CAPSULES
preliminary notes and applications from Bioanalytical Systems, Inc.

Potentiostatic Measurements of a Tc(III)/Tc(II) Couple Using an OTTLE Cell

Purpose

The formal redox potentials ($E^{o'}$) and electron stoichiometries (n) of the reduction of the Tc(III) complexes $[Tc(dmpe)_2X_2]^+$ (dmpe = 1,2-bis(dimethylphosphino)ethane; X = Cl, Br) (F1) were measured to confirm that these were one electron reductions. In addition, comparison of the formal redox potentials for the different halide shows how the weaker π-donor ability of Br affects the ease of reduction.

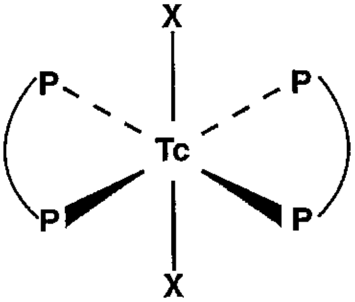

Figure 1. Structure of $[Tc(dmpe)_2Cl_2]^+$.

Reference

Technetium Electrochemistry. 2. Electrochemical and Spectroelectrochemical Studies of the Bis(tertiary phosphine) (D) Complexes *trans*-$[Tc^{III}D_2X_2]^+$ (X = Cl, Br) and $[Tc^{I}D_3]^+$, A. Ichimaru, W. R. Heineman, J-L. Vanderheyden and E. Deutsch, Inorg. Chem. 23 (1984) 1272 - 1278.

Method

This method is based on the variation of the electrode surface concentrations (C^S_O and C^S_R) of the oxidized and reduction components of a redox couple with the applied potential E, as required by the Nernst equation

$$E = E^{o'} + \log(59/n)(C^S_O / C^S_R)$$

The cell used for electrolysis was a spectroscopic cell containing an Optically Transparent Thin Layer (working) Electrode (OTTLE), F2 (which is either a fine metallic mesh or a thin metallic layer on an optically transparent material) (1,2). This allows the spectroscopic monitoring of the electrolysis process i.e. the electrolysis is carried out in the spectrometer. In the potentiostatic experiment, the potential is changed in several steps from a value at which no electrolysis occurs to a value at which there is complete conversion to another oxidation state. The potential is held at each value until there is equilibration of the solution concentrations of O and R, which are then measured spectroscopically (i.e. the solution concentrations are the same as the electrode surface concentrations required by the applied potential). Since the cell volume is small, only a short time is required for equilibration at each potential (a few minutes). A plot of E vs. $\log(C^S_O / C^S_R)$ has a gradient of 59/n mV and an intercept of $E^{o'}$ on the E axis. Although cyclic voltammetry is a much easier method for measuring $E^{o'}$ and n (indeed, the range of potentials used is calculated from the cyclic voltammogram), potentiometry is a way to confirm these values.

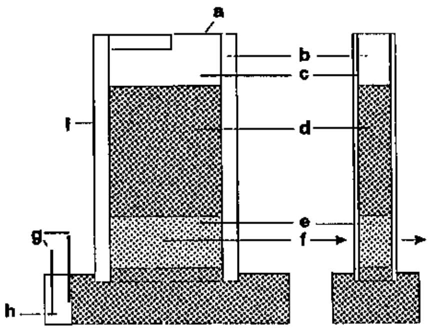

Figure 2. Optically transparent thin layer electrode cell. a) point of suction application to change solution b) Teflon tape spacers c) microscope slides d) solution e) transparent gold minigrid f) optical path of spectrometer g) reference and auxiliary electrodes h) solution cup and i) epoxy holding cell together (2).

Results

F3 shows the UV-vis spectra of $[Tc(dmpe)_2Cl_2]^+$ at different potentials. The Tc(III) complex shows an absorption maximum at 469 nm, whereas the maximum for the Tc(II) complex is at 414 nm. The different spectra show how the concentrations of O and R vary with the applied potential. The isosbestic point indicates clean interconversion between the different oxidation states. F4 shows the plot of the Nernst equation using concentrations derived from the absorption at 469 nm. As expected, this is a straight line, and gives values of n = 0.95 and $E^{o'}$ = -0.232 V (vs. Ag/AgCl) (compared with the value of -0.231 V from cyclic voltammetry measurements). The more positive value for the Br analogue (-0.108 V) is consistent with the poorer π-donor ability of Br compared with Cl.

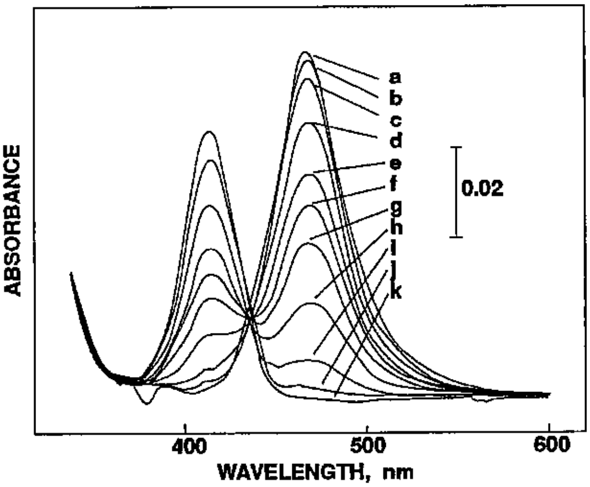

Figure 3. Spectra recorded during the spectropotentiostatic experiment on $[Tc(dmpe)_2Cl_2]^+$ for various applied potentials (a = 0.0 V, k = -0.450 V).

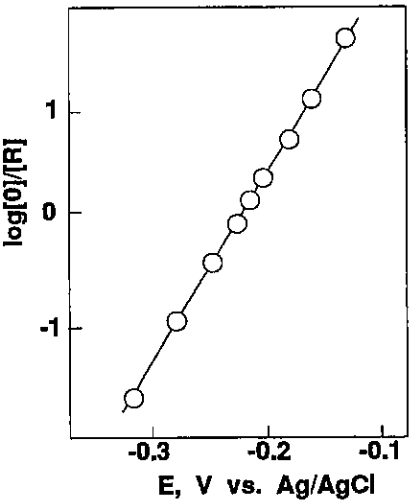

Figure 4. Nernst plot of data at 469 nm from Figure 3.

Additional References

1) W. R. Heineman, J. Chem. Ed. 60 (1983) 305 - 308.

2) T. P. DeAngelis and W. R. Heineman, J. Chem. Ed. 53 (1976) 594 - 597.