J. Am. Chem. Soc. **1994,** *116,* 1155–1156 1155

Isotope Effects on the Electron-Transfer Dynamics of the Benzene and Chlorine Oxide Donor–Acceptor Complex

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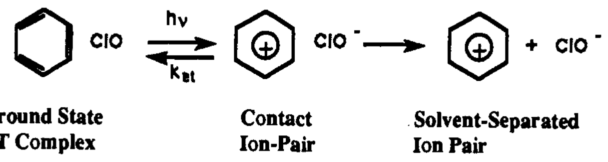
Received June 16, 1993
Revised Manuscript Received November 15, 1993

The dynamics of electron transfer in the Marcus inverted region have been the subject of several recent papers.[1-8] These highly exothermic processes are generally described as a radiationless transition, and the rate expression explicitly includes the vibrational modes of the reactants and products. Calculation of the rate constant requires knowledge of the vibrational modes that couple to the reaction coordinate. In many of the studies reported in the literature, skeletal modes are assumed to be dominant. In this communication, the intermolecular electron-transfer reaction following photoexcitation of the ClO–benzene donor–acceptor complex is examined.[9] Owing to the relative simplicity of this system, a study of the effect of temperature and isotopic substitution on the reaction rate is able to provide new insight into the role of specific modes on the reaction rate constant.

The photoinduced reaction dynamics of the ClO–benzene donor–acceptor complex are shown in Scheme 1. Excitation of the charge-transfer band ($\lambda \sim 450$–600 nm) generates a contact ion-pair (CIP). Subsequently, back electron transfer, k_{et}, competes with ion-pair separation.

The transient absorption dynamics at 556 nm following the excitation of the ClO–benzene complex at 532 nm at two different temperatures in acetonitrile solution are shown in Figure 1. Excitation forms the CIP and therefore causes a decrease in absorption at 556 nm at time $t = 0$. With increased time delay, the signal recovers but does not achieve the level observed at negative time delay. This indicates that ion-pair separation competes with electron transfer. The kinetic model shown in Scheme 1 can be solved analytically to determine k_{et} from the transient absorption data. For the ClO–benzene complex in acetonitrile, a temperature-independent rate of $k_{et} = 3.0 \pm 0.3 \times 10^9$ is found. A temperature-independent rate is expected for inverted electron-transfer reactions.

Scheme 1



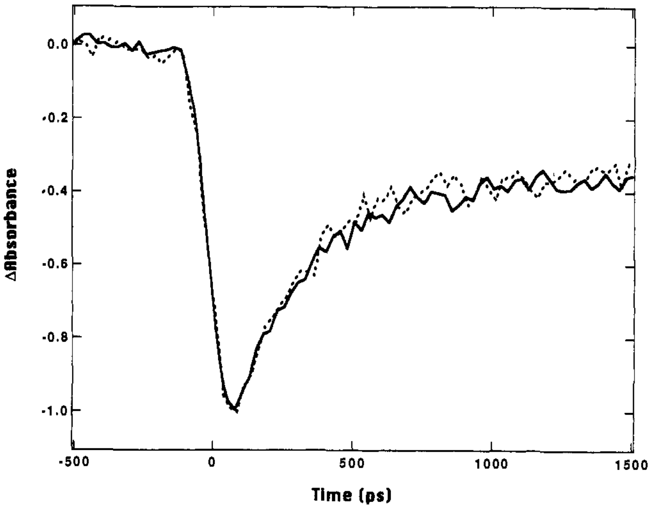


Figure 1. Transient absorption dynamics at 556 nm plotted as a function of time following the excitation of the ClO–benzene donor–acceptor complex in acetonitrile solution at 295 and 310 K. The bleach in absorption observed at $t = 0$ corresponds to photogeneration of the ClO^- benzene$^+$ contact ion-pair. The recovery in signal reflects competition between back electron transfer and ion-pair separation.

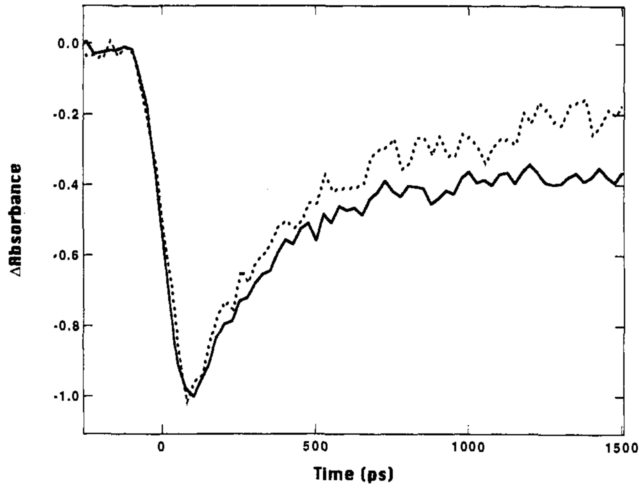


Figure 2. Transient absorption dynamics at 556 nm plotted as a function of time following the excitation of the ClO–benzene-h_6 (solid curve) and ClO–benzene-d_6 (dotted curve) donor–acceptor complex in acetonitrile solution. Deuteration of the benzene ring accelerates the electron transfer.

