

Analysis of the reduction mechanisms of technetium in NaClO₄ combining spectro-electrochemical methods and electrochemical analysis

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The reduction of technetium (Tc) from Tc(VII) to Tc(IV) in NaClO₄ solution has been studied as a function of pH by spectro-electrochemical methods and electrochemical analysis. The results show that the reduction of Tc(VII) to Tc(IV) occurs directly at pH > 4, whereas it goes through a Tc(V) intermediary species at pH 2.

⁹⁹Tc is a long-lived fission product ($\tau_{1/2} \sim 2.14 \times 10^5$ years) of ²³⁵U and ²³⁹Pu. Tc migration in ground water is highly dependent on its oxidation state. The reduction of Tc(VII)O₄⁻ to Tc(IV) hampers Tc migration since either a low soluble solid (TcO₂) and/or cationic species ready to interact with minerals are formed. This reduction step is electrochemically induced or by reductants such as Fe(II)- or S(-II)-minerals.^[1-3] However, the molecular mechanisms of this step had not been yet fully understood. Despite the clear environmental relevance, this is important from a fundamental chemical point of view. In this work, we have explored the reduction mechanism of Tc(VII) in non-complexing NaClO₄ solutions by spectro-electrochemical methods, Raman microscopy, X-ray photoelectron spectroscopy (XPS), and electrochemical analysis.^[4]

EXPERIMENTAL. Solutions of 0.5 mM K₂Tc(VII)O₄ solutions were analyzed. The electrodes used in the electrochemical procedures were glassy carbon electrode as working electrode (both in stationary or rotational mode), platinum as counter electrode, and Ag/AgCl (3 M KCl) as reference electrode. Tc(VII) electrochemical reduction was monitored in parallel by UV-vis spectroscopy in an N₂ glovebox.^[5] Cyclic voltammetry (CV) was performed at five different scan rates (from 5 to 25 mV/s) at pH 2.0 and pH 10.0. The current of the peaks associated to reduction processes (cathodic peaks) in a window of potential interest were scanned using a rotating disc electrode at six angular velocities (from 100 to 3,000 rpm) (884 Professional VA instrument, Metrohm). The precipitate obtained in the electrochemical reduction was analyzed by Raman spectroscopy (Aramis, Horiba), and by XPS (PHI 5000 VersaProbe II, ULVAC-PHI Inc.).

RESULTS. Figure 1 shows the CV performed in Tc solutions at pH 2.0 and pH 10.0 at different scan rates. CV carried out from pH 4.0 to 8.0 are comparable to that recorded at pH 10.0. It is observed that the number of peaks present in the CV is dependent on pH, which is related to a change in the number of electroactive species. As well, in the range from -0.9 to +1.2 V, a change is observed in the potential values related to oxidation and reduction processes. Spectro-electrochemical reduction experiments at pH 2.0 and pH 10.0 show a decrease on the intensity of the Tc(VII)O₄⁻ signals at 247 and 289 nm, but no additional bands are observed. In the electrochemical reduction experiments, the formation of a solid is observed at both pH values.^[4] XPS identified Tc(IV) in the solids, which also present two characteristic peaks in the Raman spectra (374 and 1107 cm⁻¹).^[4] Thus, with the aim to analyze the reduction mechanism of Tc(VII) at pH 2.0 and 10.0, we have measured the current for potentials in the region of interest of cathodic peaks using a rotating disk electrode. Randles-Sevcik and Levich equations were applied to the results to determine the number of

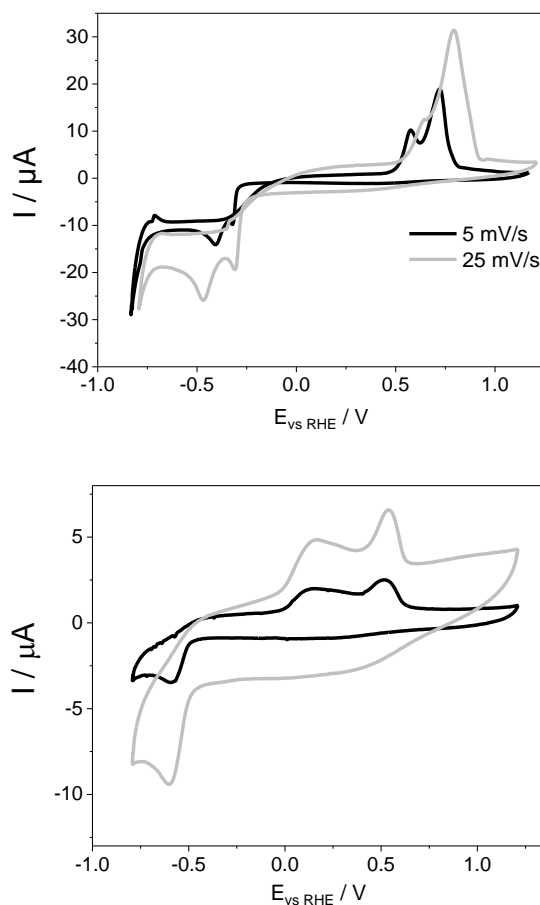


Figure 1. Cyclic voltammograms of 0.5 mM K₂TcO₄ solutions at pH 2.0 (top) and pH 10.0 (bottom). Potential values have been converted to those for reversible hydrogen electrode (RHE).

electrons exchanged and the diffusion coefficient of the electroactive species, respectively. Details are given elsewhere.^[4] At pH 2.0, the reduction occurs in two steps with the initial gain of 2.3 ± 0.3 electrons by Tc(VII) to obtain Tc(V), which subsequently receives 1.3 ± 0.3 electrons to form Tc(IV). At pH 10.0 Tc(VII) is directly reduced to Tc(IV) with the transfer of 3.2 ± 0.3 electrons.

These results narrow a significant gap in the fundamental knowledge of Tc aqueous chemistry and are important to understand Tc speciation. They provide basic steps on the way from non-complexing to complex media.

ACKNOWLEDGEMENTS. Funding from the Federal Ministry for Economic Affairs and Climate Action (BMWK) is acknowledged (02E11607B).

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