding curves given by  $\text{CO}_3^{2-}$  (Fig. 2*a*) and  $\text{S}^{2-}$  (Fig. 2*c*) both of which have two steps, and also from the one-step curves given by  $\text{HO}^-$  and by  $\text{HCO}_3^-$  (Fig. 2*d*), since the equivalence point occurs at significantly different potentials in these cases. There is, however, a remarkable resemblance between the trithiocarbonate titration curve and that given by  $\text{HS}^-$  (Fig. 2*f*), and both are like the curve given by an equimolar mixture of  $\text{HS}^-$  and  $\text{HCO}_3^-$  ions (Fig. 2*e*). Moreover, if fresh solutions containing sodium trithiocarbonate and either sodium hydrogen sulphide or sodium hydrogen carbonate are titrated with acid, the curves obtained (not reproduced here) are almost indistinguishable from each other and from those given separately by  $\text{CS}_3^{2-}$ ,  $\text{HS}^-$ , or a mixture of  $\text{HS}^-$  and  $\text{HCO}_3^-$  ions.

These results show that, under suitable conditions, reaction (3) is closely simulated by the reactions between  $\text{H}^+$  and  $\text{HS}^-$  and between  $\text{H}^+$  and  $(\text{HS}^- + \text{HCO}_3^-)$ , but that it does not involve direct reaction between  $\text{H}^+$  and either  $\text{HO}^-$  or  $\text{S}^{2-}$ . In seeking a mechanism for (3) which will meet these peculiar requirements, we have been led to conclude that the trithiocarbonate anion must react with water as follows:

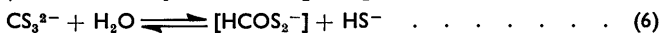


This reaction, which is analogous to the hydrolysis of the  $\text{CO}_3^{2-}$  ion, is consistent with equation (1) since it merely involves the transference of a proton from a water molecule to the  $\text{CS}_3^{2-}$  ion.

However, equation (4) must be an incomplete representation of the hydrolysis of the  $\text{CS}_3^{2-}$  ion, since it leads only to the prediction of a two-step potentiometric titration curve [like that given by  $\text{CO}_3^{2-}$  (Fig. 2*a*)] for reaction between sodium trithiocarbonate and dilute hydrochloric acid. This can be remedied by assuming that reaction (4) is followed by

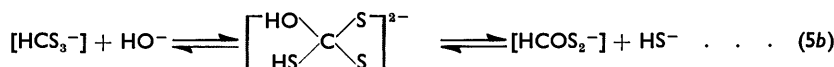
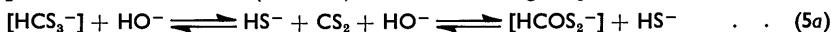


The combination of (4) and (5) leads directly to the simple equilibrium:



and this, as we shall show, is consistent with our potentiometric evidence.

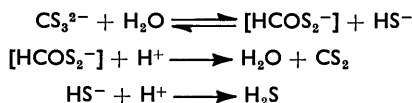
It is not inappropriate to introduce (5) in the present context, for the equilibrium  $\text{HCOS}_2^- \rightleftharpoons \text{H}^+ + \text{COS}_2^{2-}$  can be envisaged, and the occurrence of the  $\text{COS}_2^{2-}$  ion in solutions of sodium trithiocarbonate has been surmised by previous workers.<sup>18</sup> Reaction (5) may be supposed to occur in one (or both) of the following ways:



<sup>19</sup> Mills and Robinson, *J.*, 1928, 2326.

and these mechanisms emphasize that (6) is complementary to (4) and not merely a convenient alternative reaction. In choosing a reaction to follow (4), we have preferred (5) to  $[\text{HCS}_3^-] + \text{H}_2\text{O} \rightleftharpoons [\text{HCOS}_2^-] + \text{H}_2\text{S}$  because it is simpler; and, of course, we have rejected the combination of  $[\text{HCS}_3^-] \rightleftharpoons \text{CS}_2 + \text{HS}^-$  and (4) because this would yield equal molar concentrations of  $\text{HO}^-$  and  $\text{HS}^-$  ions, which is contrary to the potentiometric evidence.

