

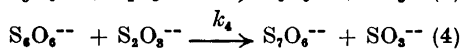
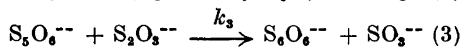
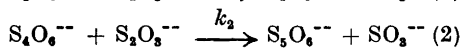
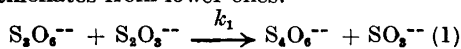
Displacement of Sulphite Groups of Polythionates by Thiosulphate

OLAV FOSS and IVAR KRINGLEBOTN

*Chemical Institute, University of Bergen,
Bergen, Norway*

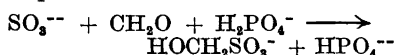
Polythionate ions higher than trithionate react with sulphite ion to give the next lower polythionate, and thiosulphate¹. In these reactions, which are nucleophilic displacements of thiosulphate groups of polythionates by sulphite^{2,3}, a shortening of the divalent sulphur chain of the polythionates takes place.

The reverse reactions, *i.e.*, nucleophilic displacements of sulphite groups of polythionates by thiosulphate^{4,5}, correspondingly lead to a building-up of higher polythionates from lower ones:



and so forth. The equilibria lie to the left side of the equations, and so the building-up process occurs only if sulphite is removed from the equilibria, as hydrogensulphite or sulphurous acid under acid conditions¹, or by means of formaldehyde⁶.

We have studied the kinetics of the reaction of potassium tetrathionate with sodium thiosulphate, eqn. (2), between 20 and 40°C in presence of formaldehyde as sulphite acceptor, in phosphate buffer to prevent the solutions from becoming alkaline. In presence of excess of formaldehyde the second step of the change, *i.e.*, the removal of sulphite as hydroxymethane sulphonate:



is more rapid than the first step (2) as indicated by the fact that variation in the amount of formaldehyde present (from *ca.* 0.13 M to *ca.* 0.26 M) had no influence on the rate. Neither had the addition of potassium hydroxymethane sulphonate, or variation of pH by half a unit to both sides of pH = 6.8. The reaction proceeds without change of ionic strength. It shows a positive salt effect, as expected for a reaction between ions of the same sign in the rate-

determining step (2). Therefore, the experiments were carried out at a constant ionic strength of 1.15 adjusted with sodium sulphate.

The rate of disappearance of thiosulphate, as followed by iodometric titration, was found to be:

$$-dS_2/dt = k_2 a S_2 \quad (5)$$

where S_2 is the concentration of thiosulphate at time t and a is the *initial* concentration of tetrathionate. Integration, when $S_2 = b$ at $t = 0$, gives:

$$S_2 = b \exp(-k_2 a t) \quad (6)$$

At 25°C and an ionic strength of 1.15, $k_2 = 1.3 \times 10^{-3}$ l.mole⁻¹sec⁻¹, when a has been varied from 0.05 to 0.10 M and b from 0.025 to 0.05 M. The activation parameters are: $E_a = 12.0$ kcal/mole, $\Delta H^\ddagger = 11.4$ kcal/mole and $\Delta S^\ddagger = -34$ cal/mole degree.

We interpret this rate law as indicating that the pentathionate formed in the first step (2) from tetrathionate and thiosulphate, reacts with thiosulphate to give hexathionate, eqn. (3), which then reacts with thiosulphate to give heptathionate, eqn. (4), and so forth, with the same or approximately the same bimolecular rate constants: $k_2 \sim k_3 \sim k_4$. Thus, through successive S_N2 displacements of sulphite by thiosulphate, in presence of a sulphite acceptor, a building-up of higher polythionates from tetrathionate and thiosulphate takes place.

Analysis of the reaction mixtures by the sulphite method⁶ showed that the sum of unreacted thiosulphate and thiosulphate produced by reaction with excess sulphite remained constant. The formation of pentathionate and hexathionate when solutions of thiosulphate and tetrathionate are mixed with simultaneous addition of formaldehyde has been demonstrated by a paper chromatographic method by Skarżyński and Szczepkowski⁷.

