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 *intra*molecular electron transfer.

The hypothesis of the present work is that the *global* environment also plays a significant role in determining the rate of *intra*molecular 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 *intra*molecular electron transfer.

If one is to study the impact of the *global* environment on *intra*molecular 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:
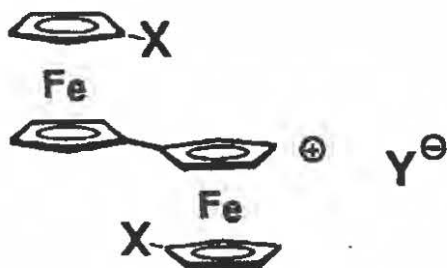
1, $X=CH_2C_6H_5$
2, $X=CH_2C_6H_5$ and $Y=PF_6^-$
3, $X=CH_2C_6H_5$ and $Y=SbF_6^-$
4, $X=CH_2C_6H_5$ and $Y=I_3^-$
5, $X=Cl$ and $Y=PF_6^-$
6, $X=Br$ and $Y=PF_6^-$
7, $X=I$ and $Y=PF_A^-$
8, $X=Cl$ and $Y=SbF_6^-$
9, $X=Br$ and $Y=SbF_A^-$
10, $X=I$ and $Y=SbF_6^-$

The symmetry of a crystalline lattice has a profound effect on the rate of *intra*molecular electron transfer. If the crystalline environment is symmetric about a mixed-valent 1',1'''-disubstituted biferrocenium cation, *intra*molecular 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 *intra*molecular 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 *intra*molecular electron transfer in biferrocenium cations. The *intra*molecular 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 *intra*molecular electron transfer rate increases dramatically.

References:

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