551. *Reaction of Thiosulphate Ion with Tetraethylthiuram Disulphide promoted by Some Metal Cations.*

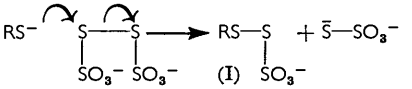
By B. SAVILLE.

Dialkyldithiocarbamate ions react readily with tetrathionate ions to give an almost quantitative yield of tetra-alkylthiuram disulphide and thiosulphate ions. The above reaction does not occur, however, when the zinc salt of diethyldithiocarbamic acid is used. This suggests that the above reaction products would react in the presence of zinc ions to give zinc dialkyldithiocarbamate and tetrathionate ions, a prediction now confirmed experimentally. Other metal cations such as Cd^{2+} and Pb^{2+} capable of yielding chelated salts with dialkyldithiocarbamic acids act similarly. Tentative mechanistic interpretations of these reactions are suggested.

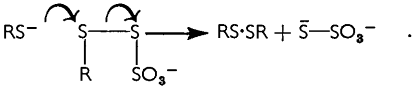
THE use of tetrathionate ion as a reagent for the oxidation of thiols or thiol-acids, ionised in the presence of an added base, to the corresponding disulphidic species was introduced by Footner and Smiles,[1] and subsequently studied by Cambron and Whitby[2] and by Bulmer and Mann.[3] This reaction, which normally proceeds very rapidly in aqueous solution at room temperature, may be plausibly interpreted in terms of two successive thiol–disulphide interchange processes symbolised thus: (*a*) thiol ionisation in presence of base (B)

$$RSH + B \rightleftharpoons RS^- + BH^+$$

(*b*) reaction of thiol anion (RS^-) with tetrathionate ion



$$RS^- \; \underset{SO_3^-}{S}-\underset{SO_3^-}{S} \longrightarrow \underset{\text{(I)}}{} \; RS-\underset{SO_3^-}{S} + \bar{S}-SO_3^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(i)}$$



$$RS^- \; \underset{R}{S}-\underset{SO_3^-}{S} \longrightarrow RS{\cdot}SR + \bar{S}-SO_3^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(ii)}$$

Since intermediates such as (I) have not been observed,* and since the disulphide (RS·SR)

---

* It has been claimed recently (Szczepkowski, *Nature*, 1958, **182**, 934) that cysteine and tetrathionate give " cysteine polythiosulphonic acids," an observation which is difficult to reconcile with the proposition made here. No idea of the proportions of these products is, however, indicated by these experiments.

[1] Footner and Smiles, *J.*, 1925, 2887.

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

[3] Bulmer and Mann, *J.*, 1945, 674.

is obtained in nearly quantitative yield, it is concluded that process (ii) is much more rapid than process (i).

Although the above reactions are, in principle, reversible, there is no evidence from studies reported here that this reversal takes place to any significant extent. For example, an initially homogeneous system containing sodium thiosulphate and a tetra-alkylthiuram disulphide gave no tetrathionate and dialkyldithiocarbamate ions as required by reaction (iii):

$$2S_2O_3^{2-} + R_2N{\cdot}C(S){\cdot}S{\cdot}S{\cdot}C(S){\cdot}NR_2 \underset{(iv)}{\overset{(iii)}{\rightleftharpoons}} S_4O_6^{2-} + 2R_2N{\cdot}CS_2^-$$

Indeed, the reverse reaction (iv) has now been shown to occur. It seems fair to conclude that in base-catalysed thiol–disulphide interchange reactions the systems reach equilibrium with the more acidic thiol predominating. Since thiosulphuric acid possesses a low pK value [4] (1·24) for ionisation of the SH group, it is clear that many thiols and thiol-acids of lower acid strength are converted into disulphides by tetrathionate ion. Now, although *ionic* diethyldithiocarbamates (*e.g.*, the Na^+, or $Et_2NH_2^+$ salts) react readily and quantitatively with tetrathionate ion in the manner described (eqn. iv), it was found that *zinc* diethyldithiocarbamate underwent no detectable change in an aqueous methanolic solvent containing an equivalent of tetrathionate. Lack of reaction is not due to the insoluble nature of zinc diethyldithiocarbamate, since independent experiment shows that it is dissolved to the extent of at least 0·5% in the hot solvent used. These observations show that reaction (v) does not occur, and suggest that this may be due to the easier reverse reaction (vi), leading to the stable combination of tetrathionate ion and zinc diethyldithiocarbamate:

$$S_4O_6^{2-} + (Et_2N{\cdot}CS_2)_2Zn \underset{(vi)}{\overset{(v)}{\rightleftharpoons}} 2S_2O_3^{2-} + (Et_2N{\cdot}CS_2)_2 + Zn^{2+}$$

