# 23. *The Reactions of Sodium Ethyl Xanthate with Ethanol and with Water.*

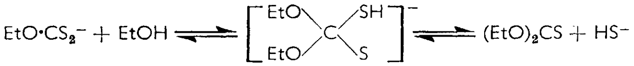
By G. Ingram and B. A. Toms.

Sodium ethyl xanthate is shown to react with both ethanol and water by addition to the thiocarbonyl linkage. With ethanol, the primary product, sodium di-*O*-ethyl dithio-orthocarbonate, yields diethyl thioncarbonate on mild oxidation and is converted into silver ethyl xanthate, or into diethyl carbonate and silver sulphide, by appropriate treatment with silver nitrate. With water, the initial production of *S*-sodium *O*-ethyl dihydrogen dithio-orthocarbonate enables silver salts of the $\mathrm{EtO{\cdot}COS_2^{3-}}$ ion to be obtained in addition to silver ethyl xanthate. Thus a new interpretation of the behaviour of the xanthate ion in aqueous solution is presented.

We have previously reported [1] that sodium trithiocarbonate reacts with ethanol to produce sodium ethyl xanthate and sodium hydrogen sulphide:

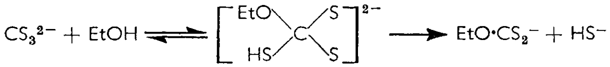
$$\mathrm{CS_3^{2-} + EtOH \longrightarrow EtO{\cdot}CS_2^- + HS^-} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

This reaction, and our belief that it proceeds by the addition of ethanol to the thiocarbonyl linkage of the $\mathrm{CS_3^{2-}}$ ion, suggested that ethanol might react analogously with sodium *O*-ethyl xanthate. We have now proved this, although the new reaction, unlike (**1**), has to be promoted. The primary products are diethyl thioncarbonate and sodium hydrogen sulphide, and we consider that they are derived from sodium di-*O*-ethyl dithio-orthocarbonate:



$$\mathrm{EtO{\cdot}CS_2^- + EtOH \rightleftharpoons \left[\begin{matrix}EtO & & SH\\ & C & \\ EtO & & S\end{matrix}\right]^- \rightleftharpoons (EtO)_2CS + HS^-} \quad . \; . \; . \; . \quad (2)$$

This mechanism supports our previous suggestion that reaction (1) might proceed through disodium *O*-ethyl trithio-orthocarbonate:

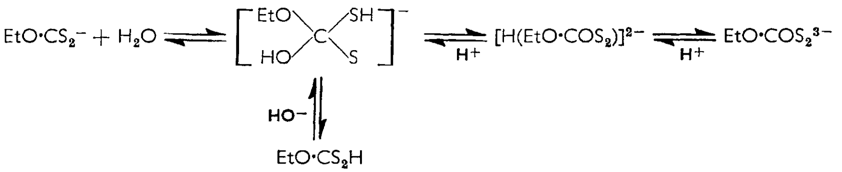


$$\mathrm{CS_3^{2-} + EtOH \rightleftharpoons \left[\begin{matrix}EtO & & S\\ & C & \\ HS & & S\end{matrix}\right]^{2-} \longrightarrow EtO{\cdot}CS_2^- + HS^-} \quad . \; . \; . \; . \quad (3)$$

The discovery of reaction (2), and the knowledge that the trithiocarbonate ion reacts uniquely with water,[1] led us to investigate the primary reaction between sodium *O*-ethyl xanthate and water because earlier work,[2,3] particularly that of Makens,[4] had indicated that the hydrolysis of alkali-metal xanthates is not adequately represented by the simple equilibrium:

$$\mathrm{RO{\cdot}CS_2^- + H_2O \rightleftharpoons RO{\cdot}CS_2H + HO^-} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

We now present new facts and argue that reaction (4) must be replaced by a more comprehensive concept based on the hydration of the xanthate ion. The essence of our hypothesis is that when sodium ethyl xanthate is dissolved in water, *S*-sodium *O*-ethyl dihydrogen dithio-orthocarbonate is produced and dissociates as follows:



$$\begin{tikzcd}[column sep=small]
\mathrm{EtO{\cdot}CS_2^- + H_2O} \arrow[r, leftrightharpoons] & \mathrm{\left[\begin{matrix}EtO & & SH\\ & C & \\ HO & & S\end{matrix}\right]^-} \arrow[r, leftrightharpoons, "H^+"'] \arrow[d, leftrightharpoons, "HO^-"'] & \mathrm{[H(EtO{\cdot}COS_2)]^{2-}} \arrow[r, leftrightharpoons, "H^+"'] & \mathrm{EtO{\cdot}COS_2^{3-}} \quad . \quad (5) \\
& \mathrm{EtO{\cdot}CS_2H} & &
\end{tikzcd}$$

These equilibria afford a rational basis for interpreting, and exploiting, the properties of sodium ethyl xanthate in aqueous media, and some examples are given here. Thus,

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[1] Ingram and Toms, *J.*, 1957, 4328.

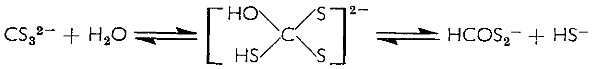
[2] Schaum, Siedler, and Wagner, *Kolloid-Z.*, 1932, **58**, 341.

[3] Klauditz, *Papier-Fabr.*, 1939, **37**, 251.

[4] Makens, *J. Amer. Chem. Soc.*, 1935, **57**, 405.

although *O*-ethyl dithio-orthocarbonic acid itself is unknown and is presumed to be highly unstable,[5] we believe that we have obtained the silver salts from the $[H(EtO{\cdot}COS_2)]^{2-}$ and $EtO{\cdot}COS_2^{3-}$ ions, although the latter product was originally regarded [4] as an equimolar mixture of silver ethyl monothiocarbonate and silver sulphide.

The hydration of the xanthate ion recalls (and supports) our previous suggestion that the hydrolysis of sodium trithiocarbonate might be effected by the formation and decomposition of di-*S*-sodium dihydrogen trithio-orthocarbonate: [1]



(6)

Thus the reactions of both sodium *O*-ethyl xanthate and sodium trithiocarbonate with both ethanol and water can all be shown to depend upon the addition of a molecule of the reactant to the thiocarbonyl linkage. There is evidence that this mechanism may also be applicable to the reactions of primary amines with metal xanthates and dithiocarbamates.

## EXPERIMENTAL

*Materials.*—Ethanol was generally " absolute alcohol B.P.," and anhydrous ethanol was obtained from this by Lund and Bjerrum's method; [6] light petroleum (b. p. 34·0—35·0°) was fractionated from " AnalaR " light petroleum (b. p. 30—40°). Other materials were of " AnalaR " quality or as specified previously.[1]

*Gas Analysis.*—Hydrogen sulphide, carbon dioxide, carbonyl sulphide, and carbon disulphide were swept from a reaction mixture by a stream of nitrogen which then passed through bubblers containing selectively absorbent liquids.[1] Carbonyl sulphide was collected in the bubblers intended for carbon dioxide and carbon disulphide respectively. The amount trapped by the aqueous sodium hydroxide was estimated by adding an excess of lead acetate–acetic acid reagent,[1] immediately after the residual sodium hydroxide had been titrated,[7] and then weighing the lead sulphide which was produced overnight; the original carbon dioxide estimation was then corrected accordingly. Carbonyl sulphide trapped by the ethanolic sodium hydroxide was estimated differentially by treating two aliquot parts as follows: (i) the combined amounts of carbonyl sulphide and carbon disulphide were determined iodometrically; (ii) after neutralization with acetic acid, thallous ethyl xanthate was precipitated and weighed (thallous ethyl monothiocarbonate is soluble in both ethanol and water).

*Gas–Liquid Chromatography.*—This method was used to detect diethyl carbonate and diethyl thioncarbonate, singly and together, in carbon tetrachloride solution and to check the purity of specimens of diethyl thioncarbonate.

A " V.P.C. Apparatus Mk. II," manufactured by Messrs. Griffin & George (London), was available. This relied on a thermal-conductivity detector and was operated at maximum sensitivity with bridge current 100 mA; the chart speed was 6 in./hr. The column, of glycerol (40% by weight) on " Celite," was 2 metres in length and was kept at 70°. The carrier gas was nitrogen and the flow rate 0·8 (±0·05) l./hr. Liquid samples (0·005—0·1 ml., depending on their nature) were injected by means of an " Agla " micrometer syringe. The " elution time " of a compound, which we determined, was the interval (min.) between the origin of the chart record and the appropriate " peak."

The apparatus was employed incidentally to detect water, ethanol, diethyl ether, benzene, carbon disulphide, diethyl xanthate (and some unidentified related compounds), and constituents of light petroleum.

*Potentiometry.*—Apparatus and procedure were as before.[1]

*Preparation of Sodium Ethyl Xanthate.*—Carbon disulphide (10 ml.) was added to a cooled, filtered solution of sodium ethoxide made from sodium (4 g.) and ethanol (125 ml.). After 5—10 min., addition of water (15 ml.) and then ether (2 l.) produced pale-green lath-shaped crystals of sodium ethyl xanthate dihydrate (Found: $H_2O$, 20·0. Calc. for $C_3H_9NaO_3S_2$: $2H_2O$, 20·0%). This product, which lost water easily, was filtered off, washed with ether, and then

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[5] Hantzsch and Bucerius, *Ber.*, 1926, **59**, 793

[6] Lund and Bjerrum, *Ber.*, 1931, **64**, 210.

[7] Martin and Green, *Ind. Eng. Chem. Analyt.*, 1933, **5**, 114.

converted into the anhydrous salt (A) (yield, 15—18 g., 65—75%) by drying overnight in a vacuum ($P_2O_5$) at room temperature (Found: C, 25·3; H, 3·6; S, 44·3; Na, 15·9. Calc. for $C_3H_5OS_2Na$: C, 25·0; H, 3·5; S, 44·4; Na, 16·0%). This was a hygroscopic pale-green powder: it was stored over $P_2O_5$ *in vacuo*.

Salt (A) dissolved readily, and completely, in acetone or water to give clear, pale-green solutions. A fresh aqueous solution gave a yellow precipitate with cupric sulphate solution and a bulky white precipitate with thallous sulphate solution, but no precipitate with barium chloride solution; addition of lead acetate (or nitrate) solution produced a pale-yellow suspension which slowly deposited a white coagulum. Dried xanthate (10 g.) which did not comply with these tests could normally be purified[8] by dissolving it in acetone (100 ml.) and then filtering the solution through sintered glass (porosity 4): addition of water (5 ml.) and then ether (500 ml.) to the filtrate produced crystals which were converted into salt (A) by drying overnight in a vacuum ($P_2O_5$) at room temperature.

*Reactions of Sodium Ethyl Xanthate in Aqueous and in Ethanolic Solution.*—(a) *With chloramine*-T. (i) In water.[9] A solution of salt (A) (7·5 g.; 0·052 mole) in water (100 ml.) was added dropwise to a rapidly stirred, cooled (about 5°) solution of chloramine-T trihydrate (15 g.; 0·053 mole) in water (1 l.). Then the mixture was saturated with sodium chloride (35 g.) and set aside at room temperature for 1 hr.

Pale-green $(C_2H_5O\cdot CS)_2S_2$ ("ethyl dixanthogen") was collected (5 g., 80%). The colourless alkaline filtrate contained toluene-*p*-sulphonamide, residual chloramine-T, carbonate ($0·5 \times 10^{-2}$ mole) and thiosulphate, but no xanthate, ethyl dixanthogen, or sulphur.

(ii) In ethanol. Reaction as in (i), but in ethanol, gave a precipitate containing sodium chloride (about 0·04 mole), and traces of carbonate and thiosulphate, but no sulphide or sulphur.

