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Review

Barrier heights in long-range electron tunneling

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ABSTRACT

Recent results regarding the importance of tunneling-barrier heights for charge transfer between distant redox partners are reviewed. Examples include studies of photoinduced hole transfer in donor–bridge–acceptor systems, as well as work on mixed valence molecules. The barrier heights imposed by different bridging units are discussed. Key examples include the comparison of biphenyl and fluorene spacers, and the comparison of *p*-xylene and *p*-dimethoxybenzene bridging units.

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1. Introduction

The rates for electron tunneling in donor–bridge–acceptor molecules or in mixed valence systems are determined to a significant extent by the heights and widths of the barriers imposed by the molecular bridges separating the two redox partners [1]. When the barrier height becomes sufficiently small, an incoherent hopping process is enabled, and an extremely shallow distance dependence of electron transfer rates may result [2]. However, the height of the barrier does also have an important influence on charge transfer rates in the tunneling regime, in which population of the bridge redox states by electrons from the donor is thermodynamically impossible [3]. This paper reviews some of our recent results obtained in this context by investigating photoinduced long-range electron transfer in donor–bridge–acceptor molecules and compares them to the results obtained by other researchers on mixed valence systems.

2. Biphenyl versus fluorene bridges

Rhenium tricarbonyl diimine and ruthenium polypyridyl complexes are very popular choices as sensitizers for phototriggered long-range electron transfer [4]. The rhenium complexes are powerful photooxidants [5], and hence are frequently used in conjunction with tertiary amine electron donors [6]. In the molecules from Fig. 1 we used phenothiazine, because its one-electron oxidized form has an optical absorption spectrum that is particularly easy to detect in transient absorption experiments [7]. Recent progress in palladium-catalyzed N–C coupling chemistry make attachment of this electron donor to aryl rings a straightforward matter [8]. The molecular bridges used to connect the electron donor to the acceptor in the three molecules from Fig. 1 all hold the two reactants at a distance of 14.9 Å and differ from one another only marginally in structure [9]. Yet, there are substantial differences between the rates for intramolecular electron transfer in these three donor–bridge–acceptor molecules. The rate is slowest for the bridge comprised of two *p*-xylene units (20 ns), increases by a factor of five to the biphenyl-bridged molecule (3.9 ns) and by another factor of two in the dyad with the fluorene bridge (1.9 ns), as determined by a combination of time-resolved luminescence and transient absorption spectroscopies [9]. This trend is broadly consistent with the decrease in twist angles between the two phenyl rings present in the three different bridges. Equilibrium torsion angles between two adjacent *p*-xylene units are on the order of 60° [10], while the two phenyl rings in biphenyl are twisted by only ~35° [11], and in fluorene they are forced into almost coplanar arrangement with twist angles below 10° [12]. The influence of torsion angles on electronic couplings between distant redox partners has been investigated by many researchers, and the general consensus seems to be that the electronic coupling matrix element (H_{AB}) exhibits a $\cos^2(\phi)$-dependence on twist angles (ϕ) [13]. Indeed, using this function, it is possible to explain quantitatively the differences observed in the distance dependence of the rates for electron tunneling across oligo-*p*-phenylene and oligo-*p*-xylene bridges [10b]. Hence, the factor of five difference observed between **1** and **2** can be explained satisfactorily by invoking only differences in twist angles. In the fluorene bridged molecule (**3**), yet another effect, which has to do with the fact that fluorene is oxidized much more readily than biphenyl, may become important. Because of the ease of bridge oxidation in **3** and because of charge transfer occurring by hole tunneling rather than electron tunneling in the donor–bridge–acceptor molecules from Fig. 1, the so-called tunneling-energy gap ($\Delta\varepsilon$ in Fig. 2) associated with hole transfer is substantially lower in **3** than in **2** [3]. According to superexchange theory, this should result in enhanced electronic coupling and faster charge transfer rates [14]. There are numerous pieces of experimental evidence for the validity of this theoretical prediction available in the literature [3,15], including studies on mixed valence systems that are closely related to those illustrated by Fig. 1.

