Thiosulphate Catalysis on Rearrangements of Higher Polythionates

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The rearrangement of tetrathionate ion into pentathionate and trithionate:

\[ 2 \text{S}_4\text{O}_6^{2-} = \text{S}_5\text{O}_6^{-} + \text{S}_3\text{O}_6^{2-} \]  

(1)
is strongly catalyzed by thiosulphate ion. The catalysis is due to nucleophilic displacements, of sulphite group of tetrathionate by thiosulphate:

\[ \text{S}_4\text{O}_6^{2-} + \text{S}_3\text{O}_3^{-} = \text{S}_4\text{O}_6^{-} + \text{SO}_4^{2-} \]  

(2)
and of thiosulphate group by sulphite:

\[ \text{S}_4\text{O}_6^{-} + \text{SO}_4^{2-} = \text{S}_3\text{O}_6^{-} + \text{S}_2\text{O}_3^{-} \]  

(3)
It is the purpose of the present note to point out that thiosulphate ion should catalyze the rearrangement into a higher and a lower polythionate, not only of tetrathionate but also of pentathionate and higher polythionates:

\[ 2 \text{S}_5\text{O}_6^{-} = \text{S}_6\text{O}_6^{-} + \text{S}_4\text{O}_6^{-} \]  

(4)
\[ 2 \text{S}_4\text{O}_6^{-} = \text{S}_5\text{O}_6^{-} + \text{S}_3\text{O}_6^{-} \]  

(5)
and so forth, through the same two-step nucleophilic displacement mechanism as in the case of tetrathionate. As shown in a previous note, the displacement which would initiate such catalytic rearrangement, i.e., the displacement of a sulphite group of pentathionate and higher polythionates by thiosulphate:

\[ \text{S}_5\text{O}_6^{-} + \text{S}_3\text{O}_6^{-} = \text{S}_5\text{O}_6^{-} + \text{SO}_4^{2-} \]  

(6)
appears to take place with the same or approximately the same rate as for tetrathionate, and the subsequent displacement of a thiosulphate group of another polythionate ion by the sulphite released in the first step:

\[ \text{S}_5\text{O}_6^{-} + \text{SO}_4^{2-} = \text{S}_4\text{O}_6^{-} + \text{S}_2\text{O}_3^{-} \]  

(7)
will occur rapidly.

Thiosulphate ion also catalyzes the change of pentathionate and higher polythionates into lower polythionates, and sulphur. Perhaps therefore, the above thiosulphate catalysis on rearrangements which should simultaneously occur, has not been directly observed. However, apparently pure pentathionate has occasionally been found to rearrange into hexa- and tetrathionate, perhaps because of minute amounts of impurities like thiosulphate, and the formation in a mixture of tetrathionate and thiosulphate, not only of trithionate and pentathionate but also of hexathionate and probably heptathionate, has been demonstrated by Skarzyński and Szczepkowski. The thiosulphate-catalyzed decomposition of pentathionate and higher polythionates into lower polythionates and sulphur may be due to the displacement, in the case of pentathionate:

\[ \text{S}_5\text{O}_6^{-} + \text{S}_3\text{O}_6^{-} = \text{S}_4\text{O}_6^{-} + \text{S} - \text{S}_2\text{O}_3^{-} \]  

(8)
This is then followed by a building-up of dithio- and polythio-thiosulphate ions \( \text{S}_2 - \text{S}_2\text{O}_3^{-} \) from the thio-thiosulphate ion released in the first step, through a series of consecutive nucleophilic displacements of thioulphate by thio-thiosulphate:

\[ \text{S} - \text{S}_2\text{O}_3^{-} + \text{S} - \text{S}_2\text{O}_3^{-} = \text{S}_2 - \text{S}_2\text{O}_3^{-} + \text{S}_2\text{O}_3^{-} \]  

(9)
\[ \text{S}_2 - \text{S}_2\text{O}_3^{-} + \text{S} - \text{S}_2\text{O}_3^{-} = \text{S}_2 - \text{S}_2\text{O}_3^{-} + \text{S}_3\text{O}_6^{-} \]  

