

## Rates of Interfacial Electron Transfer through $\pi$ -Conjugated Spacers

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The rate of interfacial electron transfer through insulating, molecular spacers is expected to depend strongly on the nature of the chemical bonding within the spacer.<sup>1</sup> This sensitivity to molecular structure should be particularly valuable for promoting or limiting specific electron-transfer reactions in amperometric sensors, organic light-emitting devices, and other interfacial structures. Here, we report measurements of the standard rate constants,  $k_0$ , for interfacial electron transfer between a gold electrode and a ferrocene group covalently connected to gold by  $\pi$ -conjugated mercaptooligo(phenyleneethynylene) (OPE) spacers.<sup>2</sup> The values of  $k_0$  are orders of magnitude larger for an OPE spacer than for a trans alkane spacer of comparable length. The slope of  $-\ln[k_0]$  vs the spacer length,  $l$ , i.e.,  $\beta$ ,<sup>1,3</sup> is  $0.57 \pm 0.02 \text{ \AA}^{-1}$  for OPE spacers compared with  $\sim 1.0 \text{ \AA}^{-1}$  for the saturated spacers.<sup>3</sup> These results are consistent with calculations using the generalized Mulliken Hush theory.<sup>4</sup>

The systems studied were self-assembled monolayers on evaporated gold films formed from solutions of one of two homologous ferrocene-terminated thiols<sup>5–7</sup> (**1**)  $\text{HS}(p\text{-C}_6\text{H}_4\text{-C}\equiv\text{C})_m(\eta^5\text{C}_5\text{H}_4)\text{Fe}(\eta^5\text{C}_5\text{H}_5)$  ( $m = 2$  or  $3$ ) and one of several diluent thiols: (**2**)  $\text{HS}(\text{CH}_2)_n\text{CH}_3$  ( $n = 9$  or  $15$ ), (**3**)  $\text{HS}(\text{CH}_2)_n\text{OH}$  ( $n = 9$  or  $16$ ), (**4**)  $\text{HS}(\text{CH}_2)_n\text{COOH}$  ( $n = 15$ ), and (**5**)  $\text{HS-}p\text{-C}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_5$ . The values of  $n$  or  $m$  are chosen so that the lengths of the spacer and of the diluent used to form a given film are comparable. Because the values of  $k_0$  for molecule **1** were too large to be measured using conventional electrochemical techniques at a macroscopic electrode, we used the indirect-laser-induced-temperature-jump (ILIT) method<sup>8</sup> previously applied to measure  $k_0$  for ferrocene tethered to gold electrodes by short saturated spacers.<sup>3,9</sup> The ferrocene coverages,  $\Gamma_{\text{Fc}}$ , were measured by cyclic voltammetry.<sup>6f</sup> All measurements were

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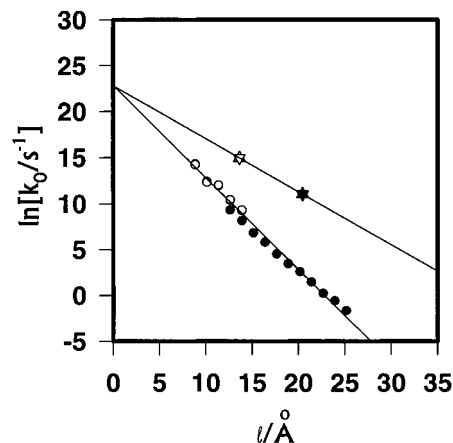
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(7) A clean electrode was placed in a chloroform solution of  $\sim 6 \times 10^{-5}$  to  $10^{-4}$  M of molecule **1** and  $\sim 4 \times 10^{-4}$  M of the diluent for 16 h. The electrode was then rinsed successively in chloroform, hexane, water, and chloroform and dried in an argon stream.

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**Table 1.** Summary of Results of ILIT Measurements

ferrocene-terminated thiol	diluent thiol	$\Gamma_{\text{Fc}}$ , mol cm <sup>-2</sup>	$T$ , K	$k_0/\text{s}^{-1}$
<b>1</b> , $m = 2$	<b>5</b>	$1.7 \times 10^{-11}$	298	$3.3 \times 10^6$
<b>1</b> , $m = 2$	<b>5</b>	$1.7 \times 10^{-11}$	281	$1.7 \times 10^6$
<b>1</b> , $m = 2$	<b>2</b> , $n = 9$	$2.0 \times 10^{-11}$	281	$1.7 \times 10^6$
<b>1</b> , $m = 2$	<b>3</b> , $n = 9$	$1.5 \times 10^{-11}$	298	$3.2 \times 10^6$
<b>1</b> , $m = 3$	<b>2</b> , $n = 15$	$0.86 \times 10^{-11}$	298	$6.7 \times 10^4$
<b>1</b> , $m = 3$	<b>3</b> , $n = 16$	$2.7 \times 10^{-11}$	298	$6.1 \times 10^4$
<b>1</b> , $m = 3$	<b>4</b>	$1.9 \times 10^{-11}$	298	$5.7 \times 10^4$
<b>1</b> , $m = 3$	<b>4</b>	$1.9 \times 10^{-11}$	281	$3.5 \times 10^4$



**Figure 1.** Comparison of  $\ln[k_0]$  vs  $l^{10}$  for OPE (Table 1) and saturated spacers. All values of  $k_0$  were corrected to 298 K using the value of  $d(\ln[k_0])/d(1/T) = -2.82 \times 10^3 \text{ K}$  deduced from the previous study.<sup>3</sup> Open star: molecule **1**,  $m = 2$ . Solid star: molecule **1**,  $m = 3$  (see Table 1 for diluents).  $\circ$  and  $\bullet$ : previously published data for  $\text{HS}(\text{CH}_2)_m\text{OC}(\text{O})(\eta^5\text{C}_5\text{H}_4)\text{Fe}(\eta^5\text{C}_5\text{H}_5)$  with  $\text{HS}(\text{CH}_2)_{m-1}\text{CH}_3$  as the diluent.<sup>3,12</sup> Error bars are significantly smaller than the size of the points.

carried out in 1 M aqueous  $\text{HClO}_4$ . Our analysis of the ILIT transients assumes a single value of  $k_0$ ; the quality of the fits to the transients supports that assumption. The results are summarized in Table 1. The temperature coefficients,  $d(\ln[k_0])/d(1/T)$ , derived from the data in Table 1 are  $-3.2 \times 10^3 \text{ K}$  (based on all runs with  $m = 2$ ) and  $-2.8 \times 10^3 \text{ K}$  for (based on all runs with  $m = 3$ ). These are in reasonable agreement with the value of  $d(\ln[k_0])/d(1/T) = -2.82 \times 10^3 \text{ K}$  determined from the study of ferrocene tethered by saturated spacers<sup>3</sup> and suggest that the reorganization energy,  $\lambda$ , is approximately the same ( $\sim 0.9 \text{ eV}$ ) for all spacers studied so far. Note also from Table 1 that the rate of electron transfer is essentially independent of the diluent molecule, whether saturated or conjugated, polar or nonpolar, suggesting that the electron transfer is dominated by coupling through the OPE spacer covalently attached to the ferrocene. Figure 1 compares plots of  $\ln[k_0]$  vs  $l^{10}$  (see Table 1) with data from previous studies of ferrocenes tethered by saturated spacers.<sup>3,12</sup> The assumptions of exponential dependence of  $k_0$  on  $l$  and of constant  $\lambda$  give  $\beta = 0.57 \pm 0.02 \text{ \AA}^{-1}$  for interfacial electron transfer through the OPE spacer.<sup>11</sup> This value is intermediate between the values for interfacial or homogeneous electron transfer through saturated spacers where

(9) The sensitivity of the ILIT response to the electron-transfer kinetics depends critically upon the values of  $dE^0/dT$  and the thermal properties of the film.<sup>3</sup> A more detailed explication will be presented elsewhere. For these systems, best results were obtained using diluents **3**, **4**, and **5**.

