Electrochemical Oxidation of [M(CO)₄(bpy)] and [M(CO)₃(bpy)(CH₃CN)] Complexes (M = Mo, W; bpy= 2,2'-bipyridine): Elucidation of the Fate of Electrogenerated Seventeen-Electron Species

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Molybdenum and tungsten complexes of the type M(CO)₄(bpy) exhibit quasi reversible one-electron oxidations in methylene chloride. Oxidations in coordinating solvents, in contrast, are irreversible due to a variety of coupled chemical reactions including ligand exchange with the solvent and disproportionation. Some of these processes have been previously reported but the reactions involved are considerably more numerous than earlier reports indicate. For example, complexes of the type [M(CO)₃(bpy)(CH₃CN)]⁺, generated by ligand exchange between the solvent and the initially formed tetracarbonyl cation, can undergo at least three distinct reactions: additional oxidation and solvent coordination to yield [M(CO)₃(bpy)(CH₃CN)]²⁺, disproportionation with a second tricarbonyl cation, and disproportionation with an electrogenerated tetracarbonyl cation. We have examined the rates and products of these various pathways using cyclic voltammetry, chronocoulometry and infrared spectroelectrochemistry. This presentation will summarize the results of these studies and will outline the relative importance of these pathways for the molybdenum and tungsten systems.