Electrochemical Oxidation of \( \text{Mo(CO)}_3(\alpha\text{-diimine})(\text{CH}_3\text{CN}) \): Infrared Spectroelectrochemical Studies of the Reactivity of \([\text{Mo(CO)}_3(\alpha\text{-diimine})(\text{CH}_3\text{CN})]^+\) Complexes

Ryan Johnson, Humair Madhani, John P. Bullock

Division of Natural Sciences and Mathematics
Bennington College
Bennington, Vermont 05201

A series of \( \text{Mo(CO)}_3(\alpha\text{-diimine})(\text{CH}_3\text{CN}) \) compounds (\( \alpha\text{-diimine} \) ligands used include 2,2'-bipyridine, 2,2'-biquinoline, 1,10-phenanthroline and substituted derivatives) was prepared from the corresponding \( \text{Mo(CO)}_4(\alpha\text{-diimine}) \) complexes via reflux in acetonitrile. These compounds all exhibit quasi-reversible one-electron oxidations in acetonitrile yielding the corresponding \([\text{Mo(CO)}_3(\alpha\text{-diimine})(\text{CH}_3\text{CN})]^+\) radicals. The electrogenerated seventeen-electron complexes can be oxidized in a second, irreversible, one-electron process which is coupled to coordination by solvent, yielding the seven-coordinate \( \text{Mo}^{2+} \) complex, \([\text{Mo(CO)}_3(\text{bpy})(\text{CH}_3\text{CN})_2]^{2+}\). In addition, the \([\text{Mo(CO)}_3(\alpha\text{-diimine})(\text{CH}_3\text{CN})]^+\) species are susceptible to nucleophilic attack by the solvent, resulting in net disproportionation reactions. These ligand-induced disproportions follow first order kinetics, the rate constants of which were found to be influenced by steric and electronic factors. In addition to the \( \text{Mo}^0 \) starting compound, disproportionation yields the same seven-coordinate \( \text{Mo}^{2+} \) species that is formed by direct oxidation of \([\text{Mo(CO)}_3(\alpha\text{-diimine})(\text{CH}_3\text{CN})]^+\). This compound is unstable toward additional acetonitrile substitution and decomposes to \([\text{Mo(CO)}_2(\alpha\text{-diimine})(\text{CH}_3\text{CN})_3]^{2+}\). The infrared spectra of the \( \text{Mo}^{2+} \) oxidation products, as well as those of the electrogenerated \( \text{Mo}^+ \) complexes, were obtained via infrared spectroelectrochemistry and will be discussed.