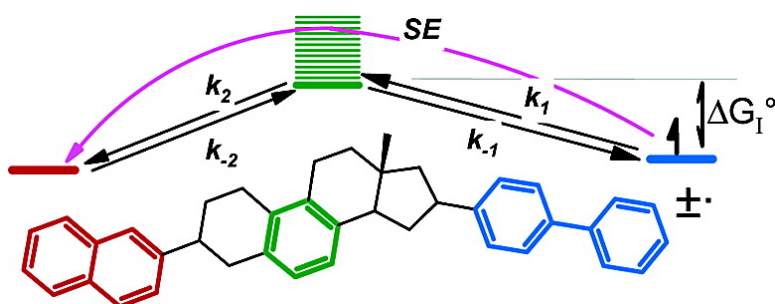


Superexchange and Sequential Mechanisms in Charge Transfer with a Mediating State between the Donor and Acceptor

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Superexchange and Sequential Mechanisms in Charge Transfer with a Mediating State between the Donor and Acceptor

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Abstract: The rate of intramolecular charge transfer from biphenyl to naphthalene was determined for the radical anions and radical cations of molecules with the general structure: (2-naphthyl)-(steroid spacer)-(4-biphenyl). Varied degrees of unsaturation (one double bond, NSenB; two double bonds, NSen₂B; and the b-ring completely aromatized, NSarB) were incorporated into the steroid spacer to examine the effect it would have on the charge transfer rate. The charge transfer rate, as inferred from the decay of the biphenyl radical ion absorption, increased in all cases relative to the completely saturated 3-(2-naphthyl)-16-(4-biphenyl)-5 α -androstane (NSB) reference molecule. For the anion charge transfer, the decay rates increased by factors of 1.4, 4.2, and 5.1, respectively, and for the cation, the decay rates increased by factors of 5, 276, and 470. To explain the results, the charge-transfer process was viewed as a combination of two independent mechanisms: a single-step, superexchange mechanism, and a two-step, sequential charge transfer. Using a low level of theory, simple models of the superexchange and two-step mechanisms were developed to elucidate the nature and differences between the two mechanisms. The critical variable for this analysis is the free energy of formation (ΔG_1°) of the intermediate state: (2-naphthyl)-[spacer]^{1±}-(4-biphenyl). The conclusion from this treatment is that superexchange is the dominant mechanism when ΔG_1° is large, but at small ΔG_1° , the sequential mechanism will dominate. This is because the superexchange rate is shown to have a weak dependence on ΔG_1° , changing 10-fold for a change in ΔG_1° of 2 eV, compared to the sequential mechanism in which the rate can change over 10³ for 0.5 V.

Introduction

Superexchange and sequential (charge hopping) mechanisms can both contribute when an electron (or ET for electron transfer in the case of the radical anions) or hole (HT for hole transfer in the case of the radical cations) is transferred from a donor to an acceptor with the assistance of an intermediate or “midway” group, as exemplified in Figure 1. In the superexchange process,^{1,2} direct, long-distance electron transfer (or simply CT for the charge transfer of either charge) is enhanced by indirect mixing of the donor and acceptor wave functions through the orbitals located between the donor and acceptor. In sequential CT, the charge temporarily resides on the midway group, while in superexchange, this intermediate state only participates by providing a virtual state. The two mechanisms have received theoretical treatments in several papers,^{3–6} and several molecules have been constructed to provide insight into the different mechanisms.^{7–11} In addition, more complex unified treatments

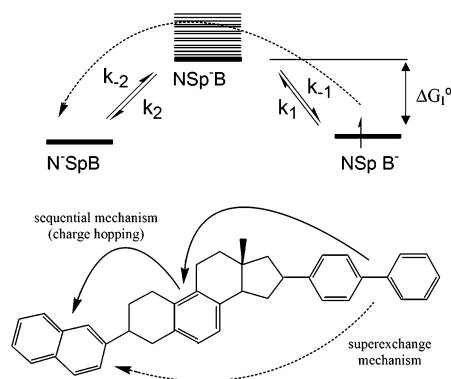


Figure 1. Sequential (charge hopping) and superexchange mechanisms illustrated for electron transfer in an anion having a phenyl group in the spacer. In its initial state, the electron resides on biphenyl NSp(B)^- . In the sequential mechanism (solid lines), the charge transfers to the phenyl in the spacer to form a thermally relaxed $\text{N(Sp)}^- \text{B}$ (heavy line) at a rate, k_1 . The reverse rate is k_{-1} , and the free energy change is ΔG_1° . In a second step, the charge transfers to the naphthalene ($\text{N}^- \text{SpB}$) with a rate, k_2 . In the superexchange mechanism (dashed arrows), the charge transfer occurs in a single-step process, but the electronic coupling is enhanced by the indirect mixing of the biphenyl and naphthalene molecular orbitals through the σ , σ^* , π , and π^* molecular orbitals of the steroid spacer.

have been developed to account for both mechanisms.⁴ The relative magnitude of these two mechanisms has been a source

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of controversy in a number of different systems. One of the most well-known and hotly debated is the charge separation step in the photosynthetic reaction center.¹² Another vigorous debate^{5,6,13} concerns the charge transport in DNA¹⁴ and whether it is a “molecular wire”. This question of mechanism also arises in molecular assemblies constructed for vectorial energy capture,^{7,15,16} in the charge transfer through polypeptides,¹⁷ and through conjugated molecules attached to electrodes.^{9–11}

One source of this controversy stems from the problem that if the charge transfer involves a temporary, intermediate, ionized species, such as the example in Figure 1, it may not be observable if the second charge-transfer step (k_2 in Figure 1) is faster than the first (k_1). The lack of an observable intermediate cannot exclude a multistep mechanism. So, in general, any result must be scrutinized carefully.

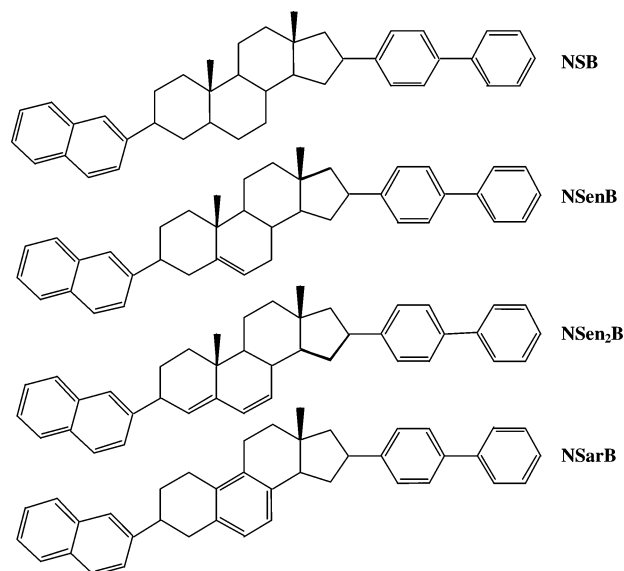


Figure 2. Series of compounds studied in this work.

