Factors Affecting the Rate of Electron Transfer in Biferrocenium Cations

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Electron transfer is a fundamental chemical process. It involves the movement of localized electronic charge from one atom, ion, or molecule to another. Despite its fundamental nature, practical importance, and several decades of active research [1-3], all of the factors which affect or control the electron transfer process are still not fully recognized or understood.

The general environment surrounding the donor and acceptor sites of the electron transfer event consists of the intervening medium and what can be termed the global environment. For intramolecular electron transfer in mixed-valence transition metal complexes, the donor and acceptor sites are typically transition metals. The intervening medium usually is the ligand that bridges between the two metal centers, while the global environment is highly variable. The global environment can include the non-bridging ligands, solvent molecules, counterions, other mixed valence molecules, zeolite cages, polymer matrices, interlamellar regions of clays, or even empty space. Much of the initial work studying electron transfer between metal sites focused on the intervening medium's role in controlling intramolecular electron transfer.

The hypothesis of the present work is that the global environment also plays a significant role in determining the rate of intramolecular electron transfer between two electron transfer sites. Various forms of spectroscopy, with their inherent timescales, were used in conjunction with X-ray diffraction and heat capacity methods to determine how variations in the global environment impact the rate of intramolecular electron transfer.

If one is to study the impact of the global environment on intramolecular electron transfer, the molecular framework has to be one in which the intervening medium remains relatively constant. The molecular framework chosen, for these studies, are the mono-oxidized, mixed-valence biferrocenium systems shown below:

1. X=CH₂C₆H₅
2. X=CH₂C₆H₅ and Y=PF₆⁻
3. X=CH₂C₆H₅ and Y=SbF₆⁻
4. X=CH₂C₆H₅ and Y=I₃⁻
5. X=Cl and Y=PF₆⁻
6. X=Br and Y=PF₆⁻
7. X=I and Y=PF₆⁻
8. X=Cl and Y=SbF₆⁻
9. X=Br and Y=SbF₆⁻
10. X=I and Y=SbF₆⁻
The symmetry of a crystalline lattice has a profound effect on the rate of intramolecular electron transfer. If the crystalline environment is symmetric about a mixed-valent 1',1''-disubstituted biferrocenium cation, intramolecular electron transfer is generally facile at thermally accessible temperatures (<350 K). However, if the crystalline environment is asymmetric, the rate of intramolecular electron transfer is rather slow.

Compound 4 crystallizes in two polymorphs [4]. In the symmetric P{$\bar{1}$} polymorph, the rate of intramolecular electron transfer in the mixed-valent dibenzylbiferrocenium cation is fast relative to the $^{57}$Fe Mössbauer timescale (valence detrapped) even at 25 K. In the less symmetric P2$_1$/n polymorph, the biferrocenium cation remains valence trapped on the Mössbauer timescale at 350 K. A similar situation exists for compound 10 [5].

In compounds 2 and 3, the 1',1''-dibenzylbiferrocenium cations crystallize in a symmetric array of hexafluorophosphate anions and in an asymmetric array of hexafluoroantimonate anions, respectively. The intramolecular electron transfer rate in the cation of 2 is always faster than it is in 3.

Dynamics in the global environment also affect the rate of intramolecular electron transfer in biferrocenium cations. The intramolecular electron transfer rate in the cations of 2 and 10 are dependent on dynamics of the hexafluorophosphate and hexafluoroantimonate anions, respectively [6]. When the relatively symmetric anions begin to reorient in the crystalline lattice the intramolecular electron transfer rate increases dramatically.

References: