CAPSULES
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Investigation of Electron Transfer Chain Catalysis using Cyclic Voltammetry

Purpose

Many electron precise organometallic carbonyl complexes are inert towards substitution (e.g., by phosphines) at room temperature. Early syntheses of substituted derivatives often involved prolonged reactions at high temperatures, which generally led to low yields and poor specificity. More recently, it has been shown that substitution reactions (and other reactions) can proceed rapidly and in high yield at room temperature after the addition of a catalytic amount of a chemical redox reagent or the passage of a small current through the solution (which electrolyzes a catalytic amount of the electroactive species) (1). There has also been considerable interest in the mechanism(s) of these Electron Transfer Chain (ETC) catalytic reactions due to the large variation in their efficiencies, and cyclic voltammetry has been extensively used in these studies.

Reference

Kinetics, Thermodynamics, and Mechanism of the Radical Chain Process for Ligand Substitution of Metal Carbonyls, J. W. Hershberger, R. J. Klinger and J. K. Kochi, J. Am. Chem. Soc. 105 (1983) 61 - 73.

Method

Initiation of ETC processes produces a reactive reduced/oxidized intermediate. Cyclic voltammetry is ideal for the qualitative investigation of such intermediates, since they can be generated on the forward scan and their fate can be probed on the reverse and subsequent scans.

Results

One molecule that has been extensively investigated is $MeCpMn(CO)_2(MeCN)$ I (F1). The cyclic voltammogram (F2a) shows a reversible oxidation. However, addition of PPh_3 causes a considerable change (F2b). The absence of a cathodic peak associated with the initial oxidation shows that the oxidized species I^+ undergoes a rapid chemical reaction. This is also shown by the appearance of the redox couple of the product of this chemical reaction, which was identified as the monosubstituted PPh_3 derivative II (F2c) (i.e., the chemical reaction is substitution of MeCN by PPh_3). Comparison of the redox potentials of the two derivatives shows that I is more easily oxidized than II. Therefore, II^+ can oxidize I.

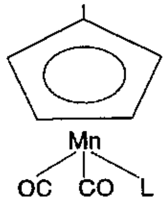

Figure 1. Structure of $MeCpMn(CO)_2L$. L = MeCN (I), L = PPh_3 (II).

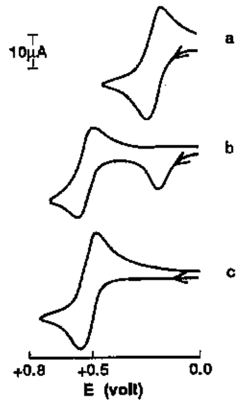

Figure 2. a) Cyclic voltammogram of I in MeCN (1 mM). b) Cyclic voltammogram of I in MeCN (1 mM) with added PPh_3. c) Cyclic voltammogram of II in MeCN (1 mM). All potentials measured with reference to ferrocene as an internal standard. Scan rate = 200 mV/s, temperature = 22° C, supporting electrolyte 0.1 M $[Et_4N][ClO_4]$. Figure adapted from Reference.

The two propagation steps in the catalytic cycle are the substitution of I^+ (to give II^+) and the electron transfer between II^+ and I (to give II and I^+) (F3). The efficiency of the catalytic process therefore depends on the rate of these two reactions (the faster the propagation reactions, the less chance there is for competing side reactions to occur). Although substitution of electronically saturated organometallic complexes is generally slow, electron deficient analogues are considerably more labile (2), so the substitution reaction is rapid. However, this is an associative reaction, so the rate depends on the steric and electronic properties of the entering and leaving ligands. The electronic properties of the ligands also affect the redox potentials. For the second reaction to be rapid, it must be exergonic (i.e., for this system, the redox potential of II must be more positive than that of I). Both steps are favorable for substitution of MeCN by phosphines and phosphites, and high catalytic efficiency was found for substitution by PPh_3 (>1000). Lower efficiencies were found for phosphites, and this was attributed to their lower nucleophilicities.

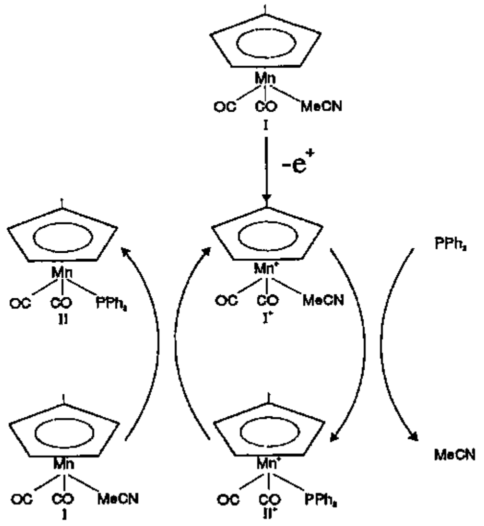

Figure 3. Scheme for catalytic substitution of I.

Additional References.

1) D. Astruc, Angew. Chem., Int. Ed. Engl. 27 (1988) 643 - 660.
2) M. Chanon, M. Julliard, J. C. Poite (eds.), Paramagnetic Organometallic Species in Activation, Selectivity, Catalysis (Kluwer Academic Publishers, Dordrecht, The Netherlands) 1989.