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Experimental Verification of the Through-Bond Mechanisms of Electron Transfer in Bridged Donor−Acceptor Complexes

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Two rigid bischromophoric systems featuring identical donor and acceptor moieties have been studied in order to directly determine the relative importance of through-space and through-bond mechanisms for electron-transfer reactions. The two molecular systems studied have the unique feature that the through-bond distance between any pair of atoms in the two molecules is held constant while the spatial distance between the donor and acceptor is changed. Time-resolved laser measurements reveal that back-electron-transfer dynamics following photoexcitation of the ground-state charge-transfer absorption band are the same in the two systems. The results provide direct evidence for the through-bond mechanism of electron transfer in bridged organic donor−acceptor systems.

Introduction

Electron-transfer reactions are ubiquitous in nature, playing a central role in biological and chemical processes. A considerable effort has focused on understanding how the distance and orientation between donors and acceptors affects the electron-transfer rate.[1−18] In recent years, studies of covalently linked donor−acceptor systems provided important information on the distance-dependent nature of electron-transfer reactions. A major goal of those studies was to determine the mechanism for the electron-transfer process. Two commonly discussed electron transfer mechanisms are the "through bond" and "through space" mechanism. In the former, the electron tunnels along the covalent bonds of the molecule and the distance between the donor and acceptor is given by the sum of the distances of the covalent bonds linking the two moieties. In the through-space mechanism, the electron tunnels through the surrounding medium and the distance between the donor and acceptor is approximated by the spatial separation between the two species. Theoretical formalism exists for each model, and each predicts a different dependence of the reaction rate on distance. To date, the applicability of a particular mechanism has solely relied on the comparison of experimental data to that predicted by the theoretical models. Specifically, for nonadiabatic electron-transfer reactions, the rate constant is generally described by eq 1[19]

$$k_{\mathrm{ET}} = (4\pi^2/h)|V|^2\mathrm{FC} \tag{1}$$

where V is the electronic coupling matrix element and FC is the Franck−Condon weighted density of states. Because the value of V depends on the spatial overlap of the molecular orbitals associated with the donor and acceptor moieties, it is sensitive to distance and is commonly modeled by[19]

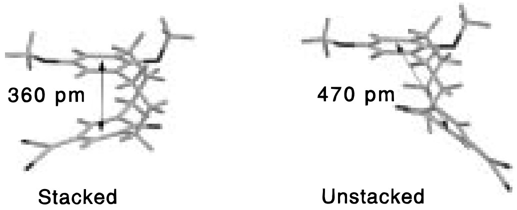

Figure 1. Two cyclophane systems studied: **1** is referred to in the text as the stacked system and **2** is referred to as the unstacked system. The donor and acceptor groups are 1,4-dimethoxybenzene and 7,7-dicyanobenzoquinone methide, respectively.

$$|V|^2 = |V_0|^2 \exp(-\beta r_{\mathrm{DA}}) \tag{2}$$

where V_0 is a constant, r_{DA} is the distance between the donor and acceptor, and β is a constant. Experimental studies imply that β is on the order of 2.8 Å^{-1} for through-space electron transfer[19d] and is on the order of 1.1 Å^{-1} for through-bond electron transfer.[1,20] Thus, evidence in support of a particular model is tied to the observed value of β and its interpretation. In this paper, we present electron-transfer data for two bridged cyclophane systems.[21] The structures of the two bridged systems are shown in Figure 1. Each system contains the same substituted benzene moieties that serve as the donor (1,4-dimethoxybenzene) and acceptor (7,7-dicyanobenzoquinone methide). The donor and acceptor are rigidly positioned relative to one another by alkyl linkers. Taken together, these two cyclophane structures have the unique feature that the through-bond distance between any pair of atoms is held constant while the spatial distance between the donor and acceptor is changed. In general, the relative importance of the through-bond and

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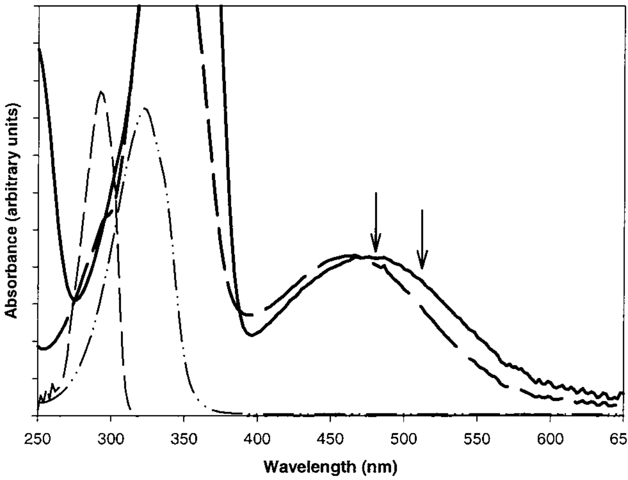

Figure 2. Absorption spectra of the stacked cyclophanes ((—) stacked, (— — —) unstacked), 1,4-dimethoxybenzene ((---) donor), and 7,7-dicyanobenzoquinone methide ((-••-) acceptor) in acetonitrile. The cyclophanes exhibit an absorption band in the visible region that is not present in the spectrum of either the donor or acceptor molecule. This broad absorption band ($\lambda_{max} = \sim 450$ nm) is assigned as a charge transfer between the donor and acceptor. The arrows indicate the two wavelengths used in this study.

through-space mechanisms for electron transfer can be gained directly from the experimental data on these molecules, without the need to do a detailed theoretical analysis.

Experimental Section

The electron-transfer dynamics were measured by performing femtosecond pump−probe absorption experiments. The experimental apparatus consists of a regeneratively amplified titanium: sapphire laser system (Spectra Physics, 1 kHz repetition rate). The output pulses from this device are 80 fs in duration and 1 mJ in energy and have a center wavelength of 800 nm. This laser beam pumps an optical parametric amplifier (OPA, Spectra Physics), which can be tuned throughout the visible and UV region of the optical spectrum. The OPA output was split into two beams using a glass plate; pump beam (95%), probe beam (5%). The two beams then traveled different paths and were recombined on the sample. The path length of one arm was controlled using a computer-controlled delay stage. After traversing the sample, the intensity of the probe beam was measured by photodiode; the diode output was directed to a lock-in amplifier, which was referenced to a mechanical chopper located in the path of the pump beam.

The electron-transfer reaction dynamics were examined in acetonitrile, deuterated acetonitrile, methanol, and chloroform solutions. The concentration of the cyclophanes was on the order of 10^{-5} M; no evidence of bimolecular complexes was manifested in the absorption spectrum. The dynamics were recorded using excitation/probe wavelengths of 480 and 515 nm. The temperature of the water-jacketed sample cell was controlled to within ±0.1 °C.

Results and Discussion

The absorption spectrum of both linked systems is characterized by a band in the visible region of the spectrum ($\lambda_{max} \approx 450$ nm), Figure 2. This band is not present in solutions of the isolated donor and acceptor. This band has been previously assigned as a charge-transfer transition in which an electron is transferred from the dimethoxybenzene to the dicyanobenzoquinone methide. The charge-transfer absorption bands have been normalized to have the same intensity so that they can easily be compared. The extinction coefficients of the two bands are markedly different for the two cyclophanes. In chloroform solution, the extinction coefficient of the charge-transfer band for the stacked and unstacked cyclophane is 3860 and 6025 M^{-1} cm^{-1}, respectively. This difference in extinction coefficients indicates that the electronic coupling between the neutral and charge-transfer states is greatest for the unstacked configuration.

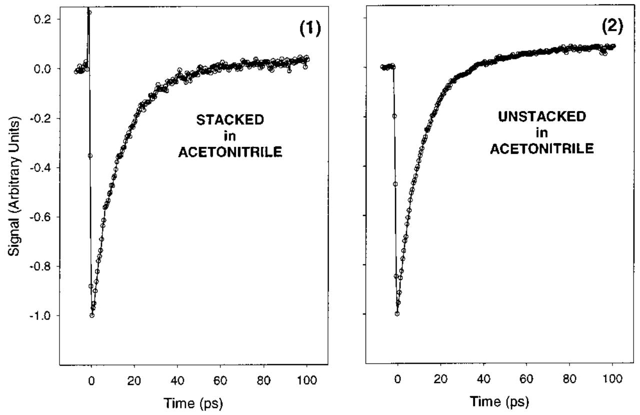

Figure 3. Degenerate pump/probe dynamics at 480 nm recorded following excitation of the charge-transfer band of the stacked (**1**) and unstacked (**2**) donor−acceptor system in acetonitrile solution at room temperature. The recovery of the ground-state absorption as a function of delay time between the pump and probe pulses reflects the back-electron-transfer dynamics. The same dynamics are observed for the two cyclophanes; the absorption recovery can be described by a single-exponential function with a time constant of 12 ± 2 ps. The kinetics of electron transfer are independent of temperature and the excitation/probe wavelength. The time constant for the electron-transfer reaction is indistinguishable from that found in CD_3CN, methanol, and chloroform solutions.

In the present study, the charge-transfer band is excited by an ultrashort laser pulse and the dynamics of the back-electron transfer to reform the ground-state molecule are monitored. The time resolution of the experimental apparatus is on the order of 100 fs. To a good approximation, the driving force for the back-electron-transfer reaction can be estimated by the onset of the charge-transfer band. In acetonitrile solution, the onset occurs at around 1.8 eV. Such a large reaction exothermicity is characteristic of the Marcus inverted region. Electron-transfer reactions in the inverted region are generally modeled in terms of quantum mechanical tunneling, and so we expect that eqs 1 and 2 are applicable to these molecular systems. It is also generally the case that electron-transfer reactions that fall into the Marcus inverted region show a weak, if any, dependence on temperature.[19] Consistent with this prediction, the observed dynamics are unaffected by the solution temperature over the range from 277 to 298 K.

