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The Iodine-Azide Reaction

VI. The Catalytic Effect of Monoseleno- and Monotelluropentathionate Ions

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Keeping in mind that, according to Foss [1], pentathionate ions must be assumed to be monosulphur di(thiosulphate) ions, it was also to be expected that monoseleno and monotelluro di(thiosulphate) ions would show a strong catalytic effect on the reaction between azide ions and iodine.

Sodium selenopentathionate, $Na_2Se(S_2O_3)_2 \cdot 3\ H_2O$, and sodium telluropentathionate, $Na_2Te(S_2O_3)_2 \cdot 2\ H_2O$, were prepared and analyzed as outlined by Foss [2, 3].

Firstly kinetic experiments were carried out in the same way as with potassium pentathionate [4]: Into a flask containing a solution of sodium azide, iodine, and starch indicator, was pipetted 10 ml 0.0002 *M* sodium selenopentathionate. Already before this solution had completely run down into the flask, all the iodine present had been consumed with a brisk evolution of nitrogen. In case of potassium pentathionate, the corresponding time of reaction was 3.18 min (ref. 4, Expt. no. 1, Table 1). A similar experiment was then carried out with 10 ml 0.00002 *M* sodium selenopentathionate solution. In this case some of the iodine was consumed immediately, thereafter nothing more happened. The two experiments show that selenopentathionate ions, when catalyzing the iodine-azide reaction, immediately are converted into substances, which are relatively inactive towards this reaction. The substances are presumably selenious acid, tetrathionate, and sulphate; at least, these three compounds could be detected after the iodine-azide reaction had taken place.

Since solutions of potassium tetra- and pentathionate react with sodium azide with the evolution of nitrogen, it was to be expected that a similar reac-

tion would take place between selenopentathionate and azide ions. This was also the case. At the same time a considerable amount of red selenium was formed. The gas was analyzed according to Christiansen and Wulff [5]; the result was 99.8 % nitrogen and 0.2 % oxygen.

Telluropentathionate was known to undergo immediate decomposition when catalyzing the iodine-azide reaction, because it is readily oxidized by iodine, to give tellurous acid and tetrathionate [3].

However, it was possible to compare the catalytic power of seleno- and telluropentathionate with that of thiosulphate by simple titrations: Into a 500 ml Erlenmeyer flask was pipetted 10 ml 0.01 *N* iodine, which was 0.02 *M* with respect to potassium iodide, 10 ml 0.1 *M* sodium azide, 1 ml 0.5 % starch solution; and water up to a total volume of 200 ml was added. This mixture was titrated by dropwise addition of thiosulphate, and, alternatively, seleno- and telluropentathionate solutions, until all iodine was consumed. The addition was performed at a rate of approximately one drop per two seconds, and the reaction mixture was briskly swirled by hand during the addition.

Table 1. The catalytic effect of seleno- and telluropentathionate on the iodine-azide reaction compared with that of thiosulphate. Temp.: ~ 20° C.

Solutions used for the titration	Amount of solution used for the titration ml		
10^{-3} *M* thiosulphate	13.87	14.03	14.37
10^{-3} *M* selenopentathionate	3.54	3.65	3.61
5.10^{-4} »	7.58	6.70	7.16
10^{-3} *M* telluropentathionate	3.56	3.66	3.62
5.10^{-4} *M* »	6.76	7.24	6.95

The results (Table 1) in duplicate runs did not agree too well, but that was presumably due to sensitiveness to variation in experimental method (method of adding the solutions and mode of stirring). Dodd and Griffith [6] also found that same sensitiveness when carrying out similar experiments with thiosulphate as the catalyst. However, it was obvious that seleno- and telluropentathionate showed quantitatively the same catalytic effect, which

was larger than that of thiosulphate. In all three cases tetrathionate and sulphate were found after the reaction had taken place. This seemed to indicate that the catalytic effect of seleno- and telluropentathionate was caused by liberated thiosulphate ions. Dodd and Griffith [6] found that when titrating a solution of iodine and sodium azide with thiosulphate, the ratio R (moles I_2 consumed/moles $Na_2S_2O_3$ consumed) increased with decreasing concentration of thiosulphate. The reason why seleno- and telluropentathionate are found to be more catalytically active than thiosulphate, could possibly be that, in a short interval of time, they are the source of a very small thiosulphate concentration.

SUMMARY

The catalytic effect of monoseleno- and monotelluropentathionate ions toward the iodine-azide reaction was found to be larger than that of thiosulphate ions. Seleno- and telluropentathionate ions are decomposed immediately when acting as catalysts, and their effect seems actually to be a thiosulphate catalysis.

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