

## Remarks on the Reactivities of the Penta- and Hexathionate Ions

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The reactions of higher polythionates with nucleophilic reagents are discussed on the basis of existing possibilities of heterolytic cleavage of the sulphur-sulphur bonds. In addition to the principal reaction type involving a release of thiosulphate from the penta- and hexathionate ions, other modes of cleavage may lead to the release of sulphite, and of thiosulphate and sulphur.

The presence of unbranched and non-planar sulphur chains in the tetra- and pentathionate ions has recently been demonstrated through crystal structure determinations of barium tetrathionate dihydrate<sup>1</sup>, orthorhombic and triclinic barium pentathionate dihydrate<sup>2,3</sup>, and a solvate of barium pentathionate with acetone<sup>4</sup>. The structure analyses, which were made by two-dimensional Fourier methods by use of the heavy atom technique, were based on X-ray data alone, without recourse to assumptions of chemical nature.

The tetra- and pentathionate chains contain two and three divalent sulphur atoms, respectively, and terminal sulphur atoms to each of which are attached three oxygen atoms. The sulphonate groups, together with the adjacent divalent sulphur atoms, constitute thiosulphate groups, which have the shape of distorted tetrahedrons. The tetrathionate ion is thus built of two thiosulphate groups, linked together through their divalent sulphur atoms, and the pentathionate ion consists of a divalent sulphur atom to which are attached, through sulphur-sulphur, bonds, two thiosulphate groups. The structures, assigned to the ions on chemical grounds<sup>5,6</sup>, are confirmed through the X-ray studies.

No structure determination of a salt of hexathionic acid has so far been reported. However, in view of chemical evidence, which speaks in favour of unbranched chains<sup>5,6</sup>, and the fact that branching of sulphur chains has never been demonstrated to occur, it appears reasonably safe to conclude that the sulphur chain of hexathionate is unbranched, like that of pentathionate and tetrathionate.

The following brief review of some features of polythionate chemistry may be pertinent to the succeeding discussion of reaction schemes.

The polythionates are chemically characterized by the ease with which they undergo heterolytic cleavage in reactions with nucleophilic reagents. This behaviour is, presumably, due to a pronounced electrophilic character of the divalent sulphur atoms of the chains. Nucleophilic attacks have been found to take place at either one of the two equivalent, divalent sulphur atoms of the tetrathionate ion, at the middle sulphur atom of the pentathionate ion, and at the middle disulphur group of the hexathionate ion. The principal reactions of the polythionates with nucleophilic reagents may be summarized as follows<sup>5-11</sup>.

Pentathionate and hexathionate behave as sulphur thiosulphates,  $S(S_2O_3)_2^{--}$  and  $S_2(S_2O_3)_2^{--}$ . In some reactions with nucleophilic reagents, both thiosulphate groups are displaced by the reagent; in other reactions, only one.

Tetrathionate behaves as a sulphur sulphite-thiosulphate, with displacement of the sulphite and the thiosulphate group by a nucleophilic reagent, or of only one of the groups. A thiosulphate group is displaced more readily than a sulphite group.

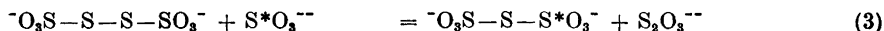
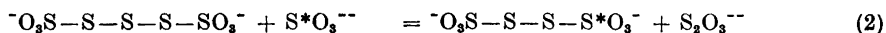
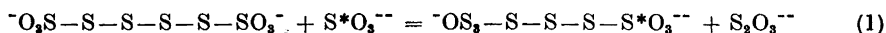
Trithionate acts as a sulphur disulphite,  $S(SO_3)_2^{--}$ , with displacement of both sulphite groups, or of only one. Trithionate may also act as a thiosulphato-sulphonate, the nucleophilic attack in this case occurring at one of the sulphonate sulphur atoms.