(10)
and so forth, with ultimate ring closure to

\[ \text{S}_6 - \text{S}_2\text{O}_3^{-} = \text{S}_6 + \text{S}_3\text{O}_6^{-} \]  

(11)
This building-up process is of the same type as proposed by Davis for the decomposition of acidified thiosulphate (there displacement of sulphite or hydrogenosulphite by thiosulphate). The acids corresponding to the species \( \text{S}_2 - \text{S}_2\text{O}_3^{-} \), the so-called sulphamonomosulphonic acids HS - \( \text{S}_2\text{O}_6\text{H} \), have been prepared and studied by Schmidt; they decompose into sulphur in presence of basic substances, probably due to a reaction sequence analogous to the above, i.e., nucleophilic attack of the terminal divalent sulphur atom of an ion \( \text{S}_2 - \text{S}_2\text{O}_3^{-} \) on a divalent sulphur atom of another, not necessarily ionized species.

The point is that a thiosulphate-catalyzed rearrangement of pentathionate into tetrathionate and hexathionate may occur also as a result of an initial displacement (8) followed by:

\[ \text{S}_3\text{O}_6^{-} + \text{S} - \text{S}_2\text{O}_3^{-} = \text{S}_4\text{O}_6^{-} + \text{S}_2\text{O}_3^{-} \]  

(12)
and correspondingly for rearrangements of still higher polythionates. In fact, any species \( \text{S}_2 - \text{S}_2\text{O}_3^{-} \), occurring in the sequence (8) - (11) or released directly from a polythionate, should be expected to attack a polythionate chain to give another polythionate, preferably a higher one since thiosulphate probably is the better leaving group relative to a thio-dithio- or poly-

thio-thiosulphate group. The $\text{S}_2\text{O}_3^{2-}$ ions are probably stronger nucleophiles than thiosulphate ion, in accordance with the lower strength of the corresponding $\text{SH}$ acids the longer the distance from the sulphonate group.

The above interactions of thiosulphate and polythionate ions, leading to rearrangements or decompositions, involve the displacement of a sulphite group of tetra-thionate or higher polythionate by thiosulphate, eqns. (2) and (6); of a thio-thiosulphate group of pentathionate or higher polythionate, eqn. (8); of a dithio-thiosulphate group of hexathionate or higher polythionate. The various modes of heterolysis of the sulphur-sulphur bonds of the tetra-, penta- and hexathionate ions in reactions with nucleophilic reagents have been discussed; the preferred, more rapid displacement appears to be that of thiosulphate, as for example in the second step of the rearrangements, eqns. (3), (7) and (12) above.


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On the Oxidation of Diselenenides and Related Compounds

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As a result of a number of recent investigations, it has been shown that disulphides are oxidized to thiosulphinates ($\text{R}—\text{SO}—\text{S}—\text{R}$) under mild conditions. In addition, Calvin and his co-workers have found that $\text{a}$-lipoic acid (I) is oxidized to the corresponding thiosulphinate (II) by ammonium persulphate under conditions in which non-cyclic disulphides are not attacked; this demonstrates the increased reactivity associated with the 1,2-dithiolane ring. Further oxidation of the thiosulphinates generally gives thiosulphonates ($\text{R}—\text{SO}_2—\text{S}—\text{R}$), although it has been supposed that this reaction occurs via fission of the sulphur-sulphur bond.

It has been reported that diselenenides are oxidized directly to seleninic acids ($\text{R}—\text{SeO}_2\text{H}$), and although several attempts to detect lower oxidation products have been made, none have ever been found. The instantaneous conversion of diselenenides to seleninic acids by reaction with bromine in aqueous solution has been clearly demonstrated by Fredga using polarimetric methods.

In a comparative study of the properties and reactions of simple molecules containing the $\text{S}—\text{S}$, $\text{Se}—\text{S}$, or $\text{Se}—\text{Se}$ bonds, the

![Chemical structures](image-url)