Solvent Mediated Coupling Across 1 nm: Not a π Bond in Sight

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Significant electronic coupling between donor (D) and acceptor (A) moieties is a prerequisite for rapid electron transfer.[1] A variety of "rigid" media are known to effect coupling between widely separated D and A units.[2] Recent reports show that fluid solvents also provide electronic coupling for highly curved D-bridge-A molecules.[3] Significant solvent-mediated coupling (SMC) has been reported in cases where (i) the covalent bridge (B) connecting the D and A provides little coupling (e.g. long bridges with non-trans σ-bond units[3,4] or symmetry-forbidden DBA topology[5]), (ii) the through solvent "path" from D to A is relatively short (<14 Å), and (iii) the solvent is aromatic or contains a high density of π bonds (e.g nitriles).[3,6] For electron transfer involving excited donors, we reported[6] a correlation between SMC magnitude, $|V|$, and solvent vertical electron affinity, EA_V.[7] Only solvents with π bonds were investigated. Transfer rate constants in saturated solvents were too small to measure for the curved DBA molecules that rely on SMC. The absence of transfer "across" saturated solvents is puzzling given numerous examples of through σ-bond coupling in other systems.[1,2] Herein, we report that saturated halocarbon solvents ($CH_{4-n}X_n$) produce D*/A couplings across 1 nm that are as large or larger than the coupling provided by any π bond containing solvent explored to date. The largest rate constants and couplings are found in brominated or chlorinated solvents with $EA_V \sim 0$. The results demonstrate that EA_V strongly influences SMC magnitudes, whether or not the solvent contains π bonds.

Charge separation (CS) rate constants, k_{CS}, in the C-shaped and linear DBA molecules, **1** and **2**, were determined from time-resolved fluorescence decays.[8] In both molecules, the donor is the lowest singlet excited state of the dimethoxyanthracene group and the acceptor is a nitroethylene group. The CS distance is 10.0 Å in **1** and 12.2 Å in **2**.[9] The rate constants at 295 K (Table 1) exhibit interesting solvent dependence. Changing from the least to the most polar solvent ($Et_2O \rightarrow CH_3CN$) produces comparable percentage increases of k_{CS} in **1** and **2**. By contrast, changing from CH_3CN to $CHCl_3$ or PhCN increases the rate 4-fold for **2** but increases the rate 21- to 26-fold for **1**. k_{CS} values for **1** are fastest in electron deficient aromatic and halocarbon solvents. In the latter, k_{CS} increases with an increase in the number of halogens and upon replacement of chlorine by bromine. These trends are not the result of heavy atom induced intersystem crossing or electron transfer to the solvent because the reported k_{CS} values account for the donor's intrinsic decay rate constant (k_{DB}) in each solvent and at each temperature.[10] k_{CS} for **2** also increase as one proceeds down the list of solvents in Table 1; however, the increase is significantly greater (up to 10-fold) for **1**. Semiclassical electron transfer theories express the transfer rate constant as the product of $|V|^2$ and the Franck−Condon weighted density of states (FCWDS).[11] It is not possible to determine $|V|$ and the FCWDS from k_{CS} at a single temperature. Values of $|V|$(D*/A) and λ_S-(295 K) for **1** and **2** can be determined by fitting the k_{CS} data as a function of temperature to the semiclassical rate expression.[11,12] The variation of λ_S and ΔG with temperature must be modeled.[12] Continuum models predict reasonable values of λ_S at room temperature but generate erroneous temperature dependence, particularly in polar solvents.[13] Instead, the temperature dependence of λ_S was evaluated using Matyushov's dipolar, polarizable hard-sphere model.[14] This model combines reorientation, λ_P, and translation, λ_D, reorganization contributions to produce λ_S. The ratio λ_P/λ_D at 295 K and the temperature dependence of λ_D were determined according to Matyushov.[12,14] The temperature dependence of λ_P was calculated by using the Pekar factor.[15] As implemented here, the model predicts $\lambda_S(T)/\lambda_S(295\ K)$ so that

