CAPSULES
notes and applications from Bioanalytical Systems, Inc.
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Characterization of (η^3-C_3H_5)Mo(CO)$_2$(NCMe)$_2$Cl Compounds using Cyclic Voltammetry

Purpose

A redox potential is a thermodynamic measure of the difference in energy between two different oxidation states of a given molecule. The oxidation state energy depends on both the molecular structure and the medium (phase, solvent, etc.). Therefore, the redox potential in a given medium is characteristic of the molecule under examination and under ideal circumstances can be used for identification. However, there are two other points to consider when using this approach:

a) redox potentials do not provide any information about molecular structure, and identification can only be achieved by comparison (i.e., fingerprinting), and

b) the resolution of the methods commonly used to measure redox potentials is poor and it is often not possible to distinguish molecules with similar redox potentials.

Reference

(η^3-Allyl)dicarbonylmolybdenum(II) Complexes: Studies of Their Redox Chemistry and Solution Equilibria by Electrochemistry, B.J. Brisdon, K.A. Conner and R.A. Walton, Organometallics 2 (1983) 1159-1163.

Method

Cyclic voltammetry is widely used for the initial characterization of the redox behavior of the molecule under investigation. It can provide qualitative information on the energies of the different oxidation states as well as the kinetic stability of these oxidation states and the rate of heterogeneous electron transfer. Comparison of cyclic voltammograms is often used to confirm the identification of organic and organometallic compounds.

Results

The cyclic voltammograms for (η^3-C_3H_5)Mo(CO)$_2$ (NCMe)$_2$Cl (I) ***(F1)*** in acetonitrile and methylene are shown in ***F2a*** and ***F2b***, respectively. The cyclic voltammogram recorded in acetonitrile shows one quasi-reversible process, whereas the voltammogram recorded in methylene shows three processes.

This dramatic difference is due to the lability of the MeCN ligands. When using acetonitrile as a solvent, dissociation of MeCN has no effect, since there is an excess of acetonitrile present. However, in methylene chloride, dissociation of MeCN leads to the formation of two additional complexes, as shown by the equation below:

$$3(\eta^3\text{-}C_3H_5)Mo(CO)_2\,(NCMe)_2Cl \rightarrow [(\eta^3\text{-}C_3H_5)Mo_2(CO)_4Cl_3]^-\,(II)^+\;[(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCMe)_3)]^+\,(III) + 3MeCN$$

The presence of the dimeric Mo anion (II) and the monomeric Mo cation (III) was confirmed by comparison with the cyclic voltammograms of authentic samples of these complexes (shown in ***F2c*** and ***F2d***, respectively).

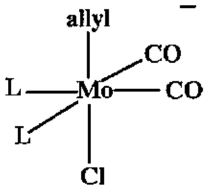

Figure 1. *Molecular structure of (η^3-C_3H_5)Mo(CO)$_2$(NCMe)$_2$Cl*

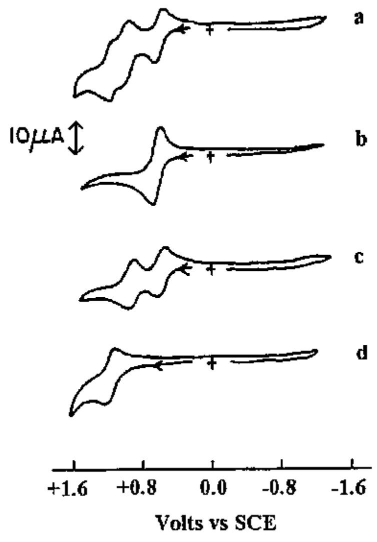

Figure 2. *Cyclic voltammograms of a) I in methylene chloride/ 0.1 M TBAH; b) I in acetonitrile/0.2 M TBAH; c) II in methylene cholride/0.2 M TBAH; and d) III in methylene chloride/0.2 M TBAH (TBAH = [^{n}Bu$_4$N][PF$_6$]). Platinum working electrode, scan rate = 200 mV s^{-1}, potentials measured with reference to the SCE. Figure adapted from reference.*