(10)  $l$  is the straight-line distance from the spacer carbon attached to the sulfur to the attached carbon of the Fc, based on mean bond distances, ref 2 (see also: Roberts, J. D.; Caserio, M. C. *Basic Principles of Organic Chemistry*; W. A. Benjamin, Inc.: New York, 1965; pp 229, 248. Weast, R. C., Ed. *Handbook of Chemistry and Physics*; CRC Press: Cleveland, OH, 1966; pp F126–129). We assume a linear spacer (cf. discussion of analogous systems in solution: Bothner-By, A. A.; Dadok, J.; Johnson, T. E.; Lindsey, J. S. *J. Phys. Chem.* **1996**, *100*, 17551).

(11) An error of  $\pm 0.05 \text{ eV}$  in  $\lambda$  would produce an error of  $\pm 0.07$  in  $\beta$ .

**Table 2.** Exponential Decay Coefficients

tether repeat unit	$\beta$ ( $\text{\AA}^{-1}$ ) (calcd) <sup>a</sup>		$\beta$ ( $\text{\AA}^{-1}$ ) (exptl)
	anion	cation	
(A) trans ( $-\text{CH}_2\text{CH}_2-$ )	1.00	0.83	$0.9 \pm 0.1^b$
(B) ( $-\text{C}_6\text{H}_4\text{C}\equiv\text{C}-$ )			
perpendicular ( $\theta_i = \pi/2$ )	1.00	0.97	$0.57 \pm 0.02^d$
uniform $\theta_i$ distribution <sup>c</sup>	0.54	0.51	
planar ( $\theta_i = 0$ )	0.43	0.39	
(C) trans ( $-\text{CH}=\text{CH}-$ )	0.32	0.31	$\geq 0.2^e$

<sup>a</sup> Present GMH, INDO/S results. <sup>b</sup> References 3 and 12–20. <sup>c</sup>  $\beta$  is based on the rms values of  $T_{\text{DA}}$ . A small torsional barrier (e.g., a value of  $\sim kT$  at room temperature found for the related diphenyl acetylene system<sup>27</sup>) would yield somewhat larger rms values of  $T_{\text{DA}}$  and smaller values of  $\beta$ . <sup>d</sup> Present work. <sup>e</sup> Reference 21.

$\beta \sim 0.9 \text{\AA}^{-1}$ <sup>3,12–20</sup> and the value observed for intramolecular electron transfer through trans polyene spacers, where  $\beta \geq 0.2 \text{\AA}^{-1}$ .<sup>21</sup> We also note that the line for the OPE spacers and the line for the saturated spacers extrapolate to a common point at  $l = 0$ , where both spacers, in principle, become identical.

According to standard theory for long distance electron transfer,<sup>1,5</sup> for an invariant  $\lambda$  (see above),  $k_0$  is proportional to the square of the donor/acceptor (D/A) electronic coupling elements ( $T_{\text{DA}}$ ). In lieu of simulating the entire electrochemical assembly,  $T_{\text{DA}}$  values were evaluated for the model radical ion systems,  $[\text{CH}_2\text{C}=\text{C}(\text{C}_6\text{H}_4\text{C}\equiv\text{C})_m\text{CH}_2]^\pm$ , using the generalized Mulliken Hush (GMH) method<sup>4</sup> and the results of INDO/s electronic structure calculations.<sup>22</sup> To obtain a compact expression for the coupling, the results of the calculations were fit to the following generalization of the McConnell superexchange model,<sup>23</sup> allowing a hole (+) or electron-attached (–) virtual electronic state in either the  $\pi$  or  $\sigma$  manifold of each phenyl group (thus yielding a superposition of  $2^m$  pathways<sup>1</sup>) and also allowing the  $i$ th benzene group to be rotated by an arbitrary angle,  $\theta_i$ , relative to the reference plane of the coplanar D and A  $\text{CH}_2$  groups:<sup>24</sup>

