KINETICS OF SOME REDOX REACTIONS OF TECHNETIUM

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Recently the interest in RedOx reactions of technetium became stronger mainly for the reason that the ions of this element negatively affect the stability of reductants in HNO_3 solutions that are used for extraction spent nuclear fuel reprocessing. Specifically, Tc(VII) accelerates the HNO_3 oxidation of U(IV) and hydrazine.

Earlier [1,2] we studied the kinetics of the Tc(VII) reduction with U(IV), hydrazine, ascorbic acid, Pu(III), the Tc(IV) and Tc(V) oxidation with nitric and nitrous acids, the reactions of Tc(V) disproportionation and reproportionation. In this paper we would like to give data on the rates of some technetium reactions that were not investigated earlier.

The Tc(VII) and Tc(IV) reduction with hydrazine in a HCl solution at a high reductant excess and high temperature (80°C) leads to a formation of a Tc(II) cluster [3,4]. As distinct from these reactions, upon the Tc(VII) interaction with hydrazine derivatives, namely, oxyethylhydrazine, the final reaction product is Tc(IV):

$$2TcO_4^- + 3HOC_2H_4N_2H_4^+ + 10Cl^- + 7H^+ = 2TcCl_5^- + 3C_2H_5OH + 3N_2 + 8H_2O \qquad (1)$$

The rate of this reaction is a HCl solution at the ionic strength $\mu = 3.1$ obeys the equation:

$$-d[Tc(VII)] / dt = k[Tc(VII)][HOC_2H_4N_2H_4^+]^{0.9}[H^+]^{1.4} \qquad (2)$$

where $k = (8.75 \pm 0.46)\cdot 10^{-3}$ $l^{2.3}/mole^{2.3}\cdot min$ at 25°C. The agreement between the orders of the Tc(VII) reactions with hydrazine and oxyethylhydrazine points to their common mechanism that involves the interaction between reductant protonated ions and TcO_4^- and TcO_3^+ ions at parallel slow stages.

Of other reactions of Tc(VII) reduction Cl- ion and sulphurous acid reactions were studied briefly. The former of these reactions is commonly used to produce Tc(V):

$$TcO_4^- + 7HCl = TcOCl_5^{2-} + Cl_2 + H^+ + 3H_2O \qquad (3)$$

The reaction is of an autocatalytic nature and its rate is described by the equation:

$$d[Tc(V)] / dt = k_1[Tc(VII)][HCl] + k_2[Tc(VII)][Tc(V)] \qquad (4)$$

where $k_1 = 2.3\cdot 10^{-3}$ l/mole·min and $k_2 = 700$ l/mole·min at [HCl] = 6 mole/l and 80°C.

Upon the interaction with sulfurous acid Tc(VII) is reduced to Tc(IV):

$$2TcO_4^- + 3H_2SO_3 + 10HCl = 2TcCl_5^- + 3H_2SO_4 + 5H_2O \qquad (5)$$