Experiments designed to test this prediction have now shown that sodium thiosulphate does not react with tetraethylthiuram disulphide (TET) alone but does so extremely readily, as shown in reaction (vi), if a soluble zinc salt capable of supplying Zn^{2+} ions is added to the system. This reaction proceeds as long as Zn^{2+} ions are present.

The reaction has been examined from the point of view of establishing the balance between reactants and products. The solvent used was methanol–water (5 : 1 v/v) in order to ensure solubility of starting materials, and temperatures were between 20° and 40°. From 0·02 mole of sodium thiosulphate, 0·01 mole of tetraethylthiuram disulphide, and 0·01 mole of zinc acetate there was obtained, after 30 min., 0·0094 mole of zinc diethyldithiocarbamate (isolated yield) and over 0·0090 mole of tetrathionate; also, 0·0196 mole of thiosulphate was consumed and a negligible amount of Zn^{2+} ions remained. That reaction only proceeds in the presence of Zn^{2+} ions was proved by allowing systems (where initially $2[S_2O_3^{2-}] > [Zn^{2+}] < [TET]$) to reach equilibrium and then measuring the correspondence between the initial quantity of zinc salt added and the thiosulphate ion which had reacted. This correspondence was found to be very good, *i.e.*, at least 1·94 g.-ions of thiosulphate react per g.-ion of zinc added.

The promotion of this otherwise unobservable interchange is by no means specific to Zn^{2+} ions. Similar reactions occur upon the addition of Cd^{2+} and Pb^{2+} ions to the thiosulphate–tetraethylthiuram disulphide combination, and there are preliminary indications that Co^{2+}, Ni^{2+}, Mn^{2+}, and Ag^+ ions behave similarly. Mg^{2+} and Ca^{2+} ions do not promote the interchange. The data do not permit definite conclusion to be drawn regarding the mechanism of these metal cation-assisted interchanges, but the following views are suggested.

A very obvious possibility is that the equilibrium (iii) $\rightleftharpoons$ (iv) is rapidly established but is normally well to the left of the equation so that reaction in the forward direction

---

[4] Kolthoff, *Rec. Trav. chim.*, 1924, **43**, 216.

(iii) is only observed experimentally if the dialkyldithiocarbamate ions are continuously removed by chelation with strongly bonding metal cations such as Zn^{2+}, Cd^{2+}, and Pb^{2+}.

A second possibility is that the metal cation is actually involved in the transition states of the substitutions at the sulphur atoms and is thereby exerting a genuine kinetic acceleration of the reaction in the forward direction.

EXPERIMENTAL

Materials.—Sodium dimethyldithiocarbamate was a pure sample kindly supplied by the Monsanto Chemical Co. Other compounds were either " AnalaR " materials or of the highest available purity. Potassium tetrathionate was made as follows: To iodine (12·7 g., 0·1 g.-atom) in ethanol (150 ml.) was added sodium thiosulphate (24·8 g., 0·1 mole) in water (30 ml.). Any iodine remaining after 10 min. was removed by cautiously adding more thiosulphate. Potassium iodide (20 g.) in water (10 ml.) was then added, and the solution cooled to 5—10°. The resultant crystalline potassium tetrathionate was recrystallised from ethanol–water (Found: S, 42·6. Calc. for $K_2S_4O_6$: S, 42·4%).

Reference Samples of Metal Dialkyldithiocarbamates.—To the sodium dialkyldithiocarbamate (0·02 mole) in water (20 ml.) were added methanol (80 ml.) and the requisite metal acetate (0·02/*n* mole, where *n* is the cationic charge) in water (20 ml.). The precipitated metal dialkyldithiocarbamate was collected, washed with methanol–water, dried, and recrystallised (usually from chloroform or toluene).

