CAPSULES
notes and applications from Bioanalytical Systems, Inc.

Investigation of E-Z Isomerization of Iron Alkenyl Complexes Using Semi-Derivative Voltammetry

Introduction

Cyclic voltammetry is a powerful technique for the qualitative investigation of the reactivity of redox active molecules. Although the technique is simple, the presentation and interpretation of data is often complicated. One way of improving the current-potential (I-E) diagram is to plot the semi-derivative of the current (sometimes called deconvolution voltammetry). This operation decreases the peak width (the peak is symmetrical rather than tailed), which improves resolution. A comparison of cyclic and semi-derivative voltammograms is shown in F1 (1).

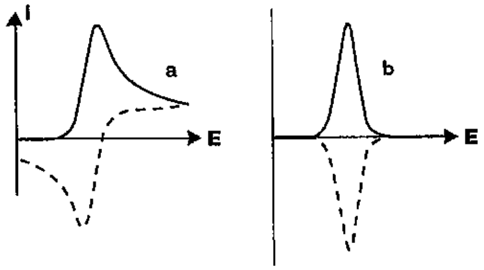

Figure 1. Comparison of a) cyclic and b) semi-derivative voltammograms (1).

One system that has been examined using deconvolution voltammetry is the oxidative isomerization of iron alkenyl complexes (F2). This occurs in the presence of a catalytic amount of an oxidizing agent at -78 °C (but does not happen in the absence of oxidizing agents). Cyclic and semi-derivative voltammograms were recorded at different temperatures for different mixtures of the E and Z isomers, using the semi-derivative output option of the BAS CV-27.

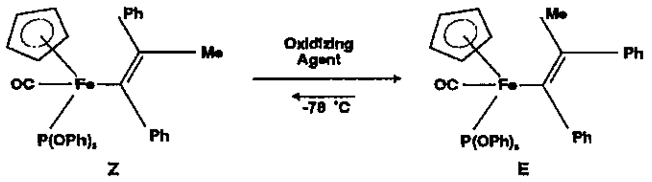

Figure 2. Structures and interconversion of E and Z isomers of the iron alkenyl complex.

Reference

Multiple Temperature Electrochemical Studies of the Oxidatively Catalyzed E-Z Isomerization Reactions in Iron Alkenyl Complexes. Improved Resolution of Closely Spaced Redox Systems Using Deconvolution Voltammetry, R. H. Philp, D. L. Reger and A. M. Bond, Organometallics 8 (1989) 1714 - 1718.

Results

At room temperature, all the different mixtures of E and Z isomers showed the same cyclic and the same semi-derivative voltammograms due to rapid interconversion of the isomers. At -87 °C, the two isomers can be differentiated. F3 shows the cyclic and semi-derivative voltammograms of the equilibrium mixture at this temperature (the ratio of E:Z is ca. 4.7:1 from NMR). The improved resolution of the semi-derivative voltammogram is apparent. The first oxidation is due to the Z isomer, and the larger oxidation peak is due to the E isomer. However, relative sizes of the reduction peaks are reversed. This shows that there is rapid conversion of the E^+ isomer to the Z^+ isomer on the timescale of the voltammetric experiment (i.e., oxidizing the complex reverses the relative stabilities of the two isomers).

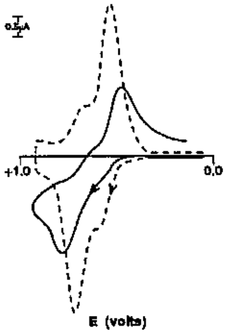

Figure 3. Cyclic (solid line) and semi-derivative (dotted line) voltammograms of an equilibrium mixture of the E and Z isomers in CH_2Cl_2 (0.5 mM) at -87 °C. Scan rate = 400 mV/s, supporting electrolyte is 0.1M [$^nBu_4N$][PF_6]. All potentials measured with reference to Ag/AgCl. Figure adapted from ref. 1.

These results show that the basis for the catalytic isomerization is the rapid interconversion of the oxidized isomers. A scheme for the formation of the E isomer from the Z isomer is shown in F4. Although Z geometry is more favorable than the E geometry for the oxidized molecule, the redox potentials are sufficiently close that there is a small but significant amount of the E^+ isomer rapidly formed when the Z isomer is oxidized. The E isomer is then formed in the thermodynamically favorable exchange reaction 3 (i.e., steps 2 and 3 are the propagation reactions). Similar isomerization reactions have been reported for other organometallic complexes (2).

$$Z \rightleftharpoons Z^+ \qquad 1$$

$$Z^+ \rightleftharpoons E^+ \qquad 2$$

$$E^+ + Z \rightleftharpoons E + Z^+ \qquad 3$$

Figure 4. Scheme for the catalytic interconversion of E and Z isomers.

Additional References

1) K. B. Oldham and R. H. Philp, Current Separations 10 (1990) 3 - 5.

2) A. M. Bond, D. J. Darensbourg, E. Mocellin and B. J. Stewart, J. Am. Chem. Soc. 103 (1981) 6827 - 6832.