The reactions, as far as their kinetics have been established, are bimolecular, and thus of the  $S_N2$  type. This applies to the following reactions involving nucleophilic displacements on divalent sulphur: Those of tetra- and pentathionate with sulphite<sup>12</sup>, hydrogensulphite<sup>13</sup> and cyanide<sup>14-16</sup> ions, of tetrathionate with azide ion<sup>17,18</sup> and of pentathionate with hydroxyl ion<sup>19</sup>, of tri- and tetrathionate with thiosulphate ion<sup>20,21</sup> and of trithionate with sulphite ion<sup>22</sup>. Likewise, nucleophilic displacements on the divalent sulphur of sulphenyl sulphites<sup>23</sup> (thiosulphate esters) and disulphides<sup>24</sup> are of the  $S_N2$  type, as is also the reaction of triphenylphosphine with elemental sulphur<sup>25</sup>.

The electrophilic species in  $S_N2$  reactions have no independent existence, and electropositive ions of divalent sulphur, even short-lived ones, do therefore not occur in the reactions.

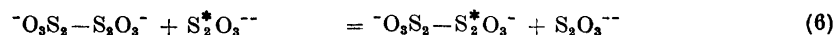
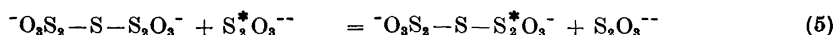
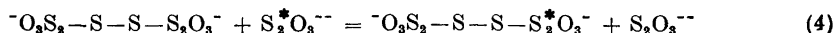
The recognition of polythionates as derivatives of divalent electropositive sulphur, and their reactions as nucleophilic displacements, removes older arguments, on chemical basis, against the unbranched chain structures<sup>6</sup>.

The occurrence of various displacement reactions, predicted on the basis of the reactivity principles outlined above, have been confirmed through experiments with sulphite and thiosulphate labelled with radioactive sulphur. Thus, the reactions of hexa-, penta- and tetrathionate with sulphite ion, to give the next lower polythionate, and thiosulphate, were formulated<sup>5</sup> as nucleophilic displacements of thiosulphate by sulphite:



The validity of this view, at any rate as far as tetra- and pentathionate are concerned, has been demonstrated by Christiansen and Drost-Hansen<sup>26,27</sup>. The reverse reactions, of tri- and tetrathionate with thiosulphate to give sulphite and the next higher polythionate, are also nucleophilic displacements<sup>10,20,21</sup>.

In a study of exchange reactions of polythionates with thiosulphate, Fava<sup>28</sup> has shown that the displacement equilibria<sup>5,10,29</sup>:

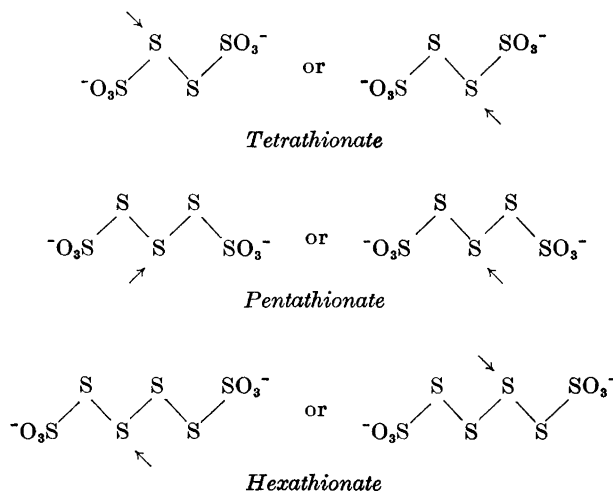


are established very rapidly at ordinary temperatures. The mechanism of the thiosulphate-catalyzed rearrangement of tetrathionate into tri- and pentathionate, formulated<sup>10</sup> as subsequent displacements of sulphite by thiosulphate and of thiosulphate by sulphite, has been confirmed by Fava and Bresadola<sup>21</sup>. Likewise, Fava and Pajaro<sup>22</sup> have found that trithionate exchanges with sulphite ion, although rather slowly.

Thus, recent studies on polythionates have established the unbranched chain structure, and the characteristic sensitivity towards basic reagents as due to nucleophilic attacks on the divalent sulphur chains. The reactivity principles recognize the electrophilic character of the middle sulphur atom of pentathionate and of the two equivalent, middle sulphur atoms of hexathionate. Nucleophilic attacks on these atoms, in directions so as to displace thiosulphate, are responsible for the principal reactions of the ions. There are, however, indications that nucleophilic attacks may occur also at other of the divalent sulphur atoms of the penta- and hexathionate ions, and in different directions.

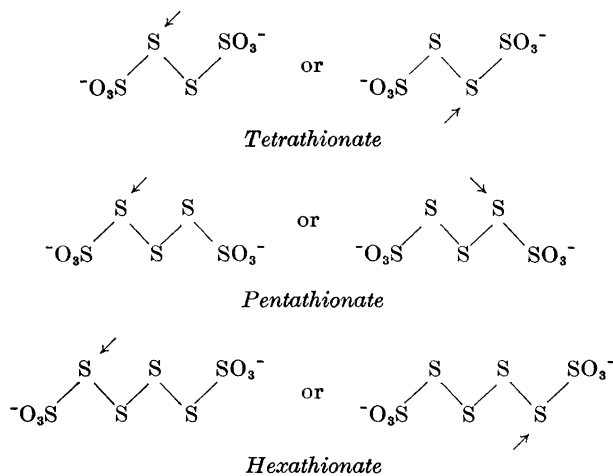
#### SCHEMES FOR THE REACTIONS OF HIGHER POLYTHIONATES WITH NUCLEOPHILIC REAGENTS

The various possibilities of nucleophilic attack on the divalent sulphur atoms of the tetra-, penta- and hexathionate ions are depicted through arrows in schemes 1 to 4 below. In each case there are two equivalent possibilities, corresponding to the two halves of the ions. The arrows are drawn so as to indicate a linear transition state, as in displacements on carbon; there is, however, as yet no definite information available concerning the configuration of the transition state.



*Scheme 1.* Principal directions of nucleophilic attack on the tetra-, penta- and hexathionate ions: Displacement of thiosulphate.

Schemes 1 and 2 lead to the displacement of thiosulphate and sulphite, respectively. The tetra-, penta- and hexathionate ions, on the action of the appropriate nucleophilic agent, eliminate thiosulphate more readily than sulphite; displacement of thiosulphate does, indeed, occur in the majority of the reactions of the ions, *e.g.*, in the reactions (1)–(6) above. Other examples include the reactions with piperidine, hydroxide, thiocarbonyl ions, and cyanide and sulphide ions.



*Scheme 2.* Alternative (less predominant) directions of nucleophilic attack on the tetra-, penta- and hexathionate ions: Displacement of sulphite.

Displacement of sulphite according to scheme 2 was first found to occur in the case of tetrathionate. In the reactions of tetrathionate with piperidine<sup>5,8</sup> and hydroxide<sup>5,30,31</sup>, displacements of thiosulphate *and* sulphite take place, to like extents but probably in two steps of which a primary displacement of thiosulphate is more predominant than a primary displacement of sulphite. With thiosulphate as the nucleophilic reagent<sup>10,21</sup>, the process is the reverse of the reaction of pentathionate with sulphite (Eqn. (2)) and takes place markedly slower than the displacement of a thiosulphate group of tetrathionate by the same reagent, as represented by Eqn. (6). Displacement of sulphite by sulphide also occurs<sup>32,33</sup>, though to a small extent compared with the simultaneous predominant reaction, which is the displacement of thio-sulphate.

For penta- and hexathionate, the probability, or ease, of reacting according to scheme 2 should be about the same as for tetrathionate. The attacks are on the divalent sulphur atoms situated next to the sulphite groups, so as to displace these, and the length of the sulphur chain on the other side of the electrophilic centre (one, two or three divalent sulphur atoms) should have relatively little influence. With thiosulphate as the nucleophilic reagent, the relevant reactions are, again, the reverse of the reactions of the next higher polythionates with sulphite.