A series of consecutive steps with equal rate constants gives for the rates of disappearance of thiosulphate and tetrathionate:

$$-dS_2/dt = k_2 S_2 (S_4 + S_5 + S_6 + S_7 + \dots) \quad (7)$$

$$-dS_4/dt = k_2 S_2 S_4 \quad (8)$$

and for the rates of formation of pentathionate and higher polythionates:

$$dS_5/dt = k_2 S_4 S_2 - k_2 S_5 S_2 \quad (9)$$

$$dS_6/dt = k_2 S_5 S_2 - k_2 S_6 S_2 \quad (10)$$

$$dS_7/dt = k_2 S_6 S_2 - k_2 S_7 S_2 \quad (11)$$

where S_4, S_5, S_6, S_7 denote the concentrations of tetra-, penta-, hexa-, heptathionate, respectively, at time t . Here, $S_4 + S_5 + S_6 + S_7 + \dots = a$, so that eqn. (7) becomes equal to eqn. (5). Integration of eqn. (8), inserting eqn. (6) and putting $S_4 = a$ at $t = 0$ gives:

$$S_4 = a \exp(-x/a) \quad (12)$$

where $x = b - S_2$ is the amount of thiosulphate reacted in moles per liter at time t . Successive integrations of eqns. (9), (10) and (11), with conditions $S_5 = S_6 = S_7 = 0$ at $t = 0$, lead to:

$$S_5 = S_4 \frac{x}{a}; S_6 = S_4 \frac{x^2}{2a^2}; S_7 = S_4 \frac{x^3}{6a^3}$$

where S_4 is given by eqn. (12). The general form of the expressions can be seen to be:

$$S_{4+n} = S_4 \frac{x^n}{n!a^n}$$

and the sum of polythionate concentrations becomes:

$$S_4 \left[1 + \frac{x}{a} + \frac{x^2}{2a^2} + \frac{x^3}{6a^3} + \frac{x^n}{n!a^n} + \dots \right]$$

The series in the bracket is the expansion of $\exp(x/a)$ so that the sum, by eqn. (12), is equal to a as should be.

Thus at any time t , the ratios of the concentrations of successively higher polythionates to that of tetrathionate are as the successively higher terms in the above series expansion of $\exp(x/a)$. The reactions were in some cases followed up to about $x/a = 0.2$ but not longer, since then often liberation of sulphur set in, probably as a result of thiosulphate-catalyzed decompositions of pentathionate and higher polythionates. At such a stage:

$$S_4 : S_5 : S_6 : S_7 = 1 : 0.2 : 0.02 : 0.0013$$

That is, the pentathionate reacting in the second step (3) amounts to 20% of the tetrathionate present, the hexathionate reacting in the third step (4) to 2% while the amount of heptathionate present is negligible. The kine-

tics followed eqn. (6) within the accuracy of the iodometric titrations up to this value of x/a . Unless reactions or effects not considered here influence the picture, the amount of pentathionate then present should be large enough to show that k_3 can not differ much from k_2 .

Experiments on the reaction of potassium trithionate with sodium thiosulphate, eqn. (1), in presence of formaldehyde under the same conditions as employed for tetrathionate, indicate that, at 25°C and an ionic strength of 1.15, the bimolecular rate constant $k_1 = 1.1 \times 10^{-4}$ l.mole⁻¹sec⁻¹. Thus, the first step in the reaction sequence (1) — (4) is markedly slower than the subsequent ones. This confirms the findings of Fava and Pajaro⁸: $k_1 = 6.2 \times 10^{-4}$ l.mole⁻¹sec⁻¹ at 51°C and $\mu = 0.816$ from the rate of isotopic exchange of trithionate with thiosulphate, and Fava and Bresadola⁹: $k_2 = 3.9 \times 10^{-3}$ l.mole⁻¹sec⁻¹ at 50°C and $\mu = 0.94$ from the rate of thiosulphate-catalyzed rearrangement of tetrathionate.

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