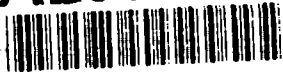


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Dynamic Solvent Effects on Electron Transfer Rates in the Inverted Regime:  
Ultrafast Studies on the Betaines

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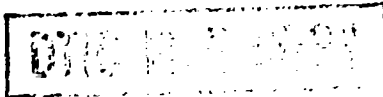
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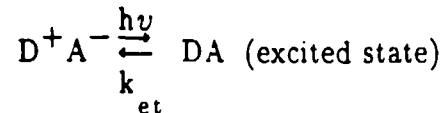
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Dynamic Solvent Effects on Electron Transfer Rates  
in the Inverted Regime:  
Ultrafast Studies on the Betaines<sup>++</sup>

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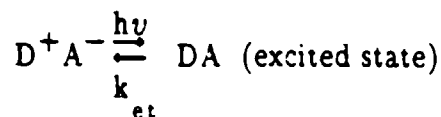
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### Abstract

Transient pump-probe measurements have been made on Betaine-30, the solvent polarity probe. Betaine-30 is composed of organic donor and acceptor groups.



The transient data has been analyzed to measure  $k_{et}$ , the electron transfer (et) rate constant, in polar solvents for this inverted regime et. The observed rate constant,  $k_{et,obs}$ , in various polar solvents is as much as a factor of  $10^5$  larger than is predicted by the standard, classical, implementation of the theory of Sumi and Marcus, using Kjaer and Ulstrup's estimates for necessary parameters. In contrast, a quantum treatment of the vibrational modes by Jortner and Bixon, which includes the dynamic solvent effect, predicts that the rate should be approximately  $k_{et,JB} \cong \frac{1}{\langle \tau_s \rangle}$ . This is close to the experimental results ( $\cong 10^{12} \text{ sec}^{-1}$ ) in typical polar aprotic solvents. However, in highly viscous, slowly relaxing solvents,  $k_{et,JB} \ll k_{et,obs}$ . This is taken as evidence that the efficient coupling modes for the et in these environments is not the "conventional solvent coordinate." It is shown that a hybrid of the Jortner/Bixon and Sumi/Marcus theories can physically account for the results. The kinetic behavior of Betaine-30 in slowly relaxing solvents is shown to be in the "diffusionless limit" of the hybrid, generalized Sumi-Marcus/Jortner-Bixon picture.

## INTRODUCTION

Recent experimental<sup>1</sup> and theoretical<sup>2-8</sup> progress has shown that the rate of electron transfer (et) reactions can be strongly influenced by the dynamics of solvent motion, especially in the electronically adiabatic limit, where the rate is given by eqn (1) if internal vibrational modes are ignored and a simple solvent model is utilized.

$$k_{\text{et}} \cong \frac{1}{\langle \tau_s \rangle} \exp(-\Delta G^\ddagger / RT) \quad (1)$$

Here,  $\langle \tau_s \rangle$  is the characteristic time for solvation dynamics and  $\Delta G^\ddagger$  is the activation energy. According to Marcus' theory

$$\Delta G^\ddagger = \frac{(\lambda + \Delta G^0)^2}{4\lambda} \quad (2)$$

where  $\lambda$  and  $\Delta G^0$  are the reorganization energy and the reaction free energy, respectively.

In the limit of  $\Delta G^\ddagger = 0$  (i.e., the barrierless case),  $k_{\text{et}} \cong \frac{1}{\langle \tau_s \rangle}$ , and the reaction is controlled by diffusion along the solvent coordinate.

Contemporary et theory includes<sup>1-8</sup>: frequency dependent solvent friction effects and interplay of barrier crossing and reactant well solvation dynamics; the dependence of dynamic solvent effects on the electronic matrix elements in the nonadiabatic, weakly adiabatic, and strongly adiabatic limits; and most importantly for this paper, the consequence of vibrational modes<sup>7,8</sup> upon solvent effects on et kinetics.

Theoretical predictions have been in reasonable agreement with a range of experimental results on dynamic solvent effects on the reaction rates of thermal and photoinduced et reactions. The most extensive and well-defined experiments have been for et reactions in the normal and barrierless regimes of Marcus theory.

### photoinduced electron transfer in betaine compounds

In contrast in this paper, we explore dynamic solvent effects on an et reaction in the

inverted regime, namely the non-radiative charge separation of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio) phenolate, betaine-30, as shown in Figure 1. The betaines have distinct Donor and Aceptor groups, separated by a single bond<sup>9</sup>. The ground state of the betaines is charge separated,  $D^+A^-$ , whereas the lowest excited state, DA, is not. For example in betaine-30, the dipole moments in the ground and excited electronic states are 15D and 6D, respectively, and point in opposite directions. The absorption spectra of betaines shift over  $10,000\text{cm}^{-1}$  as a function of solvent and this effect, in conjunction with the "reverse" state ordering, makes the betaines excellent molecular probes of solvent polarity.

In this paper we report the first et kinetics measurements on the betaines, using ultrafast spectroscopy. The et of the betaines offers an exciting opportunity to test the dramatic predictions of recent theoretical models that simultaneously include solvation and vibration dynamical degrees of freedom, such as the Jortner and Bixon<sup>9</sup> approach that treats the relevant vibrational degrees of freedom in the quantum limit, and the Sumi and Marcus<sup>7</sup> approach that treats the vibrational modes classically. Estimates for some of the necessary parameters are available from the analysis of static data by Kjaer and Ulstrup (which for a particular solvent we can summarize by model diabatic states, as in Figure 1)<sup>10</sup>. The