The almost colourless alkaline supernatant liquor (which did not contain residual chloramine-T) was decanted into a flask and distilled on a boiling-water bath under reduced pressure until only a moist yellowish solid (about 18 g.) remained; a colourless distillate (D) was collected (about 1050 ml.).

The residue was extracted with cold water (250 ml.), leaving insoluble material (1·25 g.; mainly sulphur). The filtrate was alkaline; xanthate, ethyl dixanthogen, carbonate, chloride, and thiosulphate were detected, but not sulphide or sulphate. When the filtrate was heated with an excess of 5N-hydrochloric acid, carbon disulphide ($0·9 \times 10^{-2}$ mole), carbon dioxide, and traces of carbonyl sulphide and hydrogen sulphide were liberated. On cooling, the residual acid solution yielded colourless crystals of toluene-*p*-sulphonamide (hydrochloride?).

The distillate D was divided into three equal portions which were investigated separately:

(1) D1 did not contain carbon disulphide, carbonyl sulphide, or hydrogen sulphide; saponification gave sodium carbonate and sulphide (slowly in the cold, rapidly on warming). In a quantitative experiment, an aliquot part was mixed with an excess of 0·1N-sodium hydroxide (phenolphthalein); an excess of 10% barium chloride solution was then added, and the mixture was heated under reflux until precipitation of barium carbonate ceased. Residual sodium hydroxide was determined titrimetrically; the amount of sulphide produced (weighed as lead sulphide) was found by adding the neutralized mixture to an excess of lead acetate–acetic acid reagent (warming to remove lead carbonate). The whole of fraction D1 required $3·06 \times 10^{-2}$ mole of sodium hydroxide for complete saponification, and $0·86 \times 10^{-2}$ mole of sodium sulphide was produced thereby: thus $1·10 \times 10^{-2}$ mole of sodium carbonate was obtained.

Addition of ethanolic silver nitrate solution to D1 produced a copious yellow precipitate, identified as silver thionitrate,[10] which darkened and became black (rapidly when water was added): the black residue was silver sulphide (Found: Ag, 85·1; S, 13·0. Calc. for $Ag_2S$: Ag, 87·1; S, 12·9%). The amount of silver sulphide recoverable from the whole of D1 was $0·87 \times 10^{-2}$ mole, which is almost exactly equivalent to the yield of sodium sulphide obtained by saponification (see above). The mother-liquor contained nitric acid ($1·76 \times 10^{-2}$ mole, estimated titrimetrically) equivalent to the amount of silver sulphide collected. Finally, when the neutralized mother-liquor was treated with an excess of aqueous sodium chloride solution (AgCl removed) and then heated with sodium hydroxide solution, sodium carbonate was produced, but not sodium sulphide.

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[8] Du Rietz, *Svensk Kem. Tidskr.*, 1957, **69**, 310.

[9] Cambron and Whitby, *Canad. J. Res.*, 1930, **2**, 144.

[10] Poleck and Thummel, *Ber.*, 1883, **16**, 2435; Fanto, *Monatsh.*, 1903, **24**, 477.

These results suggested that distillate D contained a (volatile) thion compound, which was not carbon disulphide or carbonyl sulphide and was readily converted, by alkaline hydrolysis or by silver nitrate, into the corresponding carbonyl compound (cf. the conversion of thioureas into ureas).

(2) Fraction D2 (1 vol.) was mixed with water (3 vol.) and extracted with carbon tetrachloride (3 × 100 ml.). The extract (E2) was washed with water (3 × 100 ml.), dried ($CaCl_2$), and filtered.

Like D, extract E2 gave a yellow precipitate with ethanolic silver nitrate solution which was converted by water into silver sulphide: the potential yield of this from the whole of E2 was $0{\cdot}85 \times 10^{-2}$ mole, which is 98% of the estimated recovery of that compound from D1 (or D2).

The remainder of extract E2 was concentrated to about one-twentieth of its original volume by distillation through a fractionating column (height, 50 cm.; diam., 1·5 cm.) packed with Fenske helices. The residual solution (about 15 ml.) was divided into two equal parts (E2/A, E2/A′) and one half was retained. E2/A′ was shaken with an excess of saturated (4%) ethanolic silver nitrate solution (50 ml.): a small quantity of water was then added, and silver sulphide (about 1 g.) was filtered off. On addition of more water to the filtrate, separation occurred, and the carbon tetrachloride layer (E2/B) was collected. E2/B was washed several times with water, dried ($CaCl_2$), and filtered.

E2/A and E2/B were then investigated by gas–liquid chromatography. Each was found to be a binary mixture consisting mainly of carbon tetrachloride (elution time, 3·7 min.); neither of them contained ethanol (elution time, 45 min.). The second constituent of E2/B (elution time, 10·2 min.) was diethyl carbonate. The second constituent of E2/A (elution time, 12·5 min.) was not diethyl carbonate (from its chromatographic behaviour). Since it had evidently reacted with silver nitrate to produce diethyl carbonate and silver sulphide (E2/A′ $\longrightarrow$ E2/B), we concluded that the unknown constituent of E2/A was probably diethyl thioncarbonate, which had been extracted from distillate D.

(3) Fraction D3 (1 vol.) was mixed with water (3 vol.) and extracted with light petroleum (b. p. 34—35°) (3 × 100 ml.). The extract (E3) was washed with water (3 × 100 ml.), dried ($CaCl_2$), and filtered.

Extract E3, like D and E2, gave a yellow precipitate with ethanolic silver nitrate; this was converted by water into silver sulphide, the potential yield of which from the whole of E3 was estimated as $0{\cdot}85 \times 10^{-2}$ mole, *i.e.*, the same as the recovery from E2 (see above).

