CAPSULES
preliminary notes and applications from Bioanalytical Systems, Inc.

Reductive Dimerization of $Cp^*W(NO)I_2$

Purpose

The organometallic complex $Cp^*W(NO)I_2$ (F1) reacts with nucleophiles to give a range of products, both monomeric and dimeric. It has been proposed that the radical anion $[Cp^*W(NO)I_2]^{\cdot -}$ is an intermediate in these reactions. This proposal was investigated by examining the reactivity of this radical using cyclic voltammetry.

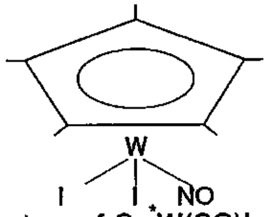

Figure 1. Structure of $Cp^*W(CO)I_2$

Reference

Reduction Behavior of the Complexes $Cp'M(NO)X_2$ (Cp' = Cp (η_5-C_5H_5) or Cp^* (η_5-C_5Me_5); M = Mo or W; X = Cl, Br, or I): Synthesis and Characterization of the $[Cp'Mo(NO)X_2]^-$ Radical Anions, F. G. Herring, P. Legzdins and G. B. Richter-Addo, Organometallics 8 (1989) 1485 - 1493.

Method

Cyclic voltammetry is a very useful method for investigating the reactions of electrogenerated intermediates, since the intermediate can be produced on the forward scan, and its fate can be examined on the reverse and subsequent scans. Quantitative kinetic data on the rate of reaction of these intermediates can be obtained from cyclic voltammograms, although other techniques (e.g., chronocoulometry) are generally preferred.

Results

The cyclic voltammograms of $[Cp^*W(NO)I_2]$ at different scan rates is shown in F2. At a scan rate of 2.64 V/s (F2a), the reduction is reversible. However, as the scan rate is decreased to 0.13 V/s (F2b), the ratio of the anodic peak current to the cathodic peak current (i_{pa}/i_{pc}) decreases (i.e., there is less of the radical anion available for oxidation on the reverse scan). This is consistent with a Chemical reaction following the Electron transfer - an EC process (the slower the scan rate, the more time there is available for the chemical reaction). The appearance of another redox process (due to the product of the chemical reaction) at a more negative potential is further evidence for an EC process. This product was shown to be $[Cp^*W(NO)I]_2$ by comparison with the cyclic voltammogram of this known dimer. It was suggested that dissociation of I^- from the radical anion was the rate determining chemical reaction, which was followed by dimerization of two of the electron-deficient radicals.

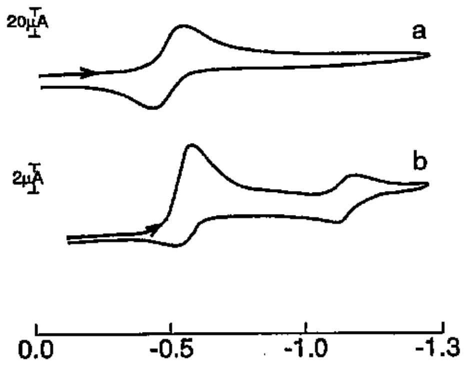

Figure 2. Cyclic voltammograms of $Cp^*W(NO)I_2$ in CH_2Cl_2 (0.5 mM) at room temperature. Scan rates = 2.64 V/s (a), 0.13 V/s (b), supporting electrolyte 0.1 M $[^nBu_4N][PF_6]$. All potentials measured with reference to the SCE. Figure adapted from Reference.

Since the size of the oxidation peak associated with the reduction of the monomer depends on the rate of the chemical reaction relative to the experimental timescale, the rate of change of the peak current ratio with the scan rate can be used to estimate the rate of I^- dissociation. A plot of i_{pa}/i_{pc} vs. scan rate is shown in F3. Working curves are available that relate such plots to the rate constant (1), and a range of values from 0.94 to 1.46 s^{-1} was obtained. A major problem with this method is the measurement of the anodic peak current, due to the uncertainty in determining the baseline anodic current.

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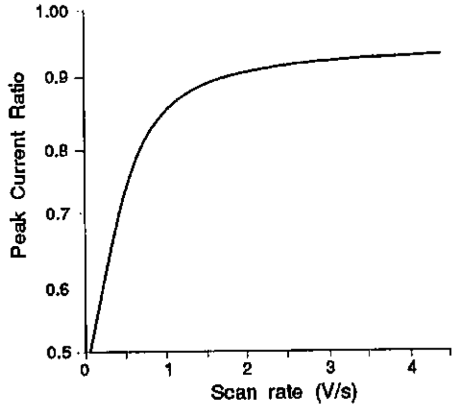

Figure 3. Variation of the peak current ratio (i_{pa}/i_{pc}) with scan rate. Figure adapted from Reference.

F4 shows the variation of i_{pa}/i_{pc} with temperature. The peak current ratio increases with decreasing temperature. This is due to the decreased rate of the chemical reactions at low temperatures.

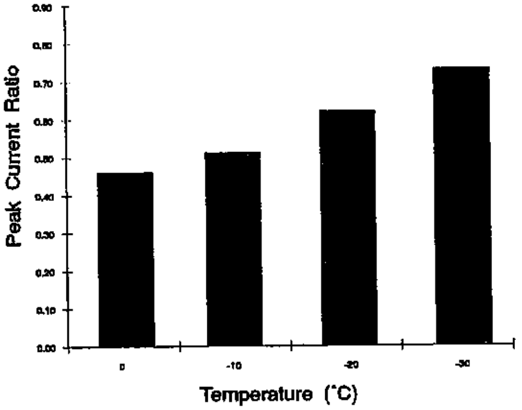

Figure 4. Variation of the peak current ratio (i_{pa}/i_{pc}) with temperature at a scan rate of 0.14 V/s. Figure adapted from Reference.

Additional Reference

1) R. S. Nicholson and I. Shain, Anal. Chem. 36 (1964) 706 - 721.