Reactions of Tetrathionate Ion with Dialkyldithiocarbamate Ions.—(i) *Dimethyldithiocarbamate ion.* To sodium dimethyldithiocarbamate ($2\frac{1}{2}H_2O$) (2·07 g., 0·011 mole) in water (50 ml.) was added potassium tetrathionate (1·51 g., 0·005 mole) in water (50 ml.). Tetramethylthiuram disulphide (1·18 g., 98·3%) was precipitated immediately and collected. It had m. p. (decomp.) *ca.* 150°, mixed m. p. 150—152° (Found: C, 30·1; H, 5·1. Calc. for $C_6H_{12}N_2S_4$: C, 30·0; H, 5·0%). The filtrate, after addition of excess of zinc acetate (to remove $Me_2N\cdot CS_2^-$ ions) and chloroform extraction, contained 0·0098 g.-ion of thiosulphate.

In a similar experiment a considerable excess of sodium dimethyldithiocarbamate (3·72 g., 0·02 mole) over the potassium tetrathionate (0·005 mole) was employed. Again, the yield of tetramethylthiuram disulphide was essentially quantitative. This reaction was therefore used to estimate gravimetrically tetrathionate produced in other reactions.

(ii) *Diethyldithiocarbamate ion.* To sodium diethyldithiocarbamate trihydrate (2·25 g., 0·01 mole) in water (50 ml.) was added potassium tetrathionate (1·51 g., 0·005 mole) in water (50 ml.), giving tetraethylthiuram disulphide (1·45 g., 98%), m. p. and mixed m. p. 69—70° (Found: C, 40·7; H, 6·9. Calc. for $C_{10}H_{20}N_2S_4$: C, 40·5; H, 6·8%). Similarly, diethylammonium diethyldithiocarbamate (from diethylamine and carbon disulphide in benzene–light petroleum) (2·22 g., 0·01 mole) gave 97% of tetraethylthiuram disulphide, m. p. 69—70°.

Stability of Zinc Diethyldithiocarbamate in Aqueous-methanolic Potassium Tetrathionate.—Zinc diethyldithiocarbamate (3·61 g., 0·01 mole) was refluxed for 3 hr. with potassium tetrathionate (3·02 g., 0·01 mole) in a mixture of methanol (100 ml.) and water (20 ml.). On cooling, the undissolved material was removed, and the filtrate evaporated under reduced pressure to remove most of the methanol. Water (50 ml.) was then added to the filtrate, and the resulting suspension extracted with chloroform (2 × 50 ml.). The undissolved material was added to the chloroform extracts which were then evaporated to dryness. Unchanged zinc diethyldithiocarbamate (3·54 g., 98%) was thus recovered, m. p. and mixed m. p. 177—178° (Found: C, 33·4; H, 5·5. Calc. for $C_{10}H_{20}N_2S_4Zn$: C, 33·2; H, 5·6. The aqueous filtrate after extraction was then analysed for tetrathionate ion as previously described (Found: 0·0075 g.-ion). The solubility of zinc diethyldithiocarbamate in the hot solvent employed was roughly checked as follows. The dithiocarbamate (2·0 g.) was used to saturate a mixture of methanol (100 ml.) and water (20 ml.) at reflux temperature. The hot mixture was rapidly filtered, and on cooling gave zinc diethyldithiocarbamate (0·61 g.), indicating a solubility of more than 0·5 g. per 100 ml. of refluxing solvent as used in the main experiment.

Reactions between Tetraethylthiuram Disulphide and Sodium Thiosulphate in the Presence of Zinc, Cadmium, and Lead Salts.—(i) *Zinc acetate.* To the disulphide (2·96 g., 0·01 mole) in warm methanol (100 ml.) was added sodium thiosulphate (4·96 g., 0·02 mole) in water (10 ml.). On addition of 10 ml. of M-zinc acetate precipitation of almost pure zinc diethyldithiocarbamate

(3·39 g., 0·0094 mole) occurred rapidly, m. p. and mixed m. p. (recrystallised from toluene) 177—178° (Found: C, 33·3; H, 5·6%). The filtrate, after evaporation under reduced pressure and extraction with chloroform, contained no ionic zinc (ethylenediaminetetra-acetic acid titration [5]) and only 2% of the original thiosulphate. It afforded tetramethylthiuram disulphide (2·12 g.), m. p. and mixed m. p. 152—154°, on treatment with excess of aqueous sodium dimethyldithiocarbamate; *i.e.*, the filtrate contained 0·0090 g.-ion of tetrathionate. The thiosulphate formed in this last process was also estimated by iodine titration as an additional check on the calculated tetrathionate value [after removal of excess of $Me_2N{\cdot}CS_2^-$ ions with zinc acetate (2·5 g.)]. (Zinc salts do not interfere with the titration of thiosulphate by iodine.) (Thiosulphate found: 0·019 g.-ion.)

