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Ultrafast studies on electron transfer in the betaines: evidence for local heating

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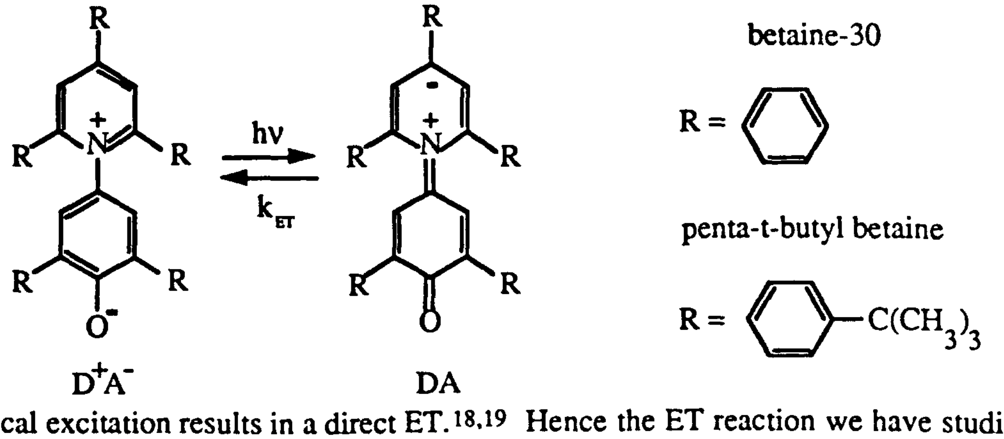
Abstract

We have made ultrafast time resolved pump probe measurements on the intramolecular electron transfer (ET) of the betaines, specifically betaine30 and penta-t-butyl betaine. The data have been analyzed to determine the ET rate in a range of solvent environments, at various temperatures and at a variety of pump and probe wavelengths. In all cases, the observed ET rate is fast, often faster than predicted by common ET theories. As a result, we have extended some common theories to successfully predict the measured ET rates. In addition to the ET dynamics, the data also display evidence for local heat deposition in the immediate vicinity of the betaine molecule which our extended model qualitatively predicts.

1. Introduction

Current electron transfer (ET) theories predict rates which depend on static and dynamic properties of both the solute and the solvent. As such, they have had remarkable success at predicting rates for many experimentally observed ET reactions.[1-11] The success of these theories demonstrates the importance of solvation dynamics and intramolecular vibrations in promoting ET. The theories differ in the emphasis they place on various different degrees of freedom. For example, in barrierless ET reactions, several theories predict that solvent friction should limit the rate.[12-14] In inverted regime reactions, intramolecular vibrational modes can accelerate the reaction by reducing the effective barrier and decreasing the energy mismatch along classical coordinates.[9-11,15-17]

In this work and previously[15-17] we have investigated the ET dynamics of two related betaine molecules, betaine 30 (2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate) and penta-t-butyl-betaine (2,6-di-tertbutylphenyl-4-(2,4,6-tri-tertbutylphenyl-1-pyridinio)phenolate). Valence bond descriptions for the structures are shown below.



Here optical excitation results in a direct ET.[18,19] Hence the ET reaction we have studied is the reverse ET or ground state recovery. This electron transfer occurs in the inverted regime. Therefore, we expect that intramolecular vibrational modes will be important in ET dynamics.

We have used ultrafast pump probe spectroscopy to investigate the ET kinetics of the lowest electronic transition in the betaines, the transition corresponding to direct photoinduced ET. We have studied the dynamics of the reverse ET in many solvents, polymer films and as a function of temperature.[15-17] The major findings of our work is that the ET rate in the betaines is always fast,

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often faster than solvation times of the solvents used and faster than current theories predict. As a result, we have developed a hybrid model capable of accurately predicting the ET rates. The dynamics of the ET reaction were also found to be highly insensitive to changes in the bulk environment including temperature and polarity of the solvent despite the extreme sensitivity of the static absorption band to these parameters.

At probe wavelengths removed from the peak of the ET absorption band, the time resolved measurements display additional dynamics on a second time scale. We have used our hybrid model to predict these dynamics on the basis of local heating in the immediate vicinity of the betaine molecule. In this paper, we discuss the results of time resolved measurements in a variety of solvents, at various temperatures and for a variety of probe wavelengths revealing the effect of local heating. We also briefly discuss the failure of current, simple ET models and the development of our hybrid model for predicting ET.

2. Experimental Methods

All the time resolved pump probe measurements have been made using an ultrafast laser system which will be described in detail elsewhere.[23] Briefly, a mode locked Nd:YAG laser synchronously pumps a home built, linear cavity dye laser to yield 150fs (FWHM) pulses at ~800nm. The dye laser pulses are amplified to ~10μJ/pulse using the doubled output of a home built Nd:YAG regenerative amplifier to pump a three stage dye amplifier. For variable color experiments, a white light continuum was generated by focussing 80-100% of the amplified dye light into a 1cm static cell of H_2O. The light is selected using a 10nm bandpass filter and further amplified in one or two stages using ~20% of the doubled light from the regenerative amplifier. The instrument response function of the apparatus is <300fs as measured by the optical Kerr effect in H_2O.

Betaine30 dye was obtained from Aldrich and was used without further purification. Penta-t-butyl betaine was a generous gift from Professor C. Reichardt and was used without further purification. All solvents used were spectral or HPLC grade and were used without further purification. In some cases, solvents were dried over activated alumina. Static spectra were collected with a Cary 17 or Shimadzu UV160 spectrophotometer.

3. Experimental Results

Both betaine30 and penta-t-butyl betaine exhibit a photoinduced ET absorption band. These absorption bands are nearly identical for the two molecules. The static absorption spectra of betaine30 in acetone and benzene and penta-t-butyl betaine in benzene are shown in Fig. 1. The lower energy bands shown correspond to direct photoinduced ET. They are extremely sensitive to the solvent polarity shifting to higher energy with increasing solvent polarity.[18,19] Indeed, the peak of this absorption band in betaine30 is the basis for the

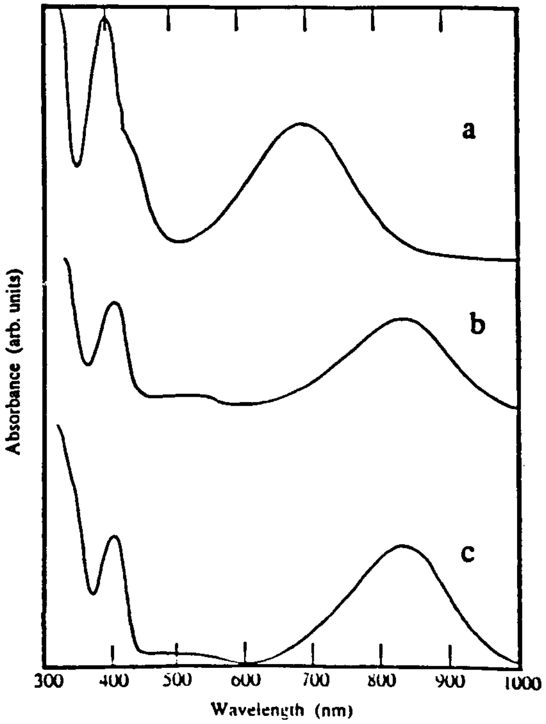

Fig. 1 Static absorption spectra for betaine30 in a) acetone, b) benzene and penta-t-butyl betaine in c) benzene.