The remainder of extract E3 was concentrated to about one-fiftieth of its original volume by distillation through the fractionating column previously described. The residual solution (about 5 ml.) was heated on a boiling-water bath under reduced pressure until no light petroleum appeared to remain: the residue (0·6—0·8 g.) was impure diethyl thioncarbonate (Found: C, 45·5; H, 7·44; S, 23·5; OEt, 61·6. Calc. for $C_5H_{10}O_2S$: C, 44·8; H, 7·46; S, 23·9; OEt, 67·2%); its b. p., determined by Siwoloboff's method,[11] was 159°/770 mm. (lit.[12,13] 161—162°) but its density (1·02 at 20°) was less than recorded (about 1·03). The equivalent weight of the oil, determined by saponification, was 43·5 [Calc. for $(C_2H_5O)_2CS$: 44·7]; the amount of sulphide so obtained (weighed as lead sulphide) corresponded to 21·6% of sulphur in the original material (a trace of mercaptan was released during saponification). A similar proportion of reactive sulphur (22·6%) was recovered as silver sulphide on treatment of the oil with ethanolic silver nitrate and water (a yellow precipitate was produced initially).

The impurities present (each in small proportion) in our product, as shown by gas–liquid chromatography, were two trace constituents of the light petroleum, diethyl carbonate, and an unidentified compound (*O*-ethyl *S*-ethyl thiocarbonate?). We removed diethyl carbonate by (small-scale) fractional distillation, but failed to obtain a specimen of diethyl thioncarbonate whose chromatogram showed no traces of the other impurities. (Other workers [14] have reported difficulty in isolating this ester.)

(b) *With silver nitrate.* (i) One equivalent of silver nitrate. Silver nitrate (6·80 g.; 0·04 mole) in water or ethanol (500 ml.) was added in 1 hr. to a stirred solution of salt (A) (5·75 g.; 0·04 mole) in the same solvent (100 ml.), giving a yellow precipitate appreciably soluble in ethanol but

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[11] Siwoloboff, *Ber.*, 1886, **19**, 795.
[12] Debus, *Ann. Chem. Pharm.*, 1850, **75**, 121.
[13] Salomon, *J. prakt. Chem.*, 1873, **6**, 433.
[14] Purvis, Jones, and Tasker, *J.*, 1910, **97**, 2287.

not in water. Then the mixture was set aside for 3 hr. and stirred occasionally. The precipitate was filtered off, washed with water, ethanol, and ether, and dried overnight in a vacuum ($P_2O_5$) at room temperature. The mother-liquor was retained.

The reaction in water [15] gave silver ethyl xanthate (8·9 g.) (Found: OEt, 20·0; Ag, 46·9. Calc. for $C_3H_5AgOS_2$: OEt, 19·65; Ag, 47·2%) (0·039 mole, 97%), which (0·30 g.) with hot 5N-hydrochloric acid (30 ml.) afforded almost 100% of silver chloride and carbon disulphide, with traces of carbonyl sulphide and hydrogen sulphide.

The reaction in ethanol also gave silver ethyl xanthate (Found: OEt, 19·1; Ag, 47·0%) (8·9 g., 97%).

(ii) Two equivalents of silver nitrate. Silver nitrate (13·6 g., 0·08 mole) in water (500 ml.) or ethanol (500 ml.) was added in 1 hr. to a stirred solution of salt (A) (0·04 mole) in the same solvent (100 ml.). A yellow precipitate was produced at first but, when more than half of the silver nitrate solution had been added, the colour changed to brown and eventually became almost black. After 3 hr., the precipitate was filtered off, washed with water only, and dried overnight in a vacuum ($P_2O_5$) at room temperature. The mother-liquor and washings were retained.

Reaction in water gave a black, plastic, unstable solid of variable composition. Silver xanthate was sometimes present. The material always appeared to contain disilver *O*-ethyl hydrogen dithio-orthocarbonate, $H(EtO{\cdot}COS_2)Ag_2$, as illustrated by two independent sets of results: (1) The product consisted mainly of the disilver salt (Found: OEt, 12·9; Ag, 62·6. Calc. for $C_3H_6O_2S_2Ag_2$: OEt, 12·7; Ag, 61·0%) (13·1 g., 0·037 mole). A sample (0·49 g., $1{\cdot}4 \times 10^{-3}$ mole) in hot 5N-hydrochloric acid (30 ml.) gave silver chloride ($2{\cdot}75 \times 10^{-3}$ mole), carbon disulphide ($0{\cdot}17 \times 10^{-3}$ mole), carbonyl sulphide ($1{\cdot}2 \times 10^{-3}$ mole), and hydrogen sulphide ($0{\cdot}77 \times 10^{-3}$ mole) but no carbon dioxide. (2) The product (11 g.) consisted of the disilver salt and silver ethyl xanthate in equal molar proportion (Found: OEt, 15·4; Ag, 55·9. Calc.: OEt, 15·4; Ag, 55·6%).

In the reaction with ethanol the yield (about 12 g.) and the composition of the solid product were variable. Moreover, the amounts of silver chloride, carbon disulphide, and hydrogen sulphide liberated by hot 5N-hydrochloric acid were also variable. Probably silver ethyl xanthate, silver hydrogen sulphide, and silver sulphide are involved in this product. The mother-liquor contained nitric acid (about 0·04 mole), but not silver or xanthate. After it had been diluted with water, carbon tetrachloride extracted diethyl carbonate (~0·015 mole) from it.

(iii) Four equivalents of silver nitrate. Silver nitrate (27·2 g.; 0·16 mole) in water (500 ml.) or ethanol (1000 ml.) was added during 1 hr. to a rapidly-stirred solution of salt (A) (0·04 mole) in the same solvent (100 ml.). The procedure of (i) was followed thereafter.

An experiment with anhydrous ethanol and exclusion of atmospheric moisture gave similar results to " absolute " ethanol.