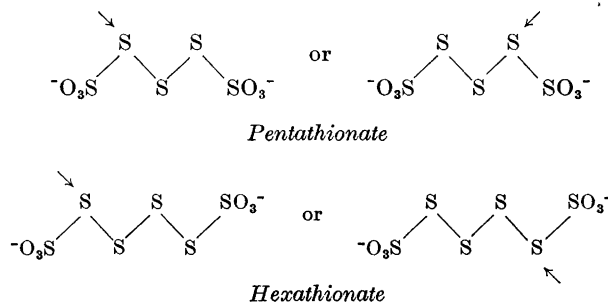
The reversal of the reactions of tetra- and pentathionate with sulphite takes place in acid solutions<sup>34,35</sup>, since under such conditions sulphite is partly removed from the equilibria, as hydrogensulphite. Corresponding reactions of the still higher polythionates were held possible by Kurtenacker and Czernotzky<sup>36</sup>, but Stamm, Seipold and Goehring<sup>34,35</sup> found no evidence for the formation of hexathionate and hydrogensulphite from pentathionate and thiosulphate in acid solutions. Nevertheless, it has been repeatedly maintained<sup>21,29,37</sup> that the reaction of hexathionate with sulphite is reversible, like those of pentathionate and tetrathionate. Preliminary experiments by the author indicate that pentathionate does react with thiosulphate, to give hexathionate and sulphite, if formaldehyde is used as a sulphite acceptor.

Like thiosulphate, other reagents with comparable or greater nucleophilicity towards divalent sulphur, *e.g.*, sulphide, cyanide or thiocarbonyl ions, should be able to displace sulphite from penta- and hexathionate, though in such cases the simultaneous, always predominant displacement of thiosulphate leads to the rapid formation of different species which do not eliminate sulphite. Thiosulphate is unique as a reagent for demonstrations of the less predominant schemes, because its participation in the preferential scheme 1 displacements leaves the polythionate unaltered, except in tracer experiments.

#### ADDITIONAL SCHEMES

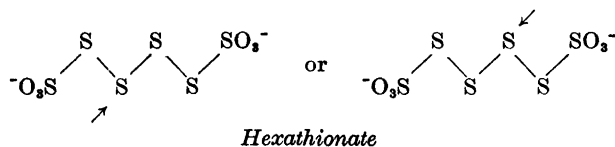
In the case of tetrathionate, schemes 1 and 2 involve attacks at the same electrophilic centre, although in different directions. This is because the two divalent sulphur atoms of tetrathionate are equivalent. In penta- and hexathionate, the two types of attack occur at different centres, corresponding to the presence of two non-equivalent divalent sulphur atoms in these ions. However, attacks on any divalent sulphur atom of the polythionate chains, also of penta- and hexathionate, may in principle occur in two directions, to displace either one of the two groups bonded to the divalent atom.

Accordingly, scheme 3 for penta- and hexathionate involves nucleophilic attacks on the same sulphur atoms as in scheme 2, but in different directions, so as to lead, not to a displacement of sulphite, but of the species  $(S-S_2O_3)^{--}$  and  $(S-S-S_2O_3)^{-}$ , which are unstable and will decompose into thiosulphate and sulphur.



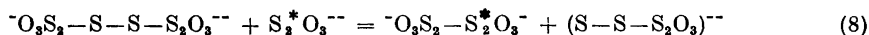
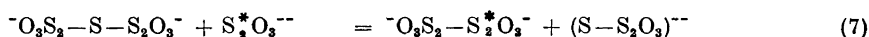
*Scheme 3.* Possible directions of nucleophilic attack on the penta- and hexathionate ions, leading to the release of thiosulphate and one or two sulphur atoms, respectively.

Similarly, scheme 4, which applies to hexathionate only, involves attacks on the same sulphur atoms as in the displacement of thiosulphate according to scheme 1, but in the other one of the two possible directions.



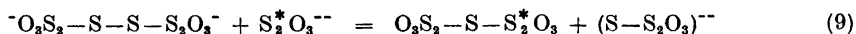
*Scheme 4.* Possible directions of nucleophilic attack on the hexathionate ion, leading to the release of thiosulphate and one sulphur atom.