In this paper, the charge-transfer rates were determined for a series of compounds (shown in Figure 2) with the structure (2-naphthyl)-steroid spacer-(4-biphenyl), NSpB. Pulse radiolysis was used to generate the radical anion or radical cation of the molecule. The transfer process was then observed photochemically.



Here, B = biphenyl, N = naphthalene, and Sp is the spacer group. The steroid spacer acts as a rigid scaffold and either is completely saturated or includes π bonds. The π bonds in the spacer can increase the charge-transfer rate by (1) improving the electronic coupling between the donor and acceptor, or (2) actually transfer charge to the intraspacer π system (Π_s) as a first step, followed by transfer to the naphthalene in a sequential “hopping” mechanism. Both mechanisms contribute to the charge-transfer process. Determining the ΔG° of the intermediate state is necessary for estimating the magnitude of the individual mechanisms, so a principal focus of this work is toward the reliable assessment of the energetics.

The compounds in the present study have the following notable features: (1) The same compounds can be used for both electron transfer and hole transfer. (2) The number of bonds separating the naphthalene from the biphenyl is the same in all of the compounds, and similarly, the distance between them remains almost constant. (3) The free energy change for the biphenyl to naphthalene charge transfer is precisely known and is similar for the electron and hole transfer reactions. (4) The electronic couplings can be estimated from a previous set of experiments. (5) The reactions are of the “charge-shift”-type (donor) $^\pm$ acceptor \rightarrow donor(acceptor) $^\pm$ (as opposed to charge separation (donor) $^+$ acceptor \rightarrow (donor) $^+$ (acceptor) $^-$). Charge

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Table 1. Rate Constants for Intramolecular Hole Transfer in Cations and Electron Transfer in Anions and Free Energies, ΔG_1° , for Charge Transfer to the Intermediate States

| compound | R_{DI} (Å) ^a | Hole Transfer | | | $\Delta\lambda_s^d$ | $\Delta\lambda_s^d$ | $\lambda_{v,I}^e$ | Electron Transfer | | |
|---------------------|---------------------------|-----------------------------|--------------------------|-----------|---------------------|---------------------|-----------------------------|-----------------------------|--------------------------------------|--|
| | | k_{HT} (s ⁻¹) | ΔG_1° (meV) | size (eV) | distance (eV) | (eV) | k_{ET} (s ⁻¹) | EA _{ETS} /gas (eV) | ΔG_1° (eV) ^g | |
| NSB | 17.4 | 1.3×10^6 | | | | | 1.9×10^6 | | | |
| NSeNB | 10.5 | 6.3×10^6 | 358 ± 100^b | 0.26 | -0.21 | 0.59 | 2.7×10^6 | -2.24 | 1.46 ± 0.3 | |
| NSen ₂ B | 10.5 | 3.5×10^8 | -20 ± 30^c | 0.08 | -0.21 | 0.55 | 8.1×10^6 | -0.62 | 0.27 ± 0.2 | |
| NSarB | 9.4 | 6.0×10^8 | 0 ± 30^c | 0.08 | -0.27 | 0.43 | 9.7×10^6 | -1.12 | $0.77 \pm 0.2, 0.79 \pm 0.08^h$ | |

^a Center-to-center distance from the donor (biphenyl) to the intermediate group (Π_s) or to the acceptor in the case of NSB. ^b From measurements on model compounds (see Table 2). ^c From participation of the spacer π group in the equilibrium in the NSpB ion. ^d Change in solvent reorganization energy for the charge-transfer reaction from biphenyl to the intermediate relative to the transfer from biphenyl to naphthalene in NSB ($\lambda_s = 0.75$ eV). * The $\Delta\lambda_s$ size of Π_s and the $\Delta\lambda_s$ distance are estimated by eqs 5a and 5b. Values of $\lambda_{s,I}$ are then 0.75, 0.80, 0.62, and 0.56 for the four compounds. ^e Computed³⁶ (B3LYP/6-31G*) internal reorganization energies for the charge transfer from biphenyl to the intermediate. The $\lambda_{v,I}$ for NSB is from refs 18 and 25. ^f Vertical electron affinities measured by electron transmission spectroscopy²⁹⁻³¹ on models for the intermediate π groups, trimethylethylene (-2.24 eV), butadiene (-0.62 eV), and benzene (-1.12 eV), in the gas phase. ^g Energy to transfer an electron from biphenyl⁻ to the intermediate group. Estimated from the difference in vertical electron affinities (EA) and corrected for the difference in solvation energies, $-\Delta\Delta G_s^\circ$, determined for cations (Table 2). $-\Delta\Delta G_s^\circ$ for the diene was taken to be the same as that for the OHP based on nearly identical computed solvation energies (PCM/b3lyp/3-21g). For biphenyl, the vertical EA (EA_{ETS} = -0.3 eV³³) was assumed to include a 0.13 eV reorganization energy from torsional vibrations³² that are of small importance in the other molecules. That amount was, therefore, added to EA(biphenyl). ^h ΔG_1° in THF is estimated from a measured equilibria for the benzene anion.⁴¹ A correction of 184 ± 80 meV for the effects of the alkyl groups was based on Lawler and Tabit's⁴² measurements of equilibria of mono- and dialkylated benzene anions. Partial additivity is assumed and is responsible for most of the uncertainty. * Strictly $\lambda_s = 0.62$ eV, but this does not affect the corrections.

shift reactions are easier to interpret because of the absence of Coulombic forces.

In this paper, the Results section presents the rates of electron and hole transfer reactions for the four NSpB compounds (eight rates in all). The first part of the Discussion section describes the methods used to estimate ΔG_1° , the electronic couplings, and the reorganization energies associated with the formation of the NSp[±]B intermediate states. The second part uses these quantities to plot the modeled sequential and superexchange rates as a function of ΔG_1° . The calculated rates are then compared with the observed rates to evaluate the theoretical models and to reach conclusions about the charge-transfer mechanism.