Reaction in water [4] gave a black solid, apparently trisilver *O*-ethyl dithio-orthocarbonate or a 1 : 1 mixture of silver ethyl monothiocarbonate and silver sulphide (Found: OEt, 10·0; Ag, 70·2. Calc. for $C_3H_5Ag_3O_2S_2$: OEt, 9·8; Ag, 70·3%) (18·5 g., $4{\cdot}0 \times 10^{-2}$ mole). Heating a sample (0·55 g., $1{\cdot}2 \times 10^{-3}$ mole) with 5N-hydrochloric acid (30 ml.) gave silver chloride ($3{\cdot}6 \times 10^{-3}$ mole), carbonyl sulphide ($1{\cdot}1 \times 10^{-3}$ mole), and hydrogen sulphide ($1{\cdot}2 \times 10^{-3}$ mole) but no carbon disulphide. The mother-liquor contained nitric acid ($7{\cdot}9 \times 10^{-2}$ mole) and silver ions ($3{\cdot}5 \times 10^{-2}$ mole), but not xanthate.

The reaction in ethanol gave 98% pure silver sulphide (Found: Ag, 85·7. Calc. for $Ag_2S$: Ag, 87·1%) (19 g., $7{\cdot}6 \times 10^{-2}$ mole). This (0·24 g.) with hot 5N-hydrochloric acid (30 ml.) gave silver chloride ($1{\cdot}84 \times 10^{-3}$ mole), hydrogen sulphide ($0{\cdot}90 \times 10^{-3}$ mole), and carbon disulphide ($0{\cdot}02 \times 10^{-3}$ mole) but no carbonyl sulphide. Evidently, the product contained about 2% of silver ethyl xanthate (Found: OEt, 0·45%). The mother-liquor contained nitric acid ($10{\cdot}5 \times 10^{-2}$ mole) and silver ions ($3{\cdot}2 \times 10^{-2}$ mole), but not xanthate. Carbon tetrachloride removed, as above, diethyl carbonate (0·04 mole), identified by gas chromatography.

(iv) When aqueous 0·1N-silver nitrate solution was added to a dilute solution of salt (A) in ethanol, a reproducible one-step potentiometric-titration curve was obtained, and the equivalence-point gave an accurate indication of the amount of xanthate present (Fig. 1). Results in solely aqueous solution were variable.

(c) *With sodium hydroxide and silver nitrate.* (i) Silver nitrate (13·6 g. g., 0·08 mole) in water

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[15] Cf. Reyschler, *Bull. Soc. chim. belges*, 1928, **37**, 166.

(500 ml.) was added in 1 hr. to a stirred solution of salt (A) (5·75 g., 0·04 mole) and sodium hydroxide (1·60 g., 0·04 mole) in water (100 ml.). The procedure of b(ii) was followed thereafter. The unstable dark-brown product appeared to be impure disilver *O*-ethyl hydrogen dithio-orthocarbonate (Found: OEt, 13·1; Ag, 62·9. Calc. for $C_3H_6O_2S_2Ag_2$: OEt, 12·7; Ag, 61·0%) (13·7 g., 0·039 mole), which (0·44 g., 1·25 × $10^{-3}$ mole) was heated with 5N-hydrochloric acid (30 ml.) to give silver chloride (2·46 × $10^{-3}$ mole), carbon disulphide (0·58 × $10^{-3}$ mole), carbonyl sulphide (0·59 × $10^{-3}$ mole), and hydrogen sulphide (0·67 × $10^{-3}$ mole) but no carbon dioxide. Thus silver and sulphur ($CS_2$ + COS + $H_2S$) were recovered in equal atomic proportion as required.

(d) *With hydrogen ions.* (i) When salt (A), or a sufficiently concentrated aqueous solution of it, was treated with a concentrated mineral acid, a heavy pale yellow oil with a characteristic pungent smell was produced: this decomposed slowly at room temperature (rapidly on warming), and was presumed to be *O*-ethyl hydrogen xanthate, $C_2H_5O{\cdot}CS_2H$.

FIG. 1. *Titration of sodium ethyl xanthate* (0·144 g.) *in ethanol* (100 ml.) *with* 0·1N-*aqueous hydrochloric acid* (○) *and silver nitrate* (●).

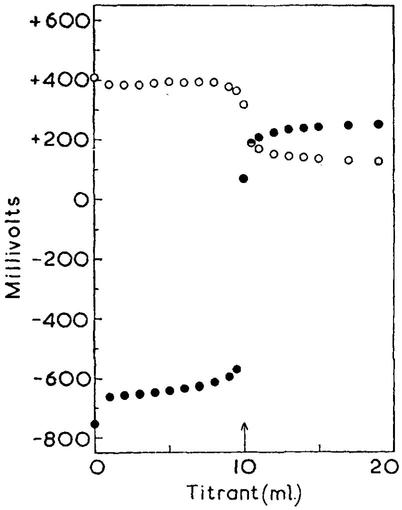
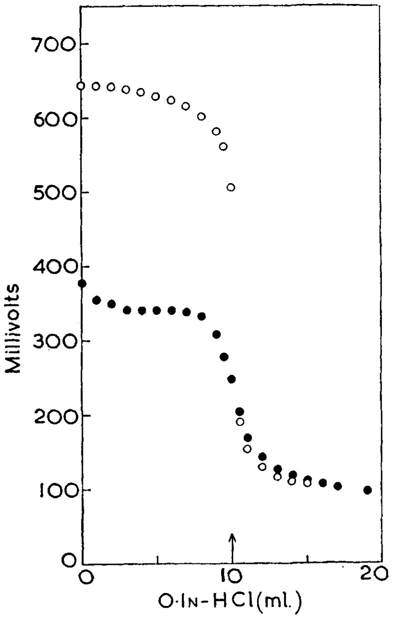


FIG. 2. *Titration of sodium hydroxide* (○) *and of sodium ethyl xanthate* (●) *in water with* 0·1N-*hydrochloric acid* (Sb *electrode*).



(ii) A fresh solution of salt (A) (0·11 g., 0·74 × $10^{-3}$ mole) in water (50 ml.) was treated with 5N-hydrochloric acid (15 ml.): carbon disulphide (0·74 × $10^{-3}$ mole) was released, but not carbonyl sulphide, carbon dioxide, or hydrogen sulphide.