$$T_{\text{DA}}^m = \sum_{\{x_i\}} (T_{\text{D1}}^{x_1}) \left[ \prod_{i=1}^{m-1} \frac{t_{i,i+1}^{x_i x_{i+1}}}{\Delta_i^{x_i}} \right] \frac{T_{\text{mA}}^{x_m}}{\Delta_m^{x_m}} \quad (1)$$

where  $x_i \equiv \pi_i$  or  $\sigma_i$  and the nearest-neighbor McConnell

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parameters are expressed as<sup>25</sup>

$$T_{\text{D1}}^{\pi_1} = (T_{\text{D1}}^{\pi_1})_0 \cos[\theta_1]$$

$$T_{\text{D1}}^{\sigma_1} = (T_{\text{D1}}^{\sigma_1})_0 \sin[\theta_1]$$

$$t_{i,i+1}^{\pi_i \pi_{i+1}} = (t_{i,i+1}^{\pi_i \pi_{i+1}})_0 (\cos[\theta_i] \cos[\theta_{i+1}] + \sin[\theta_i] \sin[\theta_{i+1}]), \text{ etc.}$$

The parameters denoted by “zero” subscripts were obtained by least-squares fits ( $\pm 10\%$ ) to the GMH results for a sample of 12 different conformers spanning the range of dihedral angles in the series  $m = 1-4$ . Results for three limiting conformational cases are displayed in Table 2. The calculated values of  $\ln[T_{\text{DA}}^2]$  vs  $m$  exhibit linear behavior (regression coefficient  $\geq 0.99$ ) within a homologous series of a given conformational type; the corresponding  $\beta$  values (Table 2) reveal a strong dependence on spacer conformation, with similar results for the anion and cation models. Note that the agreement with experimental values is quite good for both the trans ( $-\text{CH}_2\text{CH}_2-$ ) spacer and trans ( $-\text{CH}=\text{CH}-$ ).

The experimental value of  $\beta$  for the OPE spacer is seen to be intermediate between the calculated values for the perpendicular and coplanar ring geometries and in closest agreement with the calculated value for a uniform distribution of dihedral angles. For homogeneous kinetics to be obtained in the case of the uniform distribution, interconversion among the dihedral angles would have to be rapid compared to the rate of electron transfer.<sup>26</sup> Alternatively, the dihedral angles may be narrowly distributed about an intermediate value that gives a  $T_{\text{DA}}^2$  value similar to the average value of  $T_{\text{DA}}^2$  for the uniform distribution. Neither possibility can be ruled out at this point, as the barrier to rotation is known to be very small<sup>27</sup> although a distinct set of dihedral angles can be observed in the solid state.<sup>2</sup> We note that, for the uniform distribution of dihedral angles in the OPE spacers, not only the value of  $\beta$  but also the ratios of the calculated  $T_{\text{DA}}^2$  values to those for the aliphatic spacers (of the same length) correspond closely to the data in Figure 1. Thus the GMH-INDO/S method appears to be an appropriate theoretical tool for guiding the development of synthetically convenient structures for the control of interfacial electron transfer.

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(25) The use of  $\cos(\theta)$  and  $\sin(\theta)$  is an approximation motivated by the fact that, for the purpose of rotation about the spacer axis, the relevant orbitals of benzene (either HOMO or LUMO) have the nodal structure of  $2p\pi$  orbitals, in contrast to a situation involving porphyrins linked by a biphenyl spacer, as analyzed by Helms et al. (Helms, A.; Heiler, D.; McLendon, G. *J. Am. Chem. Soc.* **1991**, *113*, 4325), using the theory given by Cave et al. (Cave, R. J.; Siders, P.; Marcus, R. *J. Phys. Chem.* **1986**, *90*, 1436).

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