Experimental Section

The 3,5-cholestadiene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene were purchased from Aldrich, and the 1,2,3,4,5,6,7,8-octahydrophenanthrene was purchased from CTC Organics. The 3,5-cholestadiene was recrystallized from absolute ethanol prior to use, and the 1,2,3,4,5,6,7,8-octahydrophenanthrene was purified by passing it through activity 1 alumina with 1:9 methylene chloride/hexane. The 2-methyl-2-butene and 2,3-dimethyl-2-butene were used without any purification. 1,2-Dichloroethane (DCE) from Burdick and Jackson was distilled from P₂O₅ under an argon atmosphere and then placed in an evacuated bulb over a mixture of 4 and 3 Å sieves. Tetrahydrofuran (THF) was dried over sodium metal with benzophenone as the indicator, distilled under nitrogen, and placed in a dry evacuated bulb with a sodium-potassium alloy. After sonication for several minutes, an aqua blue color from solvated electrons appeared, indicating the solution was dry and oxygen-free.

The samples were prepared by vacuum distilling the solvents into the sample vials containing the compounds. If the compounds were volatile, the samples were cooled (-20 to -100 °C) prior to evacuation. After the solvent was transferred to the sample vial, the solutions were degassed by cooling to temperatures just above the solvent freezing point and evacuating to pressures of $<10^{-4}$ mbar.

The radical anions were generated by irradiating solutions of the NSpB compounds in THF with 30 ps, 20 MeV electron pulses from the Argonne Linac. Irradiation generates solvated electrons ($<2 \times 10^{-5}$ M) which attach to the biphenyl and naphthalene groups to form N⁻SpB and NSpB⁻. Radical cations were generated by irradiating solutions of the NSpB compounds in DCE. Irradiation of DCE produces two oxidizing species, DCE⁺⁺ and CH₂=CHCl⁺. Both react with the NSpB compounds to form N⁺SpB and NSpB⁺.

Following the charge capture, we observed the charge transfer reactions photometrically as they proceeded to equilibrium. Intramolecular rate components, reported in Table 1, were determined by concentration dependence. Electron and hole transfer reactions were followed by biphenyl radical ion absorption at λ_{max} . The HT reactions were monitored at 730 nm, and the ET reactions were monitored at 650 nm. Acquisition of transient absorption data and fitting of the data have been described elsewhere.¹⁸ During and after the charge transfer, the ions (NSpB)⁺ or (NSpB)⁻ decay principally by reaction with the counterions, Cl⁻ in DCE or the solvated protons in THF. While these decay processes are considerably slower than those of the charge-transfer reactions that are the subjects of these measurements, they were included in the kinetic model¹⁸ and are fully corrected. The intermolecular equilibrium measurements of model compounds will be described separately along with an ongoing study of their description by computational models.¹⁹

In NSpB, both the cation and anion were observed to form in a roughly equal ratio of N[±]SpB and NSpB[±] (50 ± 10%). Determination of the CT kinetics does not depend on this ratio as long as there is a sufficient change in absorption to follow the reaction as it goes to equilibrium. The equilibrium constants for charge transfer to the naphthyl group in NSpB[±] were determined from the reduction of the biphenyl ion absorption compared to that in 3-(4-biphenyl)-5 α -androstane (BS).¹⁸ The equilibrium values were verified by comparison with NSB.

For the cations, a possible source of uncertainty is the capture of additional positive charge by the Π_s groups to generate more (NSpB)⁺ ions than in the saturated reference molecules, BS and NSB. This uncertainty, included in the reported values, is very small because the molecules capture nearly all of the positive charge (DCE⁺⁺ and CH₂=CHCl⁺). This is not a consideration for the anions because the Π_s groups reduce very slowly or not at all.

Results

The charge-transfer rates are presented in Table 1. The electron transfer rates for NSeNB, NSen₂B, and NSarB increased by factors of 1.4, 4.2, and 5.1, respectively, relative to NSB, while hole transfer rates increased by factors of 5, 276, and 470, respectively. From previous studies on NSpB,^{20,21} the ΔG°

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for the charge transfer from biphenyl to naphthalene was determined from the intramolecular equilibrium to be -50 ± 10 meV for the ET and -40 ± 10 meV for the HT reactions. Identical results were found for four of the six reactions with unsaturated spacers; the ΔG° was not altered by the presence of the π groups in the spacer. For the other two cases (the HT reactions in NSen₂B and NSarB), the unsaturated spacer ion exists in the final equilibrium mixture (elaborated on later in the paper), which adds uncertainty to the assessment of ΔG° . The observations were still consistent with a $\Delta G^\circ = -40$ meV, but a change in the ΔG° for charge transfer to naphthalene of ± 20 meV would also be consistent with the observed results. Such a perturbation could conceivably come from the unsaturation in the spacer.

The observed charge-transfer rate is the sum of the superexchange (k_{SE}) and sequential charge-transfer rates (k_{2s}), $k_{CT} = k_{SE} + k_{2s}$. The methods used to assess the different rate constants are discussed next.

Nonadiabatic electron transfer theory²² has successfully described the superexchange process in molecules with saturated spacers.^{20,21,23–25} The theory describes the electron transfer rate constant using four principle factors: the electronic coupling, $V(r)$, the free energy change, ΔG° , the solvent reorganization energy, λ_s , and the internal reorganization energy, λ_v . These values were determined for a similar set of compounds^{20,25} and are used in this analysis to estimate the rates for k_{SE} and k_{2s} . Since the sequential charge-transfer mechanism is simply two discrete superexchange processes, eq 2 can be used to calculate k_1 and k_2 .

$$k_{CT} = \frac{2\pi}{\hbar} |V(r)|^2 \text{FCWD} \quad (2)$$

$$\text{FCWD} = (4\pi\lambda_s k_B T)^{-1/2} \sum_{w=0}^{\infty} \left(e^{-S} \frac{S^w}{w!} \right) \exp\{-[(\lambda_s + \Delta G^\circ + w\hbar\nu)^2 / 4\lambda_s k_B T]\}$$

$$S = \lambda_v / \hbar\nu$$

When the rate of sequential charge transfer is much slower than the superexchange rate ($k_{SE} \gg k_{2s}$), the intraspacer π system (Π_s) only alters the electronic coupling and does not change the other parameters of eq 2. In this case, the charge-transfer rate provides a simple measure of the superexchange coupling (V) as enhanced by the π bonds in the spacer.