(iii) When the reaction between an aqueous solution of salt (A) (about 0·14 g./100 ml.) and 0·1N-hydrochloric acid was followed potentiometrically (antimony or glass electrode), the results varied with the method of titration. Only if the acid was added to the xanthate solution with intervals of several minutes between 0·5 ml. increments was the titration curve reproducible (Fig. 2).

Use of 0·1N-sulphuric acid always gave a one-step titration curve, although the curves for fast and slow titrations were usually different. Moreover, if thallous sulphate solution was added to the reaction mixture immediately after an excess of sulphuric acid had been introduced, thallous ethyl xanthate was precipitated, in substantial amount after a " fast " titration, but only in traces (or none) after a " slow " one.

Evidently, when sodium ethyl xanthate reacts with hydrogen ions in aqueous solution, ethyl xanthic acid persists for an appreciable period, even when its concentration is small, and hinders potentiometry. This difficulty did not arise when 0·1N hydrochloric or sulphuric acid was added, rapidly or slowly, to a solution of sodium xanthate in ethanol (Fig. 1).

(iv) A solution of salt (A) (2·88 g.) in water (500 ml.) was prepared, and the xanthate concentration ($4{\cdot}00 \times 10^{-2}$ mole/l.) was checked by titrating an aliquot part (50 ml.) with 0·1N-iodine.

Carbon dioxide was bubbled through a portion (50 ml.) for 30 min.: afterwards the concentration of xanthate was $3{\cdot}86 \times 10^{-2}$ mole/l.

Hydrogen sulphide was bubbled through a portion (50 ml.) for 60 min., and then carbon dioxide was passed in for 30 min. in order to remove $HS^-$ ions and hydrogen sulphide. The concentration of xanthate was then $3{\cdot}81 \times 10^{-2}$ mole/l.

Evidently, unlike sodium trithiocarbonate,[1] sodium xanthate is decomposed only very slowly in aqueous solution by carbon dioxide or hydrogen sulphide.

(e) *With primary amines.* (i) Salt (A) (1·45 g., 0·01 mole), aniline (5 ml., 0·054 mole) and water (100 ml.) were heated in a sealed flask (air-space small) on a boiling-water bath for 3 hr., and then set aside at room temperature overnight. Colourless plates were collected and identified as *NN'*-diphenylthiourea (1·08 g., $0{\cdot}47 \times 10^{-2}$ mole). The filtrate (containing hydrogen sulphide) was extracted with ether (2 × 50 ml.), in order to remove residual aniline and thiocarbanilide, and then evaporated, under reduced pressure, on a water-bath. The solid so obtained was extracted with acetone (50 ml.); sodium sulphide and carbonate were filtered off. Adding ether (500 ml.) to the acetone filtrate gave colourless needles of sodium phenyldithiocarbamate (0·51 g., $0{\cdot}27 \times 10^{-2}$ mole).

(ii) In a similar experiment cyclohexylamine (5 ml.) gave *NN'*-dicyclohexylthiourea (Found: S, 12·7. Calc. for $C_{13}H_{24}N_2S$: S, 13·3%) (1·7 g., $0{\cdot}70 \times 10^{-2}$ mole), m. p. 178°, sodium cyclohexyldithiocarbamate (0·35 g., $0{\cdot}18 \times 10^{-2}$ mole), sodium sulphide, and carbonate.

## DISCUSSION

*Ethanolysis of the* $EtO{\cdot}CS_2^-$ *Ion*—Di[alkoxy(thiocarbonyl)]disulphides, $(RO{\cdot}CS)_2S_2$, are readily prepared by oxidizing alkali-metal xanthates in aqueous solution with various reagents,[9,16] and we have obtained the diethyl compound (" ethyl dixanthogen ") in 80% yield by treating sodium ethyl xanthate, in water, with chloramine-T. However, this oxidation, in ethanol solution, gave very little ethyl dixanthogen and, instead, a 1 : 1 mixture of diethyl thioncarbonate, $(EtO)_2CS$, and sulphur; this reaction, which has not been observed before, is significant in the present context.

If sodium ethyl xanthate is oxidized in ethanol, and water is present (we used chloramine-T trihydrate and " absolute " alcohol), then, since ethyl dixanthogen is stable in ethanol containing chloroamine-T and so is not an intermediate, the new reaction must depend on ethanolysis of the xanthate ion, *i.e.*, reaction (2) (p. 117) followed by

$$HS^- + \left\{\begin{matrix} H_2O \\ EtOH \end{matrix}\right\} \rightleftharpoons \left\{\begin{matrix} HO^- \\ EtO^- \end{matrix}\right\} + H_2S$$

$$H_2S + O \xrightarrow[EtOH]{} H_2O + S$$

*i.e.*, in sum,
$$EtO{\cdot}CS_2^- + EtOH + RH + O \longrightarrow (EtO)_2CS + S + R^- + H_2O \quad . \; . \; . \; . \; . \quad (7)$$
where
$$R = HO \text{ or } EtO.$$

This mechanism explains the salient experimental results, if we assume that about 80% of the available sodium ethyl xanthate was consumed in reaction (7), with most of the remainder unchanged. As regards the minor reaction products, the production of (*a*) thiosulphate and carbonate and (*b*) diethyl carbonate is consistent with the hydrolysis of small proportions of the xanthate and diethyl thioncarbonate, respectively, promoted by oxidation.