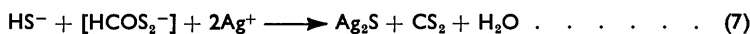
Having thus decided that the observed reaction (3) depends on the hydrolysis of the  $\text{CS}_3^{2-}$  ion in accordance with equation (6), we can formulate (3) as follows:



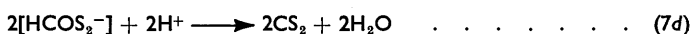
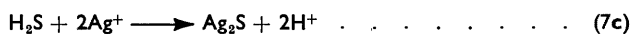
This requires hydrogen ions to react only with  $\text{HCOS}_2^-$  and  $\text{HS}^-$  ions. And so, since an equimolar mixture of these anions could well be expected to be indistinguishable, potentiometrically, from a similar mixture of  $\text{HCO}_3^-$  and  $\text{HS}^-$  ions, or from  $\text{HS}^-$  ions alone, the above mechanism evidently affords a ready, and complete, explanation of the observed potentiometric characteristics of reaction (3). It also explains how carbon dioxide or hydrogen sulphide decomposes sodium trithiocarbonate in aqueous solution: both these agents yield hydrogen ions ( $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ ;  $\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$ ), and it can be predicted that the reaction products will be  $\text{CS}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{NaHCO}_3$  or  $\text{NaSH}$  in the molar ratios 1 : 1 : 2, as we have found.

The supposition that the hydrolysis of the  $\text{CS}_3^{2-}$  ion proceeds by the consecutive reactions (4) and (5), and may therefore be represented by equation (6), is also consistent with our observations of the effects of adding  $\text{Ag}^+$ ,  $\text{Tl}^+$ , or  $\text{Pb}^{2+}$  ions to (dilute) aqueous solutions of sodium trithiocarbonate. Thallium(I) and lead each yield a characteristic sparingly soluble trithiocarbonate, but with silver only  $\text{Ag}_2\text{S}$  and hydrogen sulphide are obtained. This difference can be explained in terms of (6) and the relative solubilities of the trithiocarbonate and hydrogen sulphide of each metal (the solubility of the metal hydrogen dithiocarbonate does not appear to count, which indicates that, in each case, this salt must be more soluble than either the trithiocarbonate or the hydrogen sulphide).

Evidently, if the solution of sodium trithiocarbonate contains both  $\text{CS}_3^{2-}$  and  $\text{HS}^-$  ions, in accordance with equation (6), then the solubility product of thallos or lead hydrogen sulphide must exceed that of the corresponding trithiocarbonate. This inference is confirmed by potentiometric evidence (Figs. 4*b*, 4*c*) which shows that when  $\text{Tl}^+$  (or  $\text{Pb}^{2+}$ ) ions are added to a solution of sodium trithiocarbonate in which  $[\text{HS}^-] > [\text{HCOS}_2^-]$  (*e.g.*, because sodium hydrogen sulphide has been added deliberately, or because some decomposition of  $\text{HCOS}_2^-$  has occurred), precipitation of the heavy-metal trithiocarbonate precedes that of its hydrogen sulphide. And, of course, it follows that if a newly made solution of pure sodium trithiocarbonate is used, then  $\text{Tl}_2\text{CS}_3$  (or  $\text{PbCS}_3$ ) will be precipitated exclusively, and the corresponding potentiometric titration curve will consequently have only one step, as we have found (Fig. 4*a*). A titration curve with a single step is also obtained (ideally) when  $\text{Ag}^+$  ions are added to a solution of sodium trithiocarbonate, but in this case the equivalence point denotes completion of the alternative reaction:



We believe that this reaction occurs because the solubility product of silver hydrogen sulphide is less than that of silver trithiocarbonate (which is appreciably soluble, unlike  $\text{Tl}_2\text{CS}_3$  or  $\text{PbCS}_3$ ), and we consider that the mechanism of (7) must be as follows:



This conception of the reaction between silver ions and a solution of sodium trithiocarbonate is based primarily on our experience that, when it is followed potentiometrically, the amount of silver ions required is almost always less than expected and (paradoxically) a titration curve with *two* steps is usually obtained (Fig. 3*b*). These observations are highly significant, and we shall now show that both are consistent with the above mechanism.