Concerning these last possibilities, the following points may be made. Scheme 3 requires a heterolysis of the same sulphur-sulphur bond as in scheme 1. The latter represents a predominant type of reaction of the penta- and hexathionate ions, and has been interpreted<sup>4,5</sup> as due to a certain amount of ionic character, or polarity of the  $\sigma$  bond, in the direction of heterolysis. In scheme 3 the heterolysis is required to take place in the opposite direction of that in scheme 1 and thus in the opposite direction of the presumed polarity. Likewise, the electrophilic characters of the bond partners, *i.e.*, of the centres of nucleophilic attack in the two schemes, are probably different, so as, once more, to favour scheme 1. In view of the known tendency of sulphur-sulphur bonds to undergo heterolysis, it does not appear warranted, however, to exclude the possibility that penta- and hexathionate may react according to scheme 3, if acted upon by an appropriate nucleophilic agent. The displacements, even if occurring to a slight extent only, with small equilibrium concentrations of the primary products,  $(S-S_2O_3)^{--}$  and  $(S-S-S_2O_3)^{--}$ , will lead to continuous changes because of the instability and subsequent decomposition of these species, into thiosulphate and sulphur. Thus, with thiosulphate as the nucleophilic reagent, the reactions:



with release of sulphur from the displaced groups, will proceed continuously to the right, and cause a break-down of the penta- and hexathionate ions into tetrathionate.

For hexathionate, the possibility of reacting according to scheme 4 should be greater than for penta- and hexathionate according to scheme 3. The nucleophilic attacks are at the same electrophilic centres as in scheme 1, and the sulphur-sulphur bond required to undergo heterolysis is the middle one, and is thus non-polar, *i.e.*, there is no opposing polarity as probable in scheme 3. In presence of thiosulphate, the process:



should therefore occur more readily than the corresponding reaction (8) of hexathionate and (7) of pentathionate, although slower than the scheme 1 displacement of thiosulphate.

Scheme 4 bears resemblance to scheme 1 for tetrathionate, which also involves heterolysis of the middle sulphur-sulphur bond, and to the heterolytic cleavage of organic disulphides.

It is known that hexathionate, under the catalytic influence of thiosulphate ions, decomposes into pentathionate and sulphur<sup>29,35,38</sup>. Pentathionate, more slowly, decomposes into tetrathionate and sulphur. Whether hexathionate to some extent can decompose directly into tetrathionate, is not clear, since the analytical methods give the average sulphur content only, of hexa-, penta- and tetrathionate mixtures. It appears that the thiosulphate-catalyzed decompositions may be due to primary displacements according to schemes 3 and 4; in particular, the displacements represented by Eqns. (7) and (9). The greater lability of hexathionate as compared with pentathionate would be in accordance with the additional availability of the more probable scheme 4 for hexathionate.

The possibility of scheme 3 displacements as the cause of the catalytic decompositions was pointed out by the author<sup>29</sup> in 1949, but rejected in favour of a mechanism connected with displacements of thiosulphate according to scheme 1. Such displacements "proceed through a transition state, the energy of which is higher than that of the molecules in the initial state. The molecules are labile even in the initial state, and the increase in energy associated with the passing of the transition state serves to decrease the thermodynamic stability and accelerate the decompositions"<sup>29</sup>. The transition state complex, ordinarily unstable along one reaction coordinate only, was in this case thought to be unstable in two directions, *viz.*, in the one leading to displacements, as represented by Eqns. (4) and (5) of the present paper, and in the one leading to the release of sulphur.

Fava<sup>28</sup> in 1953 described the thiosulphate-catalyzed decompositions as due to nucleophilic attacks corresponding to schemes 3 and 4. There appears to be no way in which to decide experimentally between the possibilities. In the related case of iodide and acetate ion catalysis on the decomposition of telluropentathionate, an attack on tellurium, there substituted for the middle sulphur atom of pentathionate, is indicated<sup>29</sup>. However, the different catalysts do not necessarily act by the same mechanism, and in lack of definite information, the fact that thiosulphate does exert a catalytic influence on the decompositions serves as an indication that displacements according to schemes 3 and 4 may be possible.

In concluding, it appears that, as far as the available evidence goes, the more rapid displacement of thiosulphate according to scheme 1 will take place simultaneously with any other displacement, and in most cases dominate the reaction picture. A fuller understanding of the relative importance of the various schemes must await a knowledge of, *e.g.*, the nature of the transition state in nucleophilic displacements on divalent sulphur.

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