Equation (2) is also consistent with the diverse results we obtained by carefully adding silver nitrate in ethanol to ethanolic sodium ethyl xanthate. One equivalent (or less) of silver nitrate produced only silver ethyl xanthate and sodium nitrate:

$$EtO{\cdot}CS_2^- + Ag^+ \longrightarrow EtO{\cdot}CS_2Ag \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

But, if more than one equivalent was added, further reaction occurred until, with

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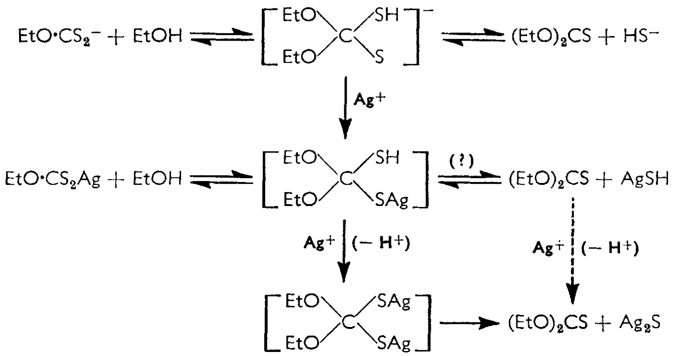
[16] Zeise, *Schweitzer's Journal*, 1822, **36**, 36; *Berzelius Journal*, 1824, **3**, 82; 1837, **16**, 306.

4 equivalents, diethyl carbonate, silver sulphide, nitric acid, and sodium nitrate were obtained in accordance with the reaction:

$$EtO{\cdot}CS_2^- + EtOH + H_2O + 4Ag^+ \longrightarrow (EtO)_2CO + 2Ag_2S + 3H^+ \quad . \quad . \quad . \quad . \quad . \quad (9)$$

A satisfactory mechanism for (9), which includes reaction (8), is based on the ethanolysis of the xanthate ion and the hydrolysis of diethyl thioncarbonate, namely:



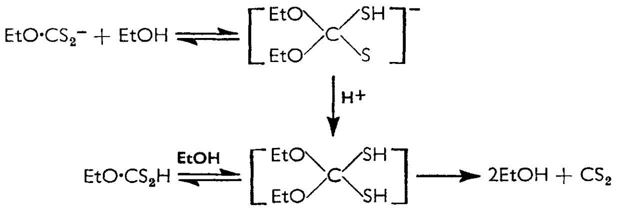
$$\left.\begin{aligned}(EtO)_2CS + H_2O &\rightleftharpoons (EtO)_2CO + H_2S\\ H_2S + 2Ag^+ &\longrightarrow Ag_2S + 2H^+\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The inclusion of reactions (10) is justified by our observation that diethyl carbonate and silver sulphide were produced when diethyl thioncarbonate was treated with ethanolic silver nitrate in the presence of water. When reaction (9) was carried out in " absolute " alcohol (water-content about 0·5%), sufficient water for reaction (10) was still present; but, when reaction (9) occurred in anhydrous ethanol, the necessary water must have been produced from ethanol and nitric acid ($EtOH + HNO_3 \rightleftharpoons EtO{\cdot}NO_2 + H_2O$) and this would account for a relatively low yield of nitric acid in that experiment.

The mechanism proposed for reaction (9) also explains the results we obtained by adding two equivalents only of silver nitrate to sodium ethyl xanthate in ethanol, namely, production of diethyl carbonate and a mixture of silver ethyl xanthate and silver hydrogen sulphide and/or sulphide in variable proportions. Since diethyl thioncarbonate was *not* found we conclude that reaction (10) proceeded so quickly that there was insufficient silver nitrate to convert all the silver xanthate into diethyl thioncarbonate and silver hydrogen sulphide or sulphide. Evidently, reaction (9) cannot be stopped at the intermediate stage:

$$EtO{\cdot}CS_2^- + EtOH + 2Ag^+ \longrightarrow (EtO)_2CS + Ag_2S + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad (9a)$$

The foregoing proof of the addition of ethanol to the thiocarbonyl linkage of the xanthate ion revives an earlier suggestion [5] that the instability of ethyl hydrogen xanthate in the presence of ethanol might be due to the formation of an unstable addition product $(EtO)_2C(SH)_2$, which decomposes rapidly into carbon disulphide and ethanol. For if that hypothesis is combined with the present concept, plausible explanations of (*a*) the reaction between sodium ethyl xanthate and hydrogen ions in ethanol or ethanol–water and (*b*) the autocatalytic decomposition of ethyl hydrogen xanthate [17] are obtained:



. . . . . . . (11)

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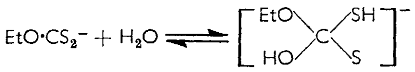
[17] von Halban and Kirsch, *Z. phys. Chem.*, 1913, **82**, 325.

*Hydrolysis of the* $EtO\cdot CS_2^-$ *Ion.*—An analogous interpretation of the hydrolysis:

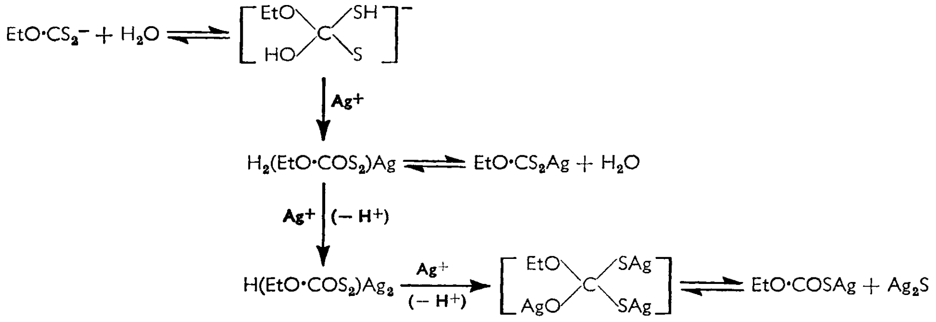


is consistent with the behaviour of sodium ethyl xanthate in water and in aqueous sodium hydroxide.