Figure 2 compares the transient absorption data obtained following photolysis of the ClO–benzene-h_6 and ClO–benzene-d_6 complexes in acetonitrile. Deuteration of the benzene ring accelerates k_{et} by 30% ($k_{et} = (3.9 \pm 0.4) \times 10^9$). This acceleration is reflected in the data both by a faster recovery of the initial bleach and by a 50% decrease in the yield of free ions.

Calculation of rate constants for inverted charge-transfer reactions relies on the golden rule. This requires knowledge of

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(9) ClO was generated *in situ* by the UV photolysis of OClO. The acetonitrile solutions contained 0.1 M benzene. The formation of the ClO–benzene complex was monitored at 556 nm. Once equilibrium was achieved, pump–probe studies were performed.

0002-7863/94/1516-1155$04.50/0

the vibrational modes of the complex that couple to the reaction coordinate. Identifying these modes has been a difficult problem. In practice, it is common to use a single vibrational mode to represent the appropriate vibrations of the molecule. A value of 1500 cm^{-1} is commonly used to approximate skeletal ring modes, which were assumed to be the modes that dominate the kinetics.[1a] However, recent work shows that higher frequency modes, C–H stretches (~3000 cm^{-1}),[3c] and low-frequency intermolecular modes (~150 cm^{-1})[3a] may also be important. Clearly, assumptions concerning the vibrational modes that control the reaction process affect the ability to elucidate quantitative information from kinetic measurements.

For the ClO–benzene system, the vibrational frequencies of the individual molecules are very well characterized. For gas-phase ClO$^-$, the bond length is 1.673 Å, and the single vibrational mode occurs at 665 cm^{-1}.[10a] Generation of the neutral diatomic decreases the bond length to 1.569 Å and blue-shifts the vibration to 853 cm^{-1}.[10bc] While these vibrational modes are of significantly lower energy than those commonly invoked in quantum-mechanical theories, they could still be important.[3a] Evaluation of the classical expression for the inner-sphere reorganization energy shows that the ClO$^-$/ClO contribution to λ_{in} is at most 0.12 eV.[11] As there is partial charge transfer in the ground-state complex, it is reasonable to conclude that this particular vibrational mode does not make a substantial contribution to λ_{in}. The reorganization energy must be largely determined by the aromatic vibrations.[12]

Deuteration of the benzene ring accelerates the rate of back electron transfer, see Figure 2. This effect can be understood by examining related results on the nonradiative electronic relaxation of molecular excited states.[13,14] Both rate processes (inverted charge transfer and nonradiative decay) are generally treated in terms of a golden rule expression. In this case, the rates depend on the interplay of the density of states and the Franck–Condon overlap. Their relative importance depends on the energy gap. Consider high-frequency modes that involve C–H stretches. When the energy gap between the two states is significantly large, the density of acceptor states is high; however, the overlap between the donor and acceptor modes is small. Decreased energy gaps result in a decrease in the density of states but larger Franck–Condon factors. Deuteration lowers the frequency of these modes and, therefore, relative to the nondeuterated molecule, both increases the density of states and decreases the overlap for a given energy gap. The decrease in nonradiative rates observed upon deuteration for large energy gaps (3–4 eV) results from the fact that the reduction in the Franck–Condon overlap is more important than the increase in the density of states.[13] On the other hand, for smaller energy gaps, deuteration can increase reaction rates. This so-called inverse isotope effect has been observed for nonradiative rates in molecules and indicates that under certain conditions the increased density of states outweighs the decreased Franck–Condon factors.[13,14]

Based on the charge-transfer absorption, the energy gap in the ClO–benzene system is at most 1.5 eV. The observed isotope effects is consistent with the conclusion that the density of acceptor states caused by deuteration dominates the rate. This results further supports the conclusion that modes involving C–H(D) displacement couple to the reaction coordinate. In analogy to the observation of deuterium isotope effects on molecular radiationless decay, the isotope effect on the ClO–benzene electron-transfer dynamics should be affected by a change in energy gap. One predicts that with an increase in the exothermicity of reaction, the isotope effect should decrease and potentially reverse. Experiments on ClO–toluene-d_8 (a more exothermic reaction) show no isotope effect ($k_H/k_D = 1.0 \pm 0.1$, compared to 0.78 ± 0.08 for benzene). We are currently examining reactions with increased exothermicity to see if a normal isotope effect results ($k_H/k_D > 1$). This relatively simple donor–acceptor complex also offers to be an excellent test case for multimode theories of electron transfer. This topic will be dealt with in detail in a later publication.[7]

Acknowledgment. This work is supported by the National Science Foundation (CHE93-06485) and the Medical and Materials Free Electron Laser Program administered by the Office of Naval Research. We thank Dr. Robert Dunn for helpful discussion on the generation of ClO.

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(11) The total inner-sphere reorganization energy, λ_{in}, is defined by $\lambda_{in} = {}^1/_2\sum_i k_i(d_s - d_p)$ where the summation is over all the vibrational modes. k_i is the average force constant and $d_s - d_p$ is the corresponding bond displacement. For ClO/ClO$^-$ this expression likely overestimates the contribution of this mode to λ_{in} as the partial donation of electron density in the ground-state complex likely decreases the vibrational frequency and causes a corresponding small increase in bond length.

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