It is reasonable to imagine that reaction (7) would yield a potentiometric titration curve of the same form (*i.e.*, with one step only) as that given by the analogous reaction between silver ions and a solution containing  $\text{HS}^-$  and  $\text{HCO}_3^-$  ions in equimolar concentrations. In seeking to explain why reaction (7) usually gives a two-step titration curve, we have been led to conclude that hydrogen ions react faster with the  $\text{HCOS}_2^-$  ion than with the  $\text{HS}^-$  ion. Consequently, since atmospheric carbon dioxide is absorbed rapidly by solid sodium trithiocarbonate (which, of course, is exceedingly hygroscopic) and by its aqueous solutions, it is difficult in practice to avoid premature decomposition of a (small) proportion of the  $\text{HCOS}_2^-$  ions produced in accordance with equation (6). Thus there will often be an excess of  $\text{HS}^-$  ions in a solution of sodium trithiocarbonate, and when there is it follows that reactions (7*a*), (7*b*), and (7*c*) will continue after (7*d*) has stopped. And so we can predict that in practice the termination of reaction (7) will tend to be the reaction between  $\text{Ag}^+$  ions and  $\text{HS}^-$  ions which, as we have found, yields a characteristic two-step titration curve (Fig. 3*a*). This also explains why the titration curve of reaction (7), as it is usually observed (Fig. 3*b*), is simulated so remarkably well (though in respect of shape only) by the two-step curve that is obtained when silver ions are added to a solution of  $\text{NaSH}$  and  $\text{NaHCO}_3$  in which the  $\text{HS}^-$  ions preponderate (Fig. 3*e*).

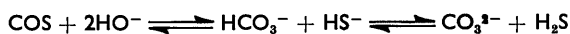
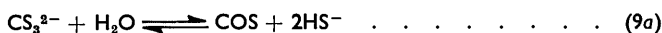
It is now obvious that, whenever a quantitative study of reaction (7) is undertaken, it is necessary to prevent an exchange of gases between the reaction mixture and the atmosphere. For if carbon dioxide enters the mixture, both  $\text{HS}^-$  and  $\text{HCOS}_2^-$  ions will be destroyed (the latter preferentially) and, of course, oxygen also will reduce the concentrations of  $\text{HS}^-$  ions ( $2\text{HS}^- \longrightarrow \text{S}_2^{2-} \longrightarrow \text{S}_2\text{O}_3^{2-}$ ). The absorption of carbon dioxide and oxygen from the air can be greatly reduced, if not prevented, by covering the mixture with a layer of toluene, but this does not always impede the escape of hydrogen sulphide sufficiently. Evidently, if part of the  $\text{H}_2\text{S}$  produced by reaction (7*b*) is lost, the quantity of  $\text{H}^+$  ions produced by (7*c*) will be insufficient for (7*d*) and, consequently, some  $\text{HCOS}_2^-$  ions will remain. It might be thought that, in the absence of hydrogen ions, these residual anions would combine with  $\text{Ag}^+$  ions (the total consumption of  $\text{Ag}^+$  ions would then be exactly equivalent to the original amount of sodium trithiocarbonate), but we consider that this does not happen because the available evidence suggests that  $\text{AgHCOS}_2$  is almost completely dissociated in aqueous solution. (We have been unable to detect combination between  $\text{Ag}^+$  ions and  $\text{HCO}_3^-$  ions potentiometrically or otherwise and, of course, neither  $\text{AgHCO}_3$  nor  $\text{AgHCOS}_2$  has been isolated.) Thus it follows that, if hydrogen sulphide is allowed to escape, the consumption of  $\text{Ag}^+$  ions in reaction (7*c*) will be reduced, while if oxygen or carbon dioxide is allowed to enter the reaction mixture, less  $\text{Ag}^+$  ions will be required in both (7*a*) and (7*c*). For these reasons, the estimation of sodium trithiocarbonate in aqueous solution by direct titration with standard silver nitrate solution may be expected to be inaccurate or unreliable (as we have found) unless very stringent precautions are taken. [In our experience it is both simplest and best to titrate a trithiocarbonate solution with standard acid (with care to exclude oxygen and carbon dioxide), or to decompose the salt with acid and collect the hydrogen sulphide evolved (weighed as  $\text{PbS}$  or, after oxidation, as  $\text{BaSO}_4$ ). Alternatively, a spectrophotometric method may be used, with appropriate precautions.]