$E_T(30)$ solvent polarity scale.[19]

We have made ultrafast time resolved pump-probe measurements of the reverse ET for betaine30 and penta-t-butyl betaine in a variety of solvent environments. Representative absorption transients for betaine30 in glycerol triacetate (GTA) and acetone are shown in Fig. 2. These solvents have similar polarities; their absorption spectra both peak near to 700nm. However, they display very different solvation dynamics. Acetone is a rapidly relaxing solvent. Its measured solvation time or the time scale for solvent fluctuations, τ_s, is approximately 0.8ps. In contrast, GTA is quite slowly relaxing, $\tau_s > 100$ps. In comparison, the ET times measured for acetone, Fig. 2b, where $\tau_{ET} \sim 1.3$ps, and GTA, Fig. 2a, $\tau_{ET} \sim 7$ps, are much closer than we would predict based on the solvation dynamics. Indeed, a comparison of the ET time versus the solvation time for a battery of solvents, as shown in Fig. 3, reveals two different kinetic regimes. For rapidly relaxing solvents, the ET time appears to be directly proportional to the solvation dynamics. But in slowly relaxing solvents, the ET times display only a mild dependence on τ_s. We have interpreted this as a manifestation of a competition between two ET mechanisms, one dominated by vibrational dynamics and one dominated by solvation dynamics. A prediction of this behavior based on our hybrid model is given below.

In addition to varying the molecule's environment, we have also made ultrafast time resolved pump-probe measurements with 700nm and 800nm excitation and 640, 700, and 800nm probe wavelengths. The measured dynamics do not appear to depend strongly on the excitation wavelength. However, we have observed a second component to the dynamics for some probe wavelengths in addition to the dynamics corresponding to the reverse ET. This component varies as a function of the probe wavelength. This effect is easily seen in Fig. 4. When we probe near the peak of the ET absorption band at 700nm, Fig. 4b, we are least sensitive to band shifting effects due to local heating hence the measured dynamics should most accurately reflect the reverse ET. However, at a wavelength longer than the absorption peak, 800nm, Fig. 4c, we observe a fast recovery of the ground state followed by an increased absorption which decays more slowly than the initial bleach. At a wavelength shorter than the absorption peak, 640nm, Fig. 4a, multiexponential dynamics are apparent

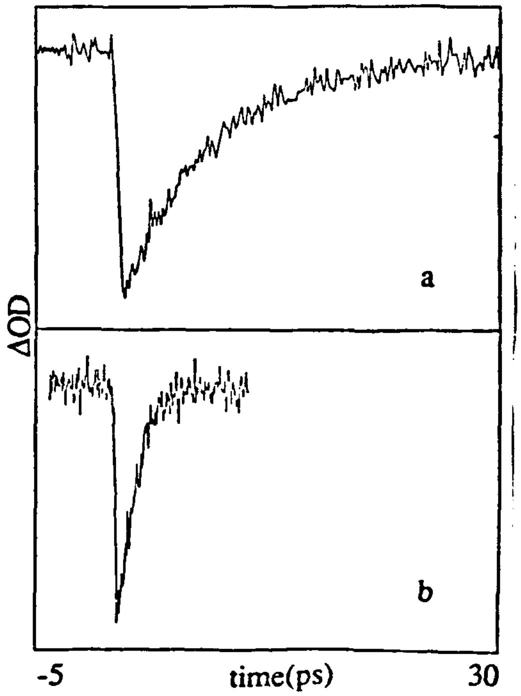

Figure 2. Absorption transients for betaine30 in a) GTA and b) acetone.

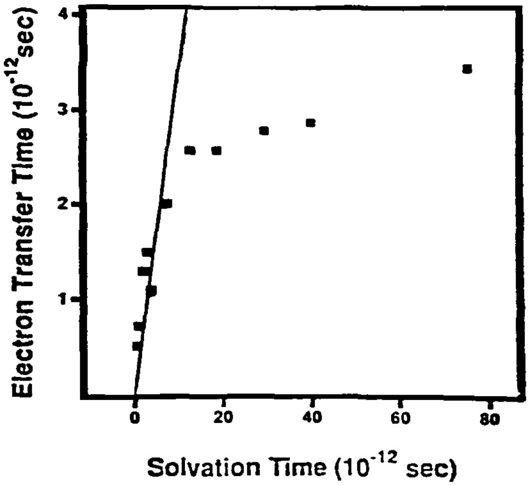

Figure 3. Electron transfer times for betaine30 in a variety of different solvents as a function of solvation time; boxes are experimental points, line indicates $\tau_{ET} = \tau_s$.