(ii) *Zinc acetate in water.* The heterogeneous reaction was performed by refluxing tetraethylthiuram disulphide (0·01 mole), sodium thiosulphate (0·02 mole), and zinc acetate (0·01 mole) in water (100 ml.) for 3 hr. The mixture was cooled, and the insoluble material extracted with acetone (2 × 25 ml.), leaving zinc diethyldithiocarbamate (2·96 g., 0·0082 mole), m. p. 175—177°. A small quantity of material, mainly unchanged disulphide, was recovered from the acetone extract. The filtrate contained zinc ions (0·002 g.-ion), thiosulphate (0·0052 g.-ion), and tetrathionate (0·0042 g.-ion).

(iii) *Cadmium acetate.* To tetraethylthiuram disulphide (0·01 mole) in warm methanol (75 ml.) was added sodium thiosulphate (0·02 mole) in water (10 ml.). Then to the warm mixture was added cadmium acetate dihydrate (2·67 g., 0·01 mole) in warm water (15 ml.). Cadmium diethyldithiocarbamate was immediately precipitated (3·94 g., 0·00965 mole), m. p. 243°, mixed m. p. 244° (Found: C, 29·3; H, 5·1. Calc. for $C_{10}H_{20}N_2S_4Cd$: C, 29·4; H, 4·9%). On crystallisation from chloroform, it had m. p. and mixed m. p. 244—245° (Found: C, 29·5; H, 4·8%). The filtrate, examined as in (i), contained tetrathionate (0·00925 g.-ion).

(iv) *Lead acetate.* In an experiment performed precisely as for (iii), but with lead acetate trihydrate (3·79 g., 0·01 mole), there was isolated lead diethyldithiocarbamate as an amorphous light yellow powder, m. p. 205°, mixed m. p. 205—206° (Found: C, 24·2; H, 4·1. Calc. for $C_{10}H_{20}N_2S_4Pb$: C, 23·8; H, 4·0%). On crystallisation from chloroform it had m. p. and mixed m. p. 206—207° (Found: C, 23·9; H, 3·9%). The filtrate contained tetrathionate (0·00914 g.-ion, based on tetramethylthiuram disulphide obtained on treatment with sodium dimethyldithiocarbamate). The final thiosulphate ion check indicated tetrathionate ≡ 0·0090 g.-ion.

Additional Quantitative Experiments on the Reaction of Sodium Thiosulphate with Tetraethylthiuram Disulphide in the Presence of Zinc Salts.—The correspondence between Zn^{2+} ions added and $S_2O_3^{2-}$ ions which finally reacted was examined as follows. To 0·02M-methanolic disulphide (50 ml.) and 0·2M-aqueous sodium thiosulphate (10 ml.) were added various volumes (0—2·00 ml.) of M-zinc acetate or sulphate. After being left overnight, the reaction mixtures were filtered, and the filtrates extracted with chloroform (3 × 50 ml.) after addition of water (150 ml.). The final aqueous phase was titrated with standard iodine. The table expresses the correlation between Zn^{2+} ions added and $S_2O_3^{2-}$ used in the reaction. Almost identical results were obtained when cadmium and lead salts were used instead of zinc salts.

Relation between Zn^{2+} [*from* $Zn(OAc)_2$ *or* $ZnSO_4$] *added and* $S_2O_3^{2-}$ *ions used for systems TET* (*initially* 0·001 *mole*) + $Na_2S_2O_3$ (*initially* 0·002 *mole*) *in approx.* 60 *ml. of methanol–water* (5 : 1 *v*/*v*).

Zn^{2+} added (g.-ion × 10^{-4})	0·0	2·5	5·0	7·5	10·0 *	20·0
Thiosulphate used (g.-ion × 10^{-4})	0·0	4·6	9·7	14·8	19·4	19·6

* Equivalent to TET and $S_2O_3^{2-}$ taken.

British Rubber Producers' Research Association,
48—56 Tewin Road, Welwyn Garden City, Herts.

[*Received, December 5th,* 1959.]

---

[5] Schwarzenbach, "Complexometric Titrations" (trs. Irving), Methuen, London, 1957, p. 83.