Our contention that the equilibrium  $\text{CS}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons [\text{HCOS}_2^-] + \text{HS}^-$  prevails in solutions of sodium trithiocarbonate is supported by other experimental evidence. For instance, we have found that, provided a trace of carbon disulphide is present initially,



Reaction (9a) includes (4) and (5b), and assumes a proton-shift within the hypothetical ortho-ion. Evidently, a high concentration of HO<sup>-</sup> ions will favour the forward reaction in each of the conventional equilibria (9b), (9c), (9d), and the back-reaction of equation (4). Thus the rate of reaction (9) will not be a simple function of the concentration of hydroxyl ions and, in fact, we have observed that, at constant temperature (25°), the rate varies inversely with [HO<sup>-</sup>]. This explains why the CS<sub>3</sub><sup>2-</sup> ion is more stable in sodium hydroxide solution than in water.

It is reasonable to suppose that (9a) remains valid when the decomposition of the trithiocarbonate ion is caused by water alone but, under these conditions, HO<sup>-</sup> ions can only be obtained by hydrolysis of HS<sup>-</sup> ions (HS<sup>-</sup> + H<sub>2</sub>O ⇌ HO<sup>-</sup> + H<sub>2</sub>S) and so (9b)—(9d) must be modified appropriately. We thus postulate the following mechanism:

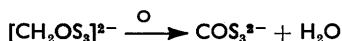


That is,

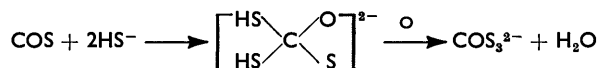


It will obviously be very difficult in practice to achieve total decomposition of the trithiocarbonate ion in accordance with (10), but the above mechanism implies that, if equilibrium is established under particular conditions, it should be possible to demonstrate that the reaction mixture then contains carbonate (HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>) and sulphide (HS<sup>-</sup>, H<sub>2</sub>S) in the molar ratio 1 : 3. We find that this is the case, and, under our experimental conditions, approximately 0.5 mole of carbonate and 1.5 moles of sulphide were obtained from 1 mole of sodium trithiocarbonate (cf. Yeoman<sup>5</sup>).

The mechanism which we have proposed for reaction (9a) is consistent with our observations of the changes which occur in the absorption spectrum of a solution of sodium trithiocarbonate in contact with air (at room temperature): two well-defined bands with their peaks at 308 and 378 mμ always develop (Fig. 1), rapidly in a dilute aqueous solution of the salt and slowly if sodium hydroxide is present. This unique spectrum (which, significantly, is not observed in solutions of sodium ethyl xanthate) is easily distinguishable from that given by solutions of sodium tetrathio-percarbonate, Na<sub>2</sub>CS<sub>4</sub>, and we suggest that it should be assigned to the trithio-percarbonate ion, COS<sub>3</sub><sup>2-</sup>, which could well be produced by oxidation of one of the ortho-ions involved in (9a):