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with the second time scale similar to that observed for the increased absorption at 800nm. We interpret this as evidence of local heating of the betaine molecule environment. Because the betaine absorption band is a strong function of temperature, the absorption band would be expected to shift its peak to longer wavelength with increasing temperature. The reverse ET deposits a large amount of energy into the molecule's environment thereby raising the effective local temperature. This effect would manifest itself in the measured dynamics as an increased absorption on the red edge of the spectrum and an additional bleach on the blue edge, which is what we observe. The recovery of the increased absorption and the additional bleach then correspond to local cooling of the molecule's environment.

4. Theoretical treatment

ET theories often treat the solvent polarization as the primary, inhomogeneous coordinate. For ET reactions occurring in the inverted regime, this is not always appropriate. We have used two current theories to try to model dynamics we observe for ET in the betaines. Both theories include a solvent mode and an intramolecular vibrational mode for promotion of the ET. Because the ET in the betaines is directly optically induced, all the parameters necessary to predict the dynamics can be directly obtained from the absorption spectrum. We expect these theories to be applicable to the ET of the betaines. However, they have often been invoked without testing whether they are appropriate for describing the experimental processes. As a result, we have tried to test them for the present experimental case.

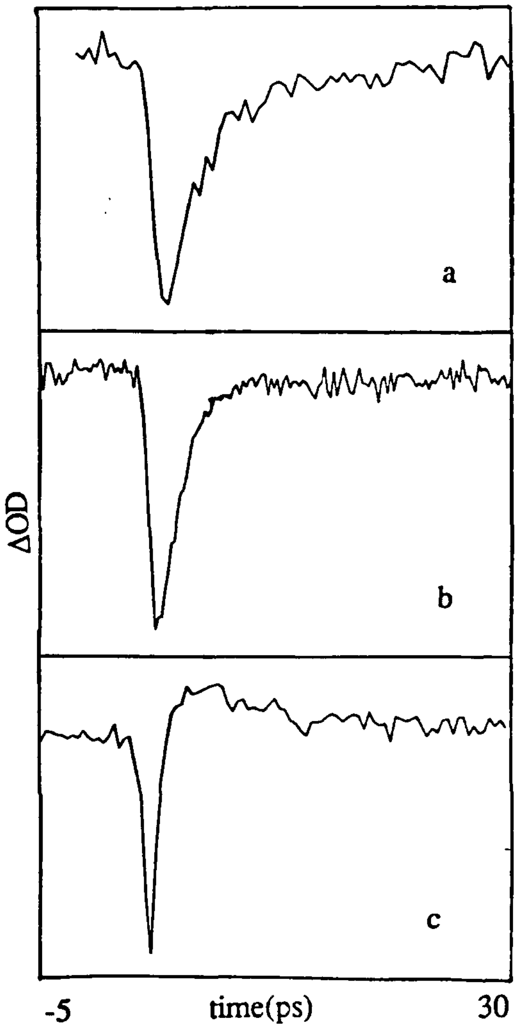

Figure 4. Absorption transients for betaine30 in acetone; 800nm excitation and a) 800nm probe, b) 700nm probe and c) 640nm probe.

Sumi and Marcus[20] presented a model that includes a classical solvent mode and an average classical intramolecular vibration as the reaction coordinate. In this model, the ET reaction occurs along vibrational coordinates with a rate constant that depends on the polarity of the local environment. Their model treats the solvent with a classical diffusion equation and vibrational coordinates are treated as a single, average classical coordinate. This theory predicts a barrier to the ET reaction. As a result, it underestimates the betaine ET rate by as much as six orders of magnitude. In fact, the theory by Sumi and Marcus always predicts rates that are orders of magnitude slower than the observed dynamics.