Kochi and coworkers determined the electronic coupling (H_{AB}) between two *p*-dimethoxytolyl redox centers in various organic mixed valence systems containing bridges with different conformation, distance and connectivity [16]. Particularly relevant for the current discussion is their comparison of the biphenyl and fluorene bridged molecules **4** and **5** (Fig. 3). Hush analysis [17] of the infrared absorption bands associated with intramolecular electron transfer in the radical cations of these molecules lead to the conclusion that $H_{AB} = 430\ \text{cm}^{-1}$ for $\mathbf{4}^{\cdot+}$ and $H_{AB} = 630\ \text{cm}^{-1}$ for $\mathbf{5}^{\cdot+}$ [16], which is in line with our abovementioned findings on molecules **2** and **3** [9]. The radical anions of the dinitroaromatic compounds **6** and **7** are class III mixed valence systems that permit determination of H_{AB} directly from their intervalence absorption band maxima [18]. The obtained values are in agreement with the results from above, but the relative difference between the biphenyl system ($\mathbf{6}^{\cdot-}$, $H_{AB} = 930\ \text{cm}^{-1}$) and the fluorene-bridged molecule ($\mathbf{7}^{\cdot-}$, $H_{AB} = 1100\ \text{cm}^{-1}$) is smaller in this case. Nelsen

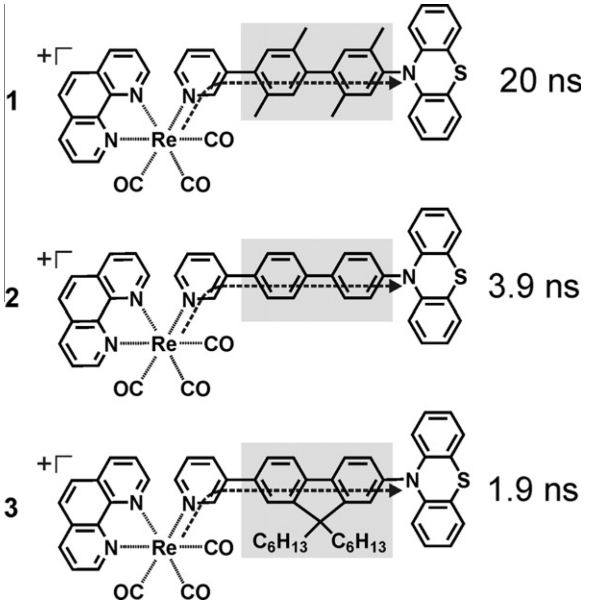

Fig. 1. Photoinduced hole tunneling and associated time constants in donor–bridge–acceptor molecules comprised of a rhenium(I) hole donor, three different but equidistant rigid rod-like bridges, and a phenothiazine (hole) acceptor [9].

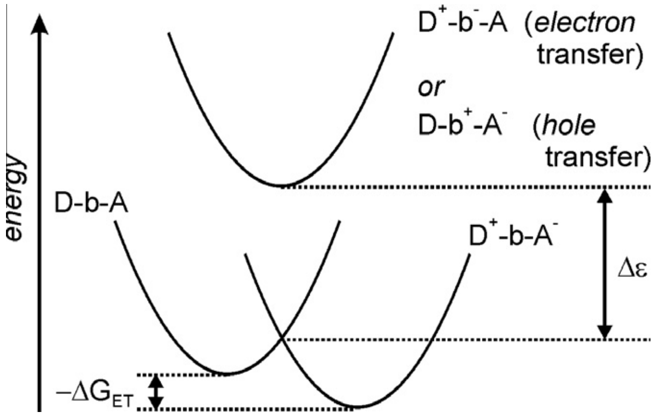

Fig. 2. Illustration of the tunneling-energy gap ($\Delta\varepsilon$). $-\Delta G_{ET}$ is the driving force for electron transfer from the donor (D) to the acceptor (A) via bridge (b) [3,14].