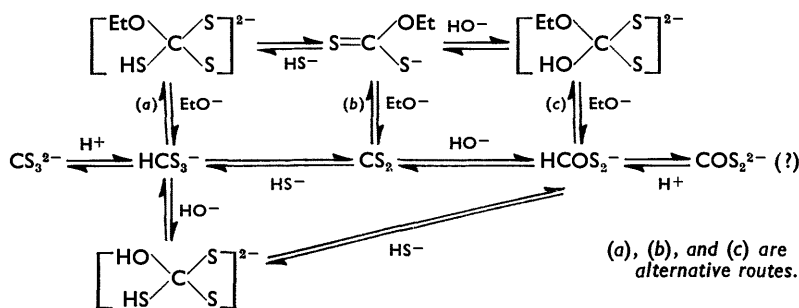
To test this hypothesis we saturated 1% solutions of both sodium hydrogen sulphide and sodium sulphide with carbon oxysulphide and then with oxygen (after which they were kept overnight at room temperature) in order to see if the following predictable reactions could be realized:



Immediately after they had been treated the solutions gave two absorption bands with peaks at 320 and 400 mμ (these bands had different relative intensities from those produced by the CS<sub>3</sub><sup>2-</sup> ion, and we have assigned them provisionally to the ortho-ion); but, when sufficient oxidation had occurred, these bands had disappeared and were replaced by another pair of bands with their peaks at 308 and 378 mμ respectively and with relative intensities similar to those of the tetrathio-percarbonate bands. These new bands were



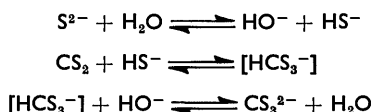
In this event, the equilibria in an aqueous ethanolic solution of sodium trithiocarbonate could be envisaged as follows:



*Formation of Sodium Trithiocarbonate.*—We have shown how crystalline  $\text{Na}_2\text{CS}_3 \cdot 2\text{H}_2\text{O}$  and amorphous  $\text{Na}_2\text{CS}_3$  can be obtained reproducibly by the action of carbon disulphide on an aqueous solution of either sodium sulphide or sodium hydroxide. We also isolated crystalline tri- and tetra-hydrates, but we did not obtain the monohydrate described by Yeoman.<sup>5</sup>

Anhydrous sodium trithiocarbonate and the dihydrate are exceedingly hygroscopic and, when moist, react rapidly with atmospheric carbon dioxide and oxygen, after hydrolysis of the  $\text{CS}_3^{2-}$  ion. Thus it is not easy to preserve this salt in a state of purity or to carry out exact quantitative work with it. The dried salt can be preserved *in vacuo*, or in dry nitrogen, or under liquid carbon disulphide, but we found it best to use fresh material whenever possible. By working quickly it is practicable to handle the salt in the open (as we did) but, for some purposes, it would be advantageous to employ a "glove-box" filled with dry nitrogen.

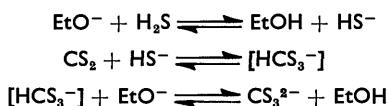
The reaction between carbon disulphide and an aqueous solution of sodium sulphide (or moist crystals of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) can be represented as follows:



That is,

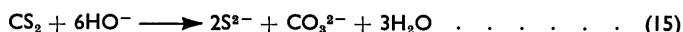


It is reasonable to assume an analogous reaction when sodium trithiocarbonate is prepared by adding carbon disulphide to a solution of sodium ethoxide in dry ethanol which has been saturated with dry hydrogen sulphide:<sup>5</sup>



In this case the loss of trithiocarbonate caused by its conversion into sodium ethyl xanthate  $[\text{CS}_3^{2-} + \text{EtOH} \rightleftharpoons \text{S}:\text{C}(\text{OEt})\text{S}^- + \text{HS}^-]$  can obviously be reduced by maintaining a high concentration of  $\text{HS}^-$  ions but, of course, it may then be difficult to obtain sodium trithiocarbonate entirely free from sodium hydrogen sulphide.

The reaction between carbon disulphide and an aqueous solution of sodium hydroxide must occur in at least two stages since  $\text{HS}^-$  ions are needed for the formation of  $\text{CS}_3^{2-}$  ions. In agreement with other workers,<sup>21</sup> we assume the first stage to be:



<sup>21</sup> Cherkasskaya, Pakshver, and Kargin, *J. Appl. Chem. (U.S.S.R.)* (U.S. translation), 1953, **26**, 55.