Figure 3 plots the dynamics observed for 480 nm degenerate pump/probe experiments on the two cyclophanes, in room temperature acetonitrile solutions. Identical dynamics are observed for the two molecules. For each molecule studied, a bleach is observed at $\Delta t = 0$ (when the pump and probe pulses are coincident on the sample), reflecting a loss in ground-state population that accompanies formation of the ion pair. With increasing delay time between the pump and probe laser pulse, the absorption signal recovers as a result of relaxation of the system back to its ground state. The recovery of the absorption signal is well described by a single-exponential function with a time constant of 12 ± 2 ps. Within experimental error, the same time constant is observed for the absorption recovery in methanol and chloroform solutions.

In principle, two processes contribute to the recovery of the absorption signal, back-electron transfer and the subsequent vibrational relaxation within the ground electronic state of the molecule. Before we analyze these data in terms of models for electron transfer, it is important to determine the relative contribution of electron transfer and vibrational relaxation to the observed signals. This is most easily done by focusing on how vibrational relaxation can be uniquely manifested in the observed transient signals. To specifically assess the importance of vibrational relaxation to the observed absorption recovery, two separate experiments were performed.

First, the transient absorption dynamics were examined using an excitation and probe wavelength of 515 nm. This corresponds to a reduction in the energy deposited in the molecule by 1400 cm^{-1} when compared to excitation at 480 nm. This energy difference is small compared to the total energy deposited (~20 000 cm^{-1}) and may not affect the observed dynamics However, by probing the dynamics at 515 nm, different Franck–Condon transitions would be excited during a vibrational relaxation process than those accessed by 480 nm light. This should be manifested by different dynamics at the two wavelengths. Specifically, with increasing probe wavelengths, faster recoveries are expected if the dynamics reflect vibrational cooling.[22] Identical dynamics are observed at the two probe wavelengths, from which we conclude that the absorption dynamics are not controlled by vibrational relaxation.

Second, the dynamics were measured in $\mathrm{CD_3CN}$, methanol, and chloroform solution. Because vibrational relaxation is critically dependent on the ability of the solute to transfer energy to the modes of the surrounding solvent, the dynamics of this process are sensitive to the frequencies of the librational and vibrational modes of the solvent molecules.[23] This range of solvents has great variation in the frequencies of normal vibrational modes, and so different rates of vibrational relaxation are expected. In addition, different spectral densities for the low-frequency modes of these solvents are revealed by nonlinear Raman spectroscopy.[24] Therefore, if the absorption dynamics were controlled by librational or vibrational relaxation processes, we would expect to observe different kinetics in these solutions. However, within experimental error, identical dynamics are observed in all solutions studied, supporting the conclusion that the observed absorption recovery relfects the electron-transfer kinetics.

Having established that the data presented in Figure 3 reflect the back-electron-transfer reaction, we can now assess the relative importance of through-bond and through-space pathways for these rigid systems. As stated earlier, the through-bond distance between any pair of atoms is essentially constant in the two structures while the center-to-center through-space distance increases by 110 pm or 25%. The observation of identical dynamics allows us to conclude that the reaction dynamics are independent of the orientation of the donor and acceptor chromophores exhibited by these two cyclophanes. This result provides compelling evidence in support of the through-bond mechanism of electron transfer.

It is important to establish that the expected difference in rate that would accompany the change in the spatial distance between the donor and acceptor could be resolved by the measurements performed. Ab initio calculations (SPARTAN25 with a 6- 31G* basis set) reveal that the center-to-center distance between the donor and acceptor aromatic rings is 360 and 470 pm for the stacked and unstacked cyclophanes, respectively. Because both cyclophanes have the same donor and acceptor, we will assume a constant value of V_0. If we set $\beta = 2.8$ Å^{-1} (the value characteristic of through-space electron transfer),[19d] eq 2 then predicts that $|V|^2$, the square of the electronic coupling matrix element for the unstacked molecule, is smaller than that for the stacked molecule by a factor of 0.06. On the basis of similar charge-transfer bands for the two cyclophanes, the Franck–Condon weighted density of states should be similar for the two molecules. Using these values in eq 1 predicts that the electron-transfer rate constants for the two cyclophanes would differ by over an order of magnitude. Such a difference in rate constants would be easily resolved by the experimental approach used.

In a recent study, the electron-transfer dynamics between chromophores attached to an oligoproline backbone reached the same conclusion from an analogous set of observations.[26] In that study, the distance between the chromophores was altered by affecting the nature of the helical chain that links them. In the particular case reported, the through-bond distance remained fixed while the through-space distance changed from 1850 to 1150 pm. The electron-transfer dynamics were unaffected by the change in the through-space distance, supporting the conclusion that the reaction occurs by a through-bond mechanism. The through-space distances in the cyclophanes studied herein are considerably smaller (~25% of that of the oligoproline molecule), and at these shorter distances, through-space and through-bond processes could occur with similar rates. Our experimental results for these cyclophanes show that the through-bond mechanism can remain the dominant reaction pathway at short donor–acceptor distances as well.

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