The superexchange coupling resulting from an intermediate virtual state, I, between the donor and acceptor can be estimated from first-order perturbation theory:

$$V_{DA} = \frac{V_{DI}V_{IA}}{E_I - E_D} \quad (3)$$

where $E_I - E_D$ is the energy required to promote an electron or hole from the donor to the intermediate, and V_{DI} and V_{IA} are electronic coupling matrix elements between the donor and intermediate Π_s and between the Π_s and acceptor states, respectively.^{2,26}

Equation 3 is the simplest possible model of the superexchange coupling through a low-lying intermediate state. It is accurate for a single intermediate state when the coupling terms in the numerator, V_{DI} and V_{IA} , are much smaller than the denominator. V_{DI} and V_{IA} can be estimated using earlier results from these labs that delineated the distance dependence of the matrix elements in saturated hydrocarbon spacers, such as the ones in the present study. In our analysis of the data, eq 3 is applied to the ground state of the charged intermediate (NSp[±]B). This method enables the use of experimental energies.

The sequential charge-transfer rate, k_{2s} , is expected to be well approximated by the first charge-transfer step (k_1 in Figure 1). The steady-state expression, $k_1 k_2 / (k_{-1} + k_2)$, used to analyze these results is a better estimate of the overall sequential rate, but the two are in very good agreement.

Determination of the ΔG_1° for Charge Transfer to π Groups in the Spacer. In principle, electrochemical redox potentials can provide estimates for ΔG_1° . Unfortunately, the electrochemical oxidations of simple olefins can be highly irreversible, so other methods were used to determine ΔG_1° .

ΔG_1° of the Cation Intermediates. Upon completion of the charge-transfer reaction, some donor ion (biphenyl[±]) will exist in the equilibrium mixture. When K_{eq} is small enough that at equilibrium a sizable population of the charge resides on the Π_s , it, and therefore ΔG_1° , can be estimated from the equilibrium absorption. Because the radical cations of the Π_s groups have much smaller extinction coefficients than those of the naphthalene or biphenyl radical cations throughout the vis–NIR spectral regions, any charge on the Π_s is readily observed as a reduction of the absorption in the equilibrium mixture. Such a reduction relative to the reference compound NSB was not observed for any of the anions but was observed in two of the cations, NSen₂B and NSarB. In each molecule, there is only one biphenyl, one naphthalene, and one Π_s group competing for the charge, so this method is only effective for $K_{eq} < \sim 10$ ($|\Delta G_1^\circ| \leq 60$ meV). The corresponding free energy changes are reported in Table 1.

ΔG_1° can also be deduced from the equilibrium constant of the hole transfer (4) from 4-cyclohexylbiphenyl (CB) and a model compound (M) whose structure is similar to that of the π system within the spacer. This method accesses a larger range of K_{eq} because concentrations can be independently adjusted. The free energy change for this reaction will be written as $\Delta G_1^\circ(M)$, indicating that it is an estimate of ΔG_1° determined from a model compound. For direct equilibria, this method is limited to $|\Delta G_1^\circ(M)| < 200$ meV, and its precision depends on

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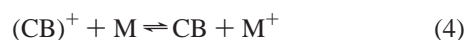
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Table 2. Ionization Potentials and Intermolecular Ion Equilibria Measured in DCE for Model Compounds Giving Estimations of ΔG_1° and Differences in Solvation Energies for Positive Ions

| compound ^a | IP (eV) ^b | Relative to CB | | $\Delta G_1^\circ(\text{M})$ corrected (meV) |
|-----------------------|----------------------|--------------------------------------|--|--|
| | | $\Delta G_1^\circ(\text{M})^c$ (meV) | $-\Delta\Delta G_s^\circ$ (meV) ^d | |
| CB | 7.71 ± 0.02 | | | |
| M ₃ Et | 8.68 ± 0.01 | >100 | <870 | 358 ± 100 ^e |
| M ₄ Et | 8.27 ± 0.01 | -52 ± 6 | 612 ± 36 | |
| Cdien | | <-90 | | |
| OHP | 7.89 ± 0.05 | 0 ± 10 | 180 ± 20 | 0 ± 10 |

^a Abbreviations: CB = 4-cyclohexylbiphenyl, M₃Et = 2-methyl-2-butene, M₄Et = 2,3-dimethyl-2-butene, Cdien = 3,5-cholestadiene, OHP = 1,2,3,4,5,6,7,8-octahydrophenanthrene. ^b Ionization potentials in the gas phase.²⁸ ^c Free energy change measured in DCE solution for charge transfer from CB⁺ to the model compound, M. ^d Differences in solvation energies relative to CB based on measured equilibria and ionization potentials: $\Delta\Delta G_s^\circ = \Delta G_1^\circ(\text{M}) - (\text{IP}_\text{M} - \text{IP}_\text{CB})$. ^e Free energy for transfer from CB to the π group in the spacer estimated as $\Delta G_1^\circ(\text{M}_3\text{Et})$ corrected with the $\Delta\Delta G_s^\circ$ from M₄Et.

how structurally and electronically similar the model compound is to the π portion of the spacer. To measure a ΔG° of -200 meV ($K_\text{eq} = 2500$) requires a concentration ratio of $[\text{CB}]/[\text{M}] > 1000$, which is feasible if the lifetimes of both ions are long. Equilibria for model compounds have been studied experimentally and theoretically¹⁹ and are reported in Table 2.



NSenB: Table 2 gives information for two model compounds, 2-methyl-2-butene (M₃Et) and 2,3-dimethyl-2-butene (M₄Et), studied by Liu.¹⁹ M₃Et is structurally more similar to the spacer π bond of NSenB than M₄Et because it has three alkyl groups attached to the π bond compared to the four in M₄Et. The equilibrium for eq 4 was far to the left for M = M₃Et, so no measurement could be obtained, but the measured equilibrium constant for the CB to M₄Et hole transfer reaction gave $\Delta G_1^\circ(\text{M}_4\text{Et}) = -52$ meV. Though the equilibrium constant of eq 4 for M₃Et could not be measured, $\Delta G_1^\circ(\text{M}_3\text{Et})$ was estimated from $\Delta G_1^\circ(\text{M}_4\text{Et})$ and the difference in ionization potentials (IP) between M₃Et and M₄Et. Using the relationship, $\Delta\text{IP}(\text{CB}, \text{M}_4\text{Et}) = \Delta G_1^\circ(\text{CB}, \text{M}_4\text{Et}) + \Delta G_s^\circ$, and assuming that the solvation energy, ΔG_s° , is roughly the same for M₃Et, $\Delta G_1^\circ(\text{CB}, \text{M}_3\text{Et})$ can be solved (Table 2).

