Electronic Supplementary Information

Sequential or superexchange mechanism in bridged electron transfer distinguished by dynamics at a bridging molecule

Keisuke Saito*, Tomoaki Kikuchi, Koichiro Mukai and Hitoshi Sumi

*E-mail address: ksaito@sci.osaka-cu.ac.jp (K. Saito)

Appendix S1: Additional parameters

In the calculation of the rate constant by the SK theory, we adopted straightforwardly parameters used by Miller et al., which are shown in Figure 2. However, some additional parameters were needed, because dephasing-thermalization of phonons in $|m\rangle$ must also be taken into account in the SK theory. Those parameters were set as follows. We took the outer-sphere reorganization energies around the midway spacer molecules at 0.35 , 0.23 , and 0.22 eV for NSenB, NSen$_2$B and NSarB, respectively. They are concerned with the total outer-sphere reorganization energies λ_1 and λ_2 associated with ET between $|d\rangle$ and $|m\rangle$ and that between $|m\rangle$ and $|a\rangle$, respectively. They were chosen so as for the rate constant calculated to best fit the experimental data of Miller et al.

Since the rate constant was observed in the THF solution in the experiment, next parameter values were set at those for THF. Thereby, the dephasing-thermalization time τ_m of phonons mentioned in I was set at 1.0 ps, which was obtained by spectroscopic measurements as the dephasing time of the excitation resonance on a dithiaanthracenophane dimer in THF [S1]. Since the spectrum of slow vibrations in the THF solution obtained by the Raman and the neutron

scattering peaks at ~90 cm^{-1} [S2], this value was set as the average energy quantum $\hbar\bar{\omega}$ of outer-sphere vibrations.

Appendix S2: The SX and the OS limit of $k_{a,d}$

In the SX limit, (4-2) turns out to be

$$k_{a,d}^{(SX)} = k_{a,d(\pi)}^{(SX)} + k_{a,d(\sigma)}, \qquad (S2\text{-}1)$$

with

$$k_{a,d(\pi)}^{(SX)} = \sum_{n=0}^{\infty} A_n k_{a,d(SK)}^{(SX)}(\Delta G_m + n\hbar\omega_l), \qquad (S2\text{-}2)$$

where $k_{a,d(SK)}^{(SX)}(\Delta G_m + n\hbar\omega_l)$ represents the rate constant in the SX limit virtually mediated by the n-th FC branch of the adiabatic potential in |m> at the π bonds in the midway molecule M, with A_n given by (3-1). Regarding the rate constant given by the SK theory [13] in the SX limit as a function of the free-energy height ΔG_m at |m> above |d> $k_{a,d(SK)}^{(SX)}(\Delta G_m + n\hbar\omega_l)$ is derived from this rate constant by replacing ΔG_m with $\Delta G_m + n\hbar\omega_l$. In (S2-1), $k_{a,d(\sigma)}$ is the rate constant mediated by the σ bonds in M always in the SX mechanism irrespectively of the value of ΔG_m in its region in Figures 4-6 in the present work.

With the same $k_{a,d(\sigma)}$ as above, the rate constant $k_{a,d}^{(OS)}$ in the OS limit is given by

$$k_{a,d}^{(OS)} = k_{a,d(\pi)}^{(OS)} + k_{a,d(\sigma)}, \qquad (S2\text{-}3)$$

with

$$k_{a,d(\pi)}^{(OS)} = \sum_{n=0}^{\infty} A_n k_{a,d(SK)}^{(OS)}(\Delta G_m + n\hbar\omega_l) \quad (S2\text{-}4)$$

where $k_{a,d(SK)}^{(OS)}(\Delta G_m + n\hbar\omega_l)$ is the rate constant in the OS limit mediated by the n-th FC branch of the adiabatic potential in |m> at the π bonds in M with the same A_n as above. Likewise as above, $k_{a,d(SK)}^{(OS)}(\Delta G_m + n\hbar\omega_l)$ is obtained by replacing ΔG_m in the OS rate constant of the SK theory [13] with $\Delta G_m + n\hbar\omega_l$. Therefore, it can be express as

$$k_{a,d}^{(OS)}{}_{(SK)}(X) = 1/[\, k^0{}_1(X)^{-1} + k_2(X)^{-1}\exp(X/k_BT)], \qquad (S2\text{-}5)$$

with

$$X = \Delta G_m + n\hbar\omega_l,$$

where $k^0_1(X)$ and $k_2(X)$ give the rate constant of ET from |d> to |m> and that from |m> to |a>, respectively, expressed as a function of energy variable X, where X represents the free-energy height of individual FC branches of the adiabatic potential in |m> above |d>. When either $k^0_1(X)$ or $k_2(X) \exp(-X/k_B T)$ can be neglected in comparison with the other for n with appreciable values of A_n, it can easily be shown that $k_{a,d(\pi)}^{(OS)}$ merges to $k_{(\pi)}^{(OS)}{}_{(M)}$ of (A-2).

References

[S1] Yamazaki, S. Akimoto, S. Sato, Y. Sakata, *J. Phys. Chem. A,* 2002, **106**, 2122.

[S2] C. Coulobeau, H. Jobic, *J. Mol. Struct. (Theochem),* 1995, **330**, 127.