In their theory, Jortner and Bixon[21] use a classical solvent coordinate but add an average, quantized vibration which allows vibronic transitions. The frequency of the quantized mode is an average of the modes coupled to the ET. This model works well for quickly relaxing solvents because the addition of vibrational levels can significantly reduce the barrier to reaction. The rate then becomes limited by the solvent fluctuations. However, the Jortner/Bixon theory[18] still significantly underestimates the observed ET rates in slowly relaxing solvents. This occurs because each vibronic transition is similar to a delta function sink, so the rate is still limited by the solvent fluctuations.

Both the Sumi/Marcus[20] and Jortner/Bixon[21] theories are applicable to this inverted regime ET, but there are discrepancies between rates predicted by these theories and the experimentally measured rates. As a result, we have developed a hybrid model[17] that is an extension of the Sumi/Marcus theory which includes a quantized vibration similar to the Jortner/Bixon theory. The hybrid model accurately predicts the ET rates for the betaines because it allows the reaction to proceed via vibronic transitions similar to Jortner and Bixon's model but fluctuations in the classical vibration can also drive the reaction. Hence the reaction is not limited by the time scale of the solvent fluctuations for solvents with very slow solvation dynamics. A comparison of the predictions from each of these three models is shown in Fig. 5 along with the observed ET rates for betaine30.

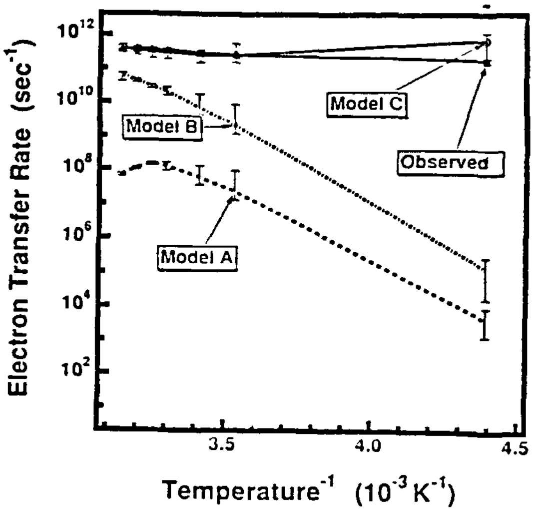

Figure 5. Electron transfer rate as a function of inverse temperature for betaine30 in GTA. Model A is the Sumi/Marcus model, Model B is the Jortner/Bixon model and Model C is the hybrid model described in the text.

To obtain the parameters for the hybrid model, we fit the absorption lineshape to a model that includes the two nuclear degrees of freedom. From the fit, we obtain values for the quantized reorganization energy, λ_{QM}, the classical reorganization energy, λ_{CL}, the driving force for the reaction, $\Delta G°$, and the quantized vibrational frequency, ν_{QM}. The classical reorganization energy is partitioned into solvent and vibrational contributions by assuming that there is no contribution to λ_{CL} in a nonpolar solvent, cyclohexane. The solvent contribution, λ_{SOLV}, is then the difference between the total λ_{CL} and the contribution from the nonpolar solvent case. The electronic matrix element, V_{EL} is estimated from the Hush relationship.[22] From the fit to the absorption spectrum, we can construct free energy curves on which to predict the dynamics.

We extended our hybrid model to predict time dependent absorption spectra.[23] This requires modelling the dynamics of the population on both the ground and the excited state surfaces. At any time, population missing from the ground state contributes to a bleach of the absorption spectrum. Population on the excited state can contribute to the signal by absorption to a higher excited state or through stimulated emission. In our analysis, we consider only the contribution from stimulated emission. All the parameters necessary for these dynamical predictions are obtained from the static absorption spectrum hence they provide a good measure of the accuracy of our hybrid model.