NSen₂B: In the full molecule, NSen₂B shows a decrease in the equilibrium absorption from NSB, indicating that the “intermediate” NS(en₂⁺)B is present at equilibrium, yielding $\Delta G_1^\circ = -20 \pm 30$ meV. Thus, the diene cation is not a high-energy intermediate, but is one of the reaction products having a free energy between that of NSen₂B⁺ and N⁺Sen₂B.

The model compound, 3,5-cholestadiene (Cdien), gave a $\Delta G_1^\circ(\text{M}) < -90$ meV. Like NSen₂B, Cdien also has two conjugated double bonds, but at different positions in the steroid scaffold. This positional difference will slightly alter the conformation around the double bonds.

The disagreement between the two ΔG_1° values could come from the conformational differences, to which IPs are known to be sensitive, but it is also possible that there are significant electronic interactions between the diene and the naphthalene which could alter their oxidation potentials. The most relevant experimental value for ΔG_1° is the one measured from NSen₂B⁺. The value $\Delta G_1^\circ = -20$ meV was deduced by assuming $\Delta G^\circ = -40$ meV for the equilibrium between NSen₂B⁺ and

N⁺Sen₂B. The strong coupling (~ 600 cm⁻¹) between the diene and naphthalene could alter the energy of N⁺Sen₂B.²⁷ The ΔG_1° uncertainty in Table 1 includes the possibility that the oxidation potential of naphthalene has been perturbed.

NSarB: The model compound used for NSarB, 1,2,3,4,5,6,7,8-octahydrophenanthrene (OHP), gave $\Delta G_1^\circ(\text{M}) = 0 \pm 10$ meV. This result is consistent with the more direct measurement, $\Delta G_1^\circ = 0 \pm 30$ meV, from the absorption difference between NSarB and NSB. As with NSen₂B⁺, the intermediate is one of the reaction products existing at equilibrium, and the possibility of electronic perturbation is considered.

The availability of the ionization potentials²⁸ and the equilibria measured here provides an opportunity to estimate the difference in solvation energy ($\Delta\Delta G_s^\circ$) between two ions. If two ions have the same solvation energy, $\Delta\Delta G_s^\circ$ is expected to be zero. Instead, the results in Table 2 indicate that there are large differences in the solvation energy between M₄Et⁺ and larger, more delocalized ions, such as methylbiphenyl⁺ or OHP⁺. The values of $\Delta\Delta G_s^\circ$ are used to estimate ΔG° I and λ_s for the intermediate anions, NSp⁻B.

ΔG_1° of the Anionic Intermediates. ΔG_1° could not be directly determined for the anions because their reduction potentials are much more negative than that of CB (by greater than 100 mV). Instead, ΔG_1° values are estimated from $\Delta\Delta G_s^\circ$ and the difference in gas-phase electron affinities (EA) of representative compounds:^{29–31} trimethylethylene (-2.24 eV), butadiene (-0.62 eV), and benzene (-1.12 eV). In contrast to ionization and oxidation potentials, EAs and reduction potentials are not very sensitive to the degree of alkyl substitution on the carbon attached to the olefin.^{29,31} For example, the EAs of 1-hexene and *tert*-butyl ethylene are within a few hundredths of an electronvolt of the EA of ethylene.³¹

Because the Π_s groups are smaller than biphenyl, their anions are stabilized to a greater degree by solvation. Therefore, the gas-phase values need to be adjusted for their differences in solvation. This adjustment can be approximated with the $\Delta\Delta G_s^\circ$ determined for the cations (Table 2). For NSarB, an alternative method was available which gave a ΔG_1° in good agreement with the methods just described (see Table 1).

One further consideration needs to be addressed to estimate ΔG_1° for the anions. The EA for biphenyl is measured to be -0.3 eV, but this value reflects the vertical transition for the electron attachment. Modeli and co-workers³² have shown that the adiabatic EA is actually > -0.2 eV (the difference of ~ 0.1 eV is due to the rotational freedom between the phenyl rings.) We have also measured this difference in the form of a low-frequency ET reorganization energy,³³ finding that this difference is 0.13 eV, in agreement with Modeli’s results. Therefore, to estimate ΔG_1° for the charge transfer from biphenyl, an EA of $-0.3 - (-0.13) = -0.17$ eV is used in Table 1.

(27) The fraction of NSen₂B⁺ observed in the equilibrium between the three species, NSen₂B⁺, N⁺Sen₂B, and NSen₂B⁻, was evaluated using $f = 1/(1 + \exp(-\Delta G_1^\circ/kT) + \exp(-\Delta G_2^\circ/kT))$.

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Reorganization Energies and Electronic Couplings for Charge Transfer to and from the Intermediate. Knowledge of the solvent reorganization energies, $\lambda_{s,I}$ and $\lambda_{v,I}$, that accompany the charge transfer from biphenyl to the Π_s groups is needed to calculate both the sequential and superexchange charge-transfer rates. In theory, the solvent reorganization energy can be calculated from Marcus' expression, $\lambda_s = e^2(\epsilon_{op}^{-1} - \epsilon_s^{-1})(1/2r_D + 1/2r_A - 1/R_{DA})$, but this dielectric continuum equation often fails to accurately describe experimental results.³⁴ Instead, the $\lambda_{s,I}$ values are derived from a combination of theory and experiment.^{18,20,21,25,33} $\lambda_{s,I}$ is estimated starting with the experimental value of λ_s for NSB (0.75 eV) and adjusting for (1) the difference in size ($\Delta\lambda_s(\text{size})$) in going from a naphthalene to the smaller unsaturated groups, and (2) the difference in separation ($\Delta\lambda_s(\text{distance})$).

$$\Delta\lambda_s(\text{distance}) = e^2(\epsilon_{op}^{-1} - \epsilon_s^{-1})(1/R_{DA} - 1/R_{DI}) \quad (5a)$$

$$\Delta\lambda_s(\text{size}) = \Delta\Delta G_s(\epsilon_{op}^{-1} - \epsilon_s^{-1})(1 - \epsilon_s^{-1})^{-1} \quad (5b)$$

The distance correction (eq 5a) is derived from Marcus' expression for λ_s , while the size correction combines the Marcus expression with the Born equation,³⁵ $\Delta G_s = e^2(r_D(1 - \epsilon_s^{-1}))^{-1}$, to relate $\Delta\lambda_s(\text{size})$ to the change in solvation free energy, $\Delta\Delta G_s$. The $\Delta\Delta G_s$ values for positive ions of model compounds are reported in Table 2, and the corresponding contributions to λ_s are shown in Table 1. The present procedure has the advantage that most of the reorganization energy is obtained from experiment, with corrections of smaller magnitude coming from the dielectric continuum expressions. The use of the experimental values (e.g., λ_s and $\Delta\Delta G_s$) has the added advantage that it is likely to include some of the contributions recognized by Matyushov,³⁴ even though the corrections rely on the form of the continuum model. Matyushov's theory includes translation of solvent molecules not described by the continuum expression of Marcus.

