

CHEMISTRY SEMINAR

“The Design of Highly Oxidizing Excited States & Rhenium-Terpyridyl Complexes”

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12:00 p.m.

WSB-122



Abstract:

The usefulness of transition metal excited states for solar energy conversion is intimately tied to their excited state redox properties. Our recent work has focused upon the discovery and photophysical characterization of transition metal excited states that are either “highly oxidizing” by conventional standards and transition metal complexes that can absorb the entire visible spectrum.

$[\text{Re}(\text{dmpe})_3]^{2+}$ (dmpe is 1,2-bis-(dimethylphosphino)ethane) and its derivatives possess substantial visible absorption and a convenient preparative chemistry that should allow linkages to surfaces and molecular assemblies. Luminescence quenching experiments with chloride ion and aromatic hydrocarbons demonstrate the extreme oxidizing power $[\text{Re}(\text{dmpe})_3]^{2+*}$. Of particular note is that *toluene* and *benzene* are oxidized. A Rehm-Weller (R-W) rate constant/ driving force relationship derived from steady-state quenching of $[\text{Re}(\text{dmpe})_3]^{2+*}$ by a series of substituted aromatic hydrocarbons can be used to estimate an excited state potential (ESP) of +2.58 V (vs. SCE). Unrestricted, open-shell DFT/TDDFT calculations on $[\text{Re}(\text{dmpe})_3]^{2+*}$ show that the emission is indeed *ligand-to-metal charge transfer* (LMCT) in character. These results suggest that future derivatives with LMCT character will have ESPs capable of rapid oxidation of kinetically slow substrates like water or chlorocarbons, in addition to the capability to oxidize high potential substrates such as aromatic hydrocarbons.

Complexes of the type *fac*- $\text{Re}(\text{N}\cup\text{N})(\text{CO})_3\text{Cl}$ (where $\text{N}\cup\text{N}$ is a α,α' -diimine/bis-chelating ligand such as 2,2'-bipyridine) have been traditionally used in many photochemical and photophysical studies and applications. This is due in part to the electron rich nature of $\text{Re}(\text{I})$. However, these systems only absorb a small portion of the available visible light, typically, the near ultraviolet (UV; ~ 400 nm and below). The tris-chelating tpy (tpy is 2,2':6',2''-terpyridine) ligand has established prominence in recent electro & photocatalytic studies. The terpyridyl ligand possesses a two-fold axis of symmetry which lends itself nicely to synthetic modification free of isomerization for surface attachment to electrode surfaces (*i.e.*, electrocatalysis). In addition the utilization of the terpyridyl ligand has resulted in the ability to *absorb more* of the visible wavelength. These results suggest that derivatives capable of both electro & photocatalytic activity can be prepared to perform important redox reactions, such as the reduction of carbon dioxide (CO_2).

This talk will cover: (1) the recent photophysical characterization of the highly oxidizing excited states (HOES) of the $[\text{Re}(\text{dmpe})_3]^{2+*}$; (2) the design of new HOES based on the d_5 -metal core as suggested by DFT/TDDFT calculations; (3) the use of HOES for the oxidation of the valence band of semiconductors like TiO_2 ; and (4) recent results pertaining to the preparation of rhenium-terpyridyl complexes.

DR. HIGHTOWER WILL MEET WITH STUDENTS AT 1:00 P.M. IN WSB-344