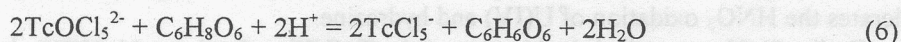


at the rate controlled by the constant $k=4.2 \cdot 10^{-2} \text{ min}^{-1}$ in 2 mole/l HCl solution at $[\text{H}_2\text{SO}_3] = 0.1 \text{ mole/l}$ and 60°C .

The final product of the formerly studied Tc(VII) reactions with ascorbic acid [5] and U(IV) [6] is Tc(IV) and the transition of Tc(V) to Tc(IV) under the experimental conditions (high concentration of a reductant) proceeds quickly. By bringing down the concentration of the reductant one succeeds in determining the rates of those quick reactions. Specifically, the reaction:



follows the kinetics equation

$$d[\text{Tc(IV)}] / dt = k[\text{Tc(V)}][\text{C}_6\text{H}_8\text{O}_6][\text{H}^+] \quad (7)$$

where $k = 280 \pm 30 \text{ l}^2/\text{mole}^2 \cdot \text{min}$ at 25°C and $\mu = 2$.

The apparent slowing down and deviation from equation (7) by the end of the reaction is explained by an increase of the Tc(IV) optical density (which was used to follow the reaction course) due to a side reaction of anation:



The specific feature of the quick reaction



is a change of its order relative to Tc(V) from the first to the second one with an increase of the reagent concentration and temperature. In this case the rate of reaction (9) obeys the equation:

$$\frac{d[\text{Tc(V)}]}{dt} = \frac{k[\text{Tc(V)}]^2[\text{U(IV)}]}{[\text{H}^+]} \quad (10)$$

where $k=1.5 \cdot 10^5 \text{ l/mole} \cdot \text{min}$ at 25°C and $\mu = 2$ and the activation energy is $\sim 105 \text{ kJ/mole}$.

Equation (10) agrees with the assumption of an intrasphere charge transfer in the ionic pair formed by the equation:



The alternative hypothesis of Tc(V) disproportionation as a limiting stage of reaction (9) is unsound, since under the experimental conditions ($[\text{H}^+] \geq 1 \text{ mole/l}$) the Tc(V) disproportionation proceeds at the lowest rate [7].

The reaction of the Tc(V) \rightarrow Tc(VII) oxidation proceed at a high rate, specifically, it results to reactions of Tc(V) with HNO_2 and HNO_3 [8,9]. Based on the latest data it is to be