Charge transfers to and from the intermediates are accompanied by internal reorganization energies ($\lambda_{v,I}$) different from the 0.45 eV value for transfer from biphenyl to naphthalene. Estimates of $\lambda_{v,I}$ for the NSpB $^{\pm}$ to NSp $^{\pm}$ B CT were computed³⁶ (B3LYP/6-31G*) and are reported in Table 1 and Figure 3 (the values for ET and HT $\lambda_{v,I}$ were averaged for simplicity.) The largest, $\lambda_{v,I} = 0.59$ eV for NSenB, decreased the sequential rates by a factor of 4 relative to the 0.45 eV reference value, while barely affecting (-4%) the superexchange rates. These variations in $\lambda_{v,I}$ have only moderate effects on the appearance of Figure 3.

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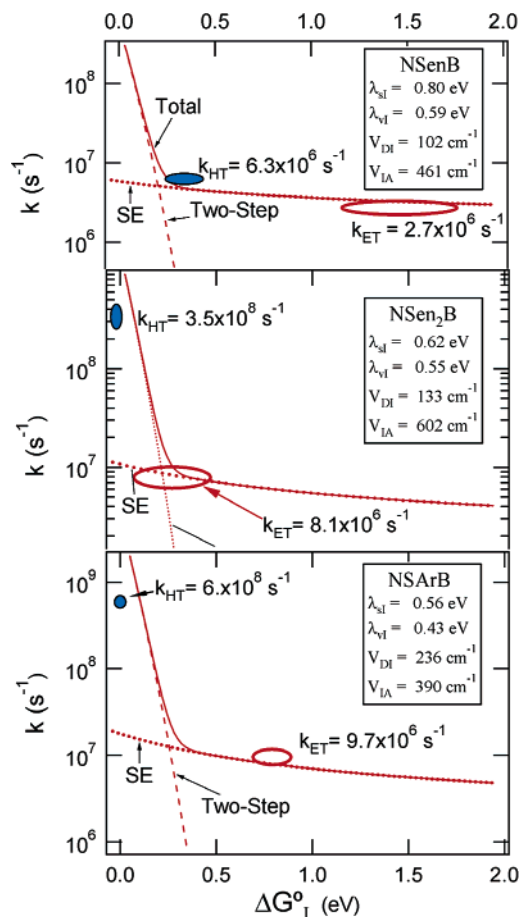


Figure 3. Rate constants for the HT measured in DCE and ET measured in THF. Measured and calculated rates are presented as functions of the free energy, ΔG_1^0 , of formation of the intermediate state from the reactant. The vertical sizes of the oval shaped points represent uncertainties in the measurements of rates; the horizontal sizes give uncertainties in ΔG_1^0 . The dotted and dashed lines are the calculated superexchange and two-step reaction rates; the solid line is the sum of the two rates. The text boxes in each of the panels give estimates of the electronic couplings and reorganization energies. The uncertainty in the computed rates is estimated to be a factor of 2.5, due principally to the uncertainty of the electronic couplings.

Table 3. Estimated Electronic Couplings between the Biphenyl and the Intermediate, Π_s Group (V_{DI}), and between the Π_s and Naphthalene (V_{IA}) used to Calculate the Two-Step Charge-Transfer Rate and the Superexchange Couplings $V_{SE}(\pi)$ used to Calculate the Superexchange Hole and Electron Transfer Rates

| compound | n^a | γ/γ_N^b | V_{DI}^c (cm^{-1}) | V_{IA}^c (cm^{-1}) | $ V_{SE}(\pi) ^d$ (cm^{-1}) | HT | ET |
|---------------------|-------|---------------------|------------------------------------|------------------------------------|--|-----|----|
| NSenB | 6, 3 | 2.2 | 102 | 461 | 3.3 | 2.0 | |
| NSen ₂ B | 5, 2 | 1.7 | 133 | 602 | 8.6 | 6.9 | |
| NSArB | 4, 3 | 1.9 | 236 | 390 | 11.5 | 6.5 | |

^a Number of saturated bonds in the shortest path from biphenyl to the intermediate group, Π_s and from Π_s to naphthalene in the compounds shown in Figure 2. ^b Ratio of the Π_s to naphthalene MO coefficients at the point of connection which gives the shortest chain of saturated bonds to biphenyl (from AM1 calculations on alkenes of Decalin or OHP.) ^c $V = 950 \text{ cm}^{-1}/1.654 \times \gamma/\gamma_N$. Uncertainties are estimated to be a factor of 1.3. ^d Additional superexchange coupling resulting from the π bonds within the spacer (excluding the $|V_{SE}(\sigma)| = 6.2 \text{ cm}^{-1}$ from the coupling through the σ bonds), as calculated by eq 6.

The electronic couplings for the charge transfer from biphenyl to the Π_s (V_{DI}) and from the Π_s to naphthalene (V_{IA}) are estimated in Table 3 based on the results from previous measurements of the distance dependence.^{18,21,25} Those studies

concluded that through n saturated bonds, $V = 950 \text{ cm}^{-1}/1.65^n$ for both ET and HT. The estimated couplings in the present molecules also include a factor for the larger orbital coefficients of the Π_s groups. Scaling V based on the MO coefficients is not well verified and contributes to the estimated uncertainties by a factor of 1.3. Because the MO coefficients for the anions and cations are within 10%, they were averaged to give a common value for V_{DI} and V_{IA} .