Figure 6 displays the dynamics of the ground and excited state populations for betaine30 in acetone. The residual population in the ground state has been subtracted for clarity. At t=0 there is a Gaussian distribution in the excited state centered at X=1, the equilibrium position in the ground state and no population in the ground state. The population in the excited state moves along the solvent coordinate towards lower energy and reacts depositing population back in the ground state. However, initially the population does not return to the ground state equilibrium position. The population in the ground state appears near X=0, the equilibrium position in the excited state and moves back to X=1. At intermediate times there is more population near X=0 in the ground state than the equilibrium population there. This effect is responsible for an increased absorption on the low energy side of the absorption spectrum. The transient absorption spectrum is calculated by convoluting the time dependent excited and ground state populations with a vibrational shape function.

5. Comparison of Predictions and Experimental Measurements

Because we can independently predict and measure the dynamics of the betaines in solution for various excitation and probe wavelengths, we are able to make direct comparisons of the predictions and the experimental measurements. Comparisons of the predicted and observed absorption transients for 700nm pump and probe light are shown for betaine30 in GTA in Fig. 7. We feel that the agreement between the predicted and observed data are remarkable especially considering that there are no adjustable parameters for the predictions. We made comparisons of the observed and predicted dynamics at other wavelengths. The general trends in the predicted and observed spectra are similar, including an increased absorption at 800nm. However, the predicted spectra do not quantitatively match the time scales for the corresponding measured spectra. This may be due to our assumption throughout this model that vibrational relaxation is instantaneous.

6. Summary

We have made measurements and predictions of the dynamics accompanying the ET of the betaines in solution. In rapidly relaxing solvents, the ET rate is dominated by solvation dynamics while in slowly relaxing solvents the rate is dominated by intramolecular vibrational dynamics. In addition to the ET dynamics, we have observed evidence for local heating of the betaine molecule environment following the ET. We have extended our hybrid model[17] to include ground and excited state population dynamics thereby allowing prediction of the spectral dynamics.[23] The model predicts the ET dynamics and some local heating due to nonequilibrium population distributions following the ET reaction. The model accurately predicts the dynamics near the peak of the absorption spectrum.

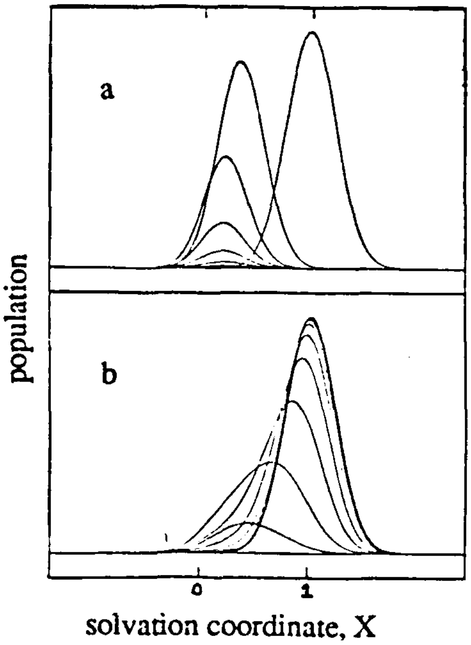

Figure 6. Time dependent a) excited state and b) ground state populations for betaine30 in acetone.

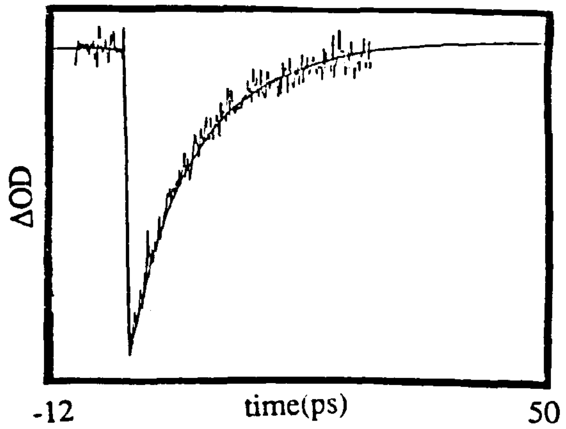

Figure 7. Observed and predicted absorption transients for betaine30 in GTA.

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