Table 1. ϵ_S, n_D, EA_V, and k_{CS} for **1** and **2** and k_{DB} at 295 K

solvent	ϵ_S[15]	n_D[15]	EA_V[7]	$k_{CS}(1)/ns^{-1}$	$k_{CS}(2)/ns^{-1}$	k_{DB}/ns^{-1}
Et_2O	4.3	1.353		0.011	2.2	0.036
CH_3CN	37.5	1.346	−2.8	0.047	6.2	0.022
THF	7.6	1.405		0.054	7.3	0.032
CH_2Cl_2	8.9	1.421	−1.2	0.39	16.	0.025
$PhCH_2CN$	18.7	1.521	−1.0	0.46	16.	0.032
$CHCl_3$	4.9	1.443	−0.35	1.0	25.	0.039
PhCN	25.2	1.526	0.2	1.2	24.	0.033
CH_2BrCl	8.0[a]	1.483		1.2	35.	0.050
CH_2Br_2	7.4	1.555	−0.2	2.6	50	0.21

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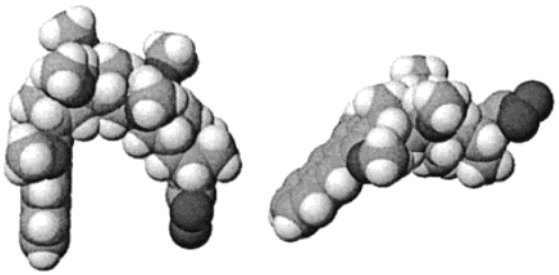
Chart 1. Electron Transfer Molecules: **1** (left) and **2** (right)



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(8) Both **1** and **2** contain 2% of an impurity whose fluorescence lifetime is the same as that of a donor only (DB) model compound.
(9) CS distance determined using the Generalized Mulliken Hush method; Cave, R. J.; Newton, M. D. *Chem. Phys. Lett.* **1996**, *249*, 15.
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Table 2. Regression Values of $|V|$ and λ_S(295 K) [λ_S(295 K) Predicted by a Two Sphere Continuum Model, for the Same Range of Radii, Are Also Shown]

DBA	solvent	$\|V\|$ (cm^{-1}) [a]	λ_S (eV) [a]	$\lambda_{continuum}$ (eV) [a]
1	CH_3CN	3.6 ± 0.1	1.45 ± 0.01	1.09 ± 0.07
1	CH_2Cl_2	4.4 ± 0.4	0.99 ± 0.01	0.79± 0.05
1	$PhCH_2CN$	5.2 ± 0.1	1.17 ± 0.01	0.78 ± 0.05
1	$CHCl_3$	6.7 ± 1.3	0.75 ± 0.02	0.57 ± 0.04
1	PhCN	6.8 ± 0.1	1.13 ± 0.01	0.81 ± 0.05
1	CH_2Br_2	13.5 ± 1.5	0.99 ± 0.01	0.59 ± 0.04
2	Et_2O	20 ± 6	0.79 ± 0.03	0.75 ± 0.04
2	CH_3CN	18 ± 1	1.20 ± 0.01	1.23 ± 0.07
2	PhCN	20 ± 1	0.96 ± 0.01	0.91 ± 0.05

[a] The range of values obtained for different r_A values is indicated by the number following the ± symbol.

λ_S(295 K) scales λ_S at all temperatures.[16] The solvent and temperature dependence of ΔG was calculated according to Weller.[17]

D and A radii are needed to calculate ΔG and λ_S as a function of solvent and temperature. The radii influence the calculated FCWDS most significantly in weakly polar solvents. Radii of 4.5 Å were used for this D and an alkene-diester A.[5b,12] The nitroethylene acceptor contains fewer atoms, suggesting a smaller value of the radius, r_A. To assist evaluation of r_A, k_{CS} for **2** was determined in cyclohexane, Bu_2O, Pr_2O, and Et_2O. Negligible transfer was detected in C_6H_{12}.[18] Weller's model predicts $\Delta G_{CS} < 0.06$ eV in C_6H_{12} for $r_A > 4.3$ Å. Measurable k_{CS} is expected for $\Delta G_{CS} < 0.06$ eV,[19] thus ΔG_{CS} must be more positive in C_6H_{12} and r_A must be smaller than 4.3 Å. The volume of the neutral acceptor group[20] corresponds to a radius of 3.3 Å. The appropriate Born radius for an anion is typically larger than the neutral radius.[21] To explore the influence of r_A on the analysis, λ_S(295 K) and $|V|$ for **2** were extracted from k_{CS}(T) data in CH_3CN, PhCN, and Et_2O. Table 2 lists the means and range of values from analyses using $r_A = 3.5$, 3.7, 3.9, and 4.1 Å. $|V|$ in Et_2O is most sensitive to the value of r_A (±30% of the mean). The $|V|$ for **2** appear constant in three solvents of very different polarity and ability to mediate coupling.[6,12] A constant, *through bond* $|V|$ is expected[2c,6,12] for a DBA with an all *s*-trans bridge. Its observation for **2** indicates the temperature dependence of the FCWDS is reasonably modeled.[6,12,13] Fixing $r_A = 3.7$ Å yields $|V| = 20 \pm 2$ cm^{-1} for **2** in all three solvents.[22]

In contrast to **2**, the $|V|$ obtained by fitting k_{CS}(T) data from **1** vary substantially with solvent (Table 2). The largest $|V|$ for **1**, in CH_2Br_2, is nearly as large as the coupling provided by the covalent bridge of **2**. The $|V|$ in the next two most effective solvents, $CHCl_3$ and PhCN, are half as large.[23] These three solvents have the most positive EA_V (Table 1). Two of these three solvents lack π bonds entirely.[24] The smallest $|V|$ for **1** are found in solvents with the most negative EA_V.[22]

Compared to **2**, the bridge in **1** contains one bend and four more σ-bonds. If only bond mediated coupling is active, $|V|(1)$ should be less than $0.07 \times |V|(2) = 1.4$ cm^{-1}.[25] The D, B, and A groups of **1** constitute the walls of a molecular cleft that is wide enough (~7 Å between the "walls") to entrain solvent molecules. These may act as a "second" bridge for the purpose of coupling. For SMC involving unfilled orbitals of a single solvent within the cleft, $|V|$ may be approximated as $\beta_{D^*S}\beta_{SA}/\Delta$, where the β are D*S and SA exchange integrals and Δ is the vertical energy gap between the CS transition state and the superexchange state, D^+S^-A.[26] The vertical energy gap is smallest for solvents with the lowest energy, unfilled orbitals (most positive EA_V). Thus, the EA_V in the halogenated methanes and PhCN enhance SMC relative to the other solvents. At this point, it is premature to ascribe $|V|$(**1**) in CH_3CN as primarily solvent or bridge mediated.

The EA_V allow coarse grouping of Δ (and SMC) for the solvents.[27] Within each group, the dependence of $|V|$ on EA_V is not monotonic (e.g., in PhCN, $CHCl_3$, and CH_2Br_2). SMC magnitudes are affected by the D*/S and S/A exchange integrals.[26] These integrals depend on solvent shape, placement, orientation and on the atomic coefficients of the active molecular orbitals, presumably the LUMO for the most positive EA_V solvents. The LUMO coefficients of PhCN are largest at C_1 and C_4 with smaller values at C_2, C_3, and CN. For a single PhCN to span the cleft requires specific solvent placement and orientation; with C_4 proximate to D(A) and CN proximate to A(D). The σ^* LUMO's of $CH_{4-n}X_n$ have large coefficients on the halogen and carbon atoms.[28] The halomethanes readily access orientations that span the cleft of **1** and place the solvent LUMO (on a Cl or Br) nearly in van der Waals contact with the D and A.[29] This should produce a larger percentage of SMC competent, "in-cleft" solvent configurations, particularly for the largest solvent, $CHCl_3$.[30] Even though $1/\Delta$ is smaller for $CHCl_3$ and CH_2Br_2 than for PhCN, larger values of $\beta_{D^*S}\beta_{SA}$ in a larger fraction of solvent configurations are likely responsible for the observed order of couplings.[31] The low energy and spatially expansive LUMO of the halomethanes give rise to substantial solvent mediated electronic coupling on the 1 nm length scale.

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Supporting Information Available: DBA line structures, tables of k_{CS}(T) and k_{DB}(T), and views of **1** with solvent in the cleft (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) λ_S for **1** are 0.2 to 0.4 eV larger than the continuum estimates. Analyses of k_{CS}(295 K) using $\lambda_{continuum}$ yield |V| in PhCN, $CHCl_3$ and CH_2Br_2 that are 3.0, 3.4 and 4.1-fold bigger than |V| in CH_3CN. The solvent dependence of |V| is robust to the model used for λ_S.

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