Charge-Transfer Reaction Mechanisms. With estimates of the salient energy terms (ΔG_1° , reorganization energies, and electronic couplings), it is possible to calculate the sequential and superexchange rates. Sequential rates are calculated as $k_1 k_2 / (k_{-1} + k_2)$, using eq 2 to calculate each k . To compute k_1 and k_{-1} , $V = V_{\text{DI}}$ and $\Delta G^\circ = \pm \Delta G_1^\circ$. To compute k_2 , $V = V_{\text{IA}}$ and $\Delta G^\circ = \Delta G_{\text{B,N}}^\circ - \Delta G_1^\circ$, where $\Delta G_{\text{B,N}}^\circ$ is the overall free energy change for charge transfer from biphenyl to naphthalene. The superexchange rates are also calculated with eq 2 using the established values for ΔG° , λ_s , and λ_v ,²⁵ but using $|V_{\text{SE}}(\sigma)| + |V_{\text{SE}}(\pi)|$ for V , where $V_{\text{SE}}(\sigma)$ represents the coupling that occurs through the σ bonds, and $V_{\text{SE}}(\pi)$ the additional coupling that results from the incorporation of the π bonds (this calculation is described later). $V_{\text{SE}}(\sigma)$ is treated as though it does not change throughout the series of compounds and is equal to the coupling in NSB (6.2 cm^{-1}).²⁵

The assumption of constructive, but not destructive, interference between the σ and π is able to explain the data. Remarkably good agreement is found by examining the ratios of the calculated superexchange rate to the observed ET rate ($k_{\text{SE}}/k_{\text{observed}}$). Assuming constructive interference ($V = |V_{\text{SE}}(\sigma)| + |V_{\text{SE}}(\pi)|$), values for this ratio are 1.3, 1.1, and 0.82 for NSenB, NSen₂B, and NSarB, respectively, but assuming destructive interference ($V = |V_{\text{SE}}(\sigma)| - |V_{\text{SE}}(\pi)|$), the same ratios are $k_{\text{SE}}/k_{\text{observed}} = 0.32, 0.003, \text{ and } 0.0004$. A similar result was observed for the NSenB HT, where $k_{\text{SE}}/k_{\text{observed}} = 0.48$, assuming constructive interference, versus 0.043, assuming destructive interference. In addition, had destructive interference occurred, the Π_s groups would have decreased the ET rates contrary to observation. The present results raise the possibility of a propensity toward constructive interference. If constructive (C) and destructive (D) interference were equally probable in each case, then for ET in NSenB and NSarB, where superexchange clearly dominates, four outcomes (CC, CD, DC, and DD) are equally likely. The observation "CC" does not necessarily indicate a propensity for C. Two more cases in Figure 3, the HT in NSenB and ET in NSen₂B, suggest constructive interference. Finding all four C, a 6.25% chance, would signal a preference for constructive interference, but this second pair of rates can easily be understood in terms of the sequential mechanism, either or both might be D. It is not clear whether constructive interference is favored. While the present results are indecisive, we may speculate that constructive interference might, in fact, be favored in systems having configurational flexibility, such as the facile rotations of B and N groups in the present molecules.

$$V_{\text{SE}}(\pi) = V_{\text{DI}} V_{\text{IA}} / (\Delta G_1^\circ + \lambda_1) \quad (6)$$

Equation 6 was used to calculate $V_{\text{SE}}(\pi)$ shown in Table 3. It is based on eq 3, but uses $\Delta G_1^\circ + \lambda_1$ as an estimate for the NSpB[±] to NSp[±]B vertical charge transfer in solution, with a

reorganization energy of $\lambda_1 = \lambda_{s,1} + \lambda_{v,1}$ to form the intermediate assessed as described above.

These assumptions and approximations presume that (1) the coupling through the σ bonds of the steroid spacer is unaffected by the change in hybridization in some of the bonds, (2) the complex nexus of σ and π interactions that give rise to $V_{\text{SE}}(\pi)$ can be described in the simple form of eqs 6 and 3, and (3) the total coupling can be partitioned into discrete σ and π components.

Figure 3 compares predictions of the simple superexchange and sequential models with the measured electron and hole transfer rates. It is evident that when ΔG_1° is large, the superexchange mechanism determines the rate, which depends only weakly on ΔG_1° . At small ΔG_1° , a sharp increase in the rate occurs as the sequential mechanism becomes dominant. The experimentally observed rate increases are explained by this simple description. The figure indicates that the modest rate increases in the anions, NSenB and NSarB, are due to enhancement of the superexchange coupling, while the large rate increases in HT reactions for NSen₂B and NSarB are clearly due to the sequential mechanism. The present results and analysis do not determine the relative importance of the two mechanisms in the remaining two (ET/NSen₂B and HT/NSenB) cases.

Sensitivity to the Parameters and Model. In the sequential mechanism, the rate calculation is very sensitive to the energy of the intermediate ΔG_1° . Fortunately, for the two cases in which the sequential mechanism dominates, ΔG_1° is well measured. Where the uncertainty in ΔG_1° is larger, the superexchange mechanism, which is relatively insensitive to ΔG_1° , determines the rate.

In the sequential mechanism, the rate is proportional to the square of V_{DI} , while in the superexchange mechanism, the rate is proportional to the square of $(V_{\text{DI}} \times V_{\text{IA}})$. Though both rate calculations are sensitive to the electronic coupling and, therefore, to its uncertainties, the superexchange calculation will be affected the most because it squares the error of both V_{DI} and V_{IA} .

The solvent reorganization energy will cause only a modest (\sim linear) change in the calculated superexchange rate but will induce a larger change in the sequential rate. A change of 0.1 eV in $\lambda_{s,1}$ alters k_{SE} and k_{2s} by factors of ~ 1.1 and 3, respectively. $\lambda_{v,1}$ has a smaller effect on the sequential rate and a minor effect on the SE rate. Discrepancies between the calculated and observed sequential rates in Figure 3 could be due either to small errors in $\lambda_{s,1}$ or to errors in our estimates of couplings.

Equation 6 estimates superexchange couplings in a crude way. A more correct treatment would integrate the enhancement of electronic couplings over all configurations of the solvent and internal coordinates with appropriate thermal weightings. Such an integral is not difficult to evaluate given the availability of an expression for the coupling produced as a function of energy, such as that in eq 3. Equation 3, however, is not adequate for this purpose. At some nuclear configurations to be included in the integral, the energy of the intermediate, E_i , is close to or equal to E_D , causing eq 3 to produce unrealistically large or infinite contributions. The approach used here combines all of those weighted contributions into the most probable state. In doing so, eq 6 provides the mean of contributions with larger and smaller values of the energy denominator, $E_i - E_D$, which

should be a reasonable approximation when ΔG_1° is large. But when ΔG_1° is small, eq 6 almost certainly underestimates the superexchange contributions. In application to the present experiments, the deficiencies of eq 6 are not noticeable. Whenever ΔG_1° is small, the rate from the sequential mechanism overwhelms that from the superexchange. This masking of the errors of eq 6 may not be unique to the present experiments.

Theory indicates that for low-energy intermediate states, where both sequential and superexchange mechanisms contribute, these distinct routes to charge-transferred products can blur into a common mechanism requiring a more complex theoretical description.⁴ Of the data shown in Figure 3, for two cases (hole transfer in NSenB⁺ and electron transfer in NSen₂B⁻), superexchange and sequential mechanisms probably both contribute, but the data appear to be described adequately by the simple sum of the two contributions.

Alternative View of Superexchange. Electronic couplings are reported to decay less rapidly ($\beta = 0.25\text{--}0.7 \text{ \AA}^{-1}$) through unsaturated spacers^{9,15i,11,16,37} than saturated spacers ($\beta \approx 0.8 \text{ \AA}^{-1}$).^{10,11,18,21,24} An alternate way of envisioning superexchange is to view it as a series resistance. For example, the spacer in NSarB could be viewed as three segments, a high-resistance σ segment through a saturated hydrocarbon, a lower-resistance π segment through the phenyl ring, followed by another high-resistance σ segment. In this view, the coupling decays by a factor of $\sim 1.6/\text{bond}$, as described above through four σ bonds, then by a factor of $\sim 1.2/\text{bond}$ through three π bonds, and then again by $1.6/\text{bond}$ through three more σ bonds. This analysis yields rates within a factor of 2 of the observed values. This may be fortuitous because it does not consider the relative energy of the Π_s , which should have some affect on the coupling.

Consideration of Conformation Changes. Trans-fusion of the four rings in androstane makes it a very rigid spacer, but introduction of the π groups into the spacer can decrease this rigidity, particularly in the case of NSarB. Possible conformational changes were investigated by molecular mechanics calculations, making use of the MM2 force field and the conformation search routines of the Spartan molecular modeling program.³⁸ This routine searches for stable conformers by rotating the dihedral angles (at specified increments) of chosen bonds, and then minimizes the MM2 energy of each. The search routine was set to save any conformer with a population greater than 0.01%. Table 4 presents results of calculations on the model compound, 3,16-diphenyl-5 α -androstane, and its three unsaturated variants, the monoene, diene, and phenyl groups. These model molecules have the same spacers as NSB, NSenB, NSen₂B, and NSarB, but have phenyls instead of naphthalene and biphenyl at the 3 and 16 positions to simplify the calculation.

The conformer search on the model molecules of NSB and NSenB determined only a single conformer. A second conformation was found for the diene with a 0.013% population, but for the NSarB model compound, several conformations were found, including one with a 2.5% population. In this conformer, the phenyl at the 3 position is in an axial-like conformation leading to a 1.2 \AA decrease of the edge-to-edge distance (defined as the distance between the carbon atoms in the aromatic groups

Table 4. Conformer Search Results for 3,16-Diphenyl-5 α -androstane and its Olefin Derivatives Containing One Double Bond, a Diene, and a Phenyl Group^a

| spacer group | conformer | MM2 energy (kcal/mol) | population | edge-to-edge separation |
|------------------|-----------|-----------------------|------------|-------------------------|
| S | 1 | 39.824 | 100.000 | 11.49 |
| Sen | 1 | 36.854 | 99.993 | 11.46 |
| Sen ₂ | 1 | 34.701 | 99.984 | 11.21 |
| | 2 | 39.999 | 0.013 | 10.79 |
| Sar | 1 | 25.463 | 96.928 | 11.47 |
| | 2 | 27.623 | 2.525 | 10.28 |
| | 3 | 28.953 | 0.268 | 11.48 |
| | 4 | 29.121 | 0.201 | 11.32 |
| | 5 | 29.876 | 0.056 | 10.49 |
| | 6 | 30.802 | 0.012 | 9.68 |

^a Search was performed with the MM2 force field using a minimum Boltzmann population cutoff at 0.01% by the Spartan Molecular Modeling Program.³⁸

closest to the spacer). A decrease in distance of 1.2 \AA typically leads to a rate increase of a factor of about 3.¹⁸ However, the change in distance occurs without a change in the number of bonds, which is a stronger determinant of the CT rate. In addition, the accompanying change in conformation pushes the biphenyl into an axial stereochemistry, and this has been shown to significantly decrease rates.³⁹ It is not clear that the rate in this conformation will be larger. If the rate of conformation change were much slower than the rate of electron or hole transfer, then this increased rate would only apply to 2.5% of the molecules; otherwise, the increase would be averaged with a 2.5% weighting. These calculations, therefore, predict that conformational changes are unlikely to contribute substantially to the observed rates in NSarB and very unlikely for the other molecules.

Conclusions

Incorporation of π bonds into the spacer always increased the biphenyl to naphthalene charge-transfer rate, although in two cases, a significant fraction of the charge in the equilibrium mixture resided on the Π_s group. The results are consistent with a low level of theory that predicts the dominant charge-transfer mechanism to be superexchange when the energy of the intermediate ΔG_1° is large and sequential when ΔG_1° is small.

In two of the six reactions (ET in NSenB and NSarB), the modest rate increases are attributed to superexchange, while the factors of 276 and 470 for hole transfer in NSen₂B and NSarB arise principally from the sequential mechanism. The increases in the other two reaction rates (ET in NSen₂B and HT in NSenB) may contain contributions from both mechanisms in undetermined ratios. Presuming the Π_s groups solely increase the electronic couplings, the change in coupling from the unsaturated spacer relative to NSB (i.e., $V/V_{\text{NSB}} = (k/k_{\text{NSB}})^{-1/2}$) for the ET reaction is 1.2, 2.1, and 2.3 for NSenB, NSen₂B, and NSarB, respectively, yielding $V = 7.4, 13, \text{ and } 14 \text{ cm}^{-1}$, respectively. In the HT reactions, both mechanisms probably contribute to the factor of 5 increase in the rate in NSenB.

The fact that the approximation for the superexchange coupling in eq 6 appears to adequately describe data for the present compounds may say more about the insensitivity of superexchange couplings to energetics at large ΔG_1° than a

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general validation of that approximation. Superexchange can be more sensitive to energetics where reorganization energies are smaller than that in the present molecules. The present results suggest the possibility that constructive interference between σ and π contributions to electronic coupling may be more probable than destructive interference.

The present experiments provide insight into the intermediate-assisted charge-transfer process. The experiments benefited from the structural similarity of the compounds and the relatively well-characterized energetics. However, in the molecules examined here, the intermediate π bonds span only a fraction of the distance between the donor and acceptor, so significant attenuation of the coupling occurs through the σ bonds. Both the superexchange and sequential mechanisms could cause a much larger increase in the rate if the π group spanned a greater region between the donor and acceptor. In larger systems,

especially those in which several intermediate states span the region between donor and acceptor,^{9–11} the sequential mechanism would be likely to be increasingly important,⁵ although it has been ruled out in one case.⁴⁰

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