When up to one equivalent of silver nitrate is added gradually to aqueous sodium (or potassium [15]) ethyl xanthate, only silver ethyl xanthate is obtained, in accordance with reaction (8). If, however, more silver nitrate is then introduced, it reacts with the silver xanthate, causing the yellow precipitate to darken until, finally, it is black. Makens [4] decided that the end-product was a 1 : 1 mixture of silver ethyl monothiocarbonate and silver sulphide:

$$EtO\cdot CS_2Ag + H_2O + 2Ag^+ \longrightarrow EtO\cdot COSAg + Ag_2S + 2H^+ \quad . \quad . \quad . \quad . \quad (12)$$

Our analytical data also are consistent with this, but we think that the product, which is unique in both appearance and consistency, could well be trisilver *O*-ethyl dithio-orthocarbonate, $EtO\cdot COS_2Ag_3$, which decomposes (*e.g.*, when heated) into $EtO\cdot COSAg$ and $Ag_2S$. If so, a mechanism for reactions (8) and (12) can be formulated as follows:

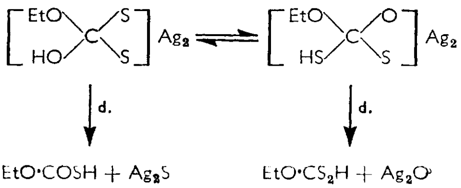


This scheme explains why pure silver xanthate is not obtained unless reaction (8) is carried out in a way which ensures that an excess of silver ions is avoided. It also suggests that reaction (12) might be stopped half-way:

$$EtO\cdot CS_2Ag + H_2O + Ag^+ \longrightarrow H(EtO\cdot COS_2)Ag_2 + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad (12a)$$

This can be achieved by treating sodium ethyl xanthate with exactly two equivalents of silver nitrate but, when the reaction occurs in water, there is a tendency for the disilver salt to be contaminated with silver xanthate; however, if one equivalent of sodium hydroxide is introduced as the reaction proceeds, hydrogen ions are removed continuously, and the salt $H(EtO\cdot COS_2)Ag_2$ is then obtained reproducibly.

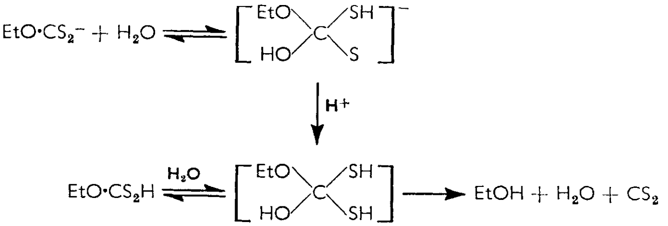
Disilver hydrogen *O*-ethyl dithio-orthocarbonate decomposes at room temperature, yielding silver sulphide and oxide, carbonyl sulphide, and carbon disulphide; when heated with hydrochloric acid, it affords carbon disulphide, carbonyl sulphide, and hydrogen sulphide. This behaviour is consistent with isomerization:



. . . . . . . . (13)

It is therefore interesting that we have isolated the disilver salt in two physical forms: a black plastic solid was obtained when reaction (12) occurred in water whereas, when sodium hydroxide was present, the product was a dark-brown powder.

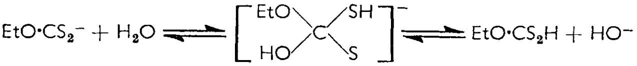
Hydration of the xanthate ion also enables the reaction between sodium ethyl xanthate and hydrogen ions in water to be understood:



. . . . (14)

This mechanism, which follows the pattern of reactions (11), includes an unstable hydrate of ethyl hydrogen xanthate, as envisaged by Hantzsch and Bucerius,[5] in order to explain why that compound is stable when dry, yet decomposes rapidly in the presence of water.[17]

The production of xanthic acid from the hydrated xanthate ion can, however, be conceived in another way [see (4)]:



. . . (15)

But although this alternative route affords a mechanism for the oxidation of the xanthate ion in water (see below), it does not explain its reaction with the hydrogen ion because (i) the complementary reaction $HO^- + H^+ \longrightarrow H_2O$ is not detected potentiometrically (Fig. 2), and (ii) the xanthate ion is not rapidly destroyed by carbon dioxide or hydrogen sulphide in aqueous solution.

When sodium ethyl xanthate is oxidized in water by means of chloramine-T or a soluble hypochlorite,[9] the oxidizing agent is presumably the $ClO^-$ ion: thus, when iodine is used, the hypoiodite ion is very probably involved. But in order that $IO^-$ ions should be available, the iodine must react with $HO^-$ ions, and this can only be arranged in accordance with (16):

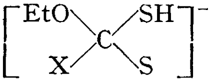
$$2EtO{\cdot}CS_2^- + 2H_2O \rightleftharpoons 2EtO{\cdot}CS_2H + 2HO^-$$

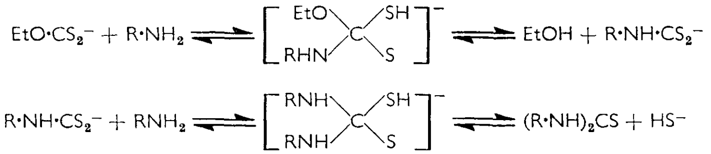
$$I_2 + 2HO^- \rightleftharpoons IO^- + I^- + H_2O$$

$$2EtO{\cdot}CS_2H + IO^- \longrightarrow (EtO{\cdot}CS)_2S_2 + I^- + H_2O$$

That is, $$2EtO{\cdot}CS_2^- + I_2 \xrightarrow{(H_2O)} (EtO{\cdot}CS)_2S_2 + 2I^- \qquad \text{. . . . . . . . (16)}$$

This mechanism explains the well-known iodometric estimation of xanthates in aqueous solution, for the amounts of iodine and xanthate consumed must be equivalent.

To sum up, it is now evident that the behaviour of sodium ethyl xanthate in both water and ethanol can be understood by supposing that the thiocarbonyl linkage is able to add on water or ethanol, and that the ortho-ion  (where X = HO or EtO) so produced is capable of dissociating in different ways according to the nature of X and the environment. Since this hypothesis has already served to explain the behaviour of sodium trithiocarbonate in ethanol and in water,[1] it may also be applicable to other thiocarbonyl compounds and in cases where XH is not ethanol or water. It appears that this is indeed the case, for the reaction between sodium ethyl xanthate and a primary amine, which produces the corresponding sodium dithiocarbamate and *NN'*-disubstituted thiourea, can be formulated as follows:



. . . (18)

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