Final Report

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The fifteen years of DOE support have encompassed two different projects, electron-transfer reactions of metal carbonyl anions and water-soluble organometallic complexes. Each of these is related to homogeneous catalysis and will be described in separate sections.

Electron Transfer. Twenty-one manuscripts resulted from our studies of electron-transfer reactions of metal carbonyl anions and acknowledge DOE support. Construction of an infrared stopped-flow system allowed us to measure rates of reactions for the extremely air-sensitive metal carbonyl anions. As for carbanions, both one-electron and two-electron processes occur for metal carbonyl anions. The most unexpected feature was examples of a very rapid two-electron process, followed by a much slower one-electron back transfer. The two-electron processes were accompanied by transfer of a ligand between two metals,

$$M\text{–}X + M'^{-} \rightarrow M^{-} + M'\text{–}X$$

with X groups of CO^{2+}, H^{+}, CH_3^{+} and Br^{+}. These transfers, which can be considered nucleophilic displacements, occurred when M'^{-} was more nucleophilic than M^{-}. The 21 published manuscripts explore one- and two-electron processes for many such organometallic complexes.

Water-Soluble Organometallic Complexes. The potential of water-soluble organometallic complexes in "green chemistry" intrigued us. Sixteen manuscripts acknowledging DOE support have appeared thus far in this field. Our research centered on sulfonated phosphine ligands, $PPh_2(m\text{-}C_6H_4SO_3Na)$ and $P(m\text{-}C_6H_4SO_3Na)_3$, to solubilize organometallic complexes in water. These analogues of PPh_3 allowed us to synthesize complexes of Ir, Rh, Ru, Ni, Pd, Pt and Ag that are water-soluble and contain such common organometallic ligands as CO, H and CH_3 in addition to halides and the phosphine ligands. These metal complexes show the ability to activate H_2, CO, C_2H_4, H_2O, SO_2, *etc* in aqueous solution. The primary conclusion is that water-soluble organometallic complexes can be prepared and show very similar reactivity in water to analogous compounds in organic solvents. Thus, organometallic complexes in aqueous solution do provide a "green" route to products currently prepared in organic solvents.

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DOE Patent Clearance Granted
MP Dvorscak 7·23·03
Mark P. Dvorscak Date
(630) 252-2393
E-mail: mark.dvorscak@ch.doe.gov
Office of Intellectual Property Law
DOE Chicago Operations Office

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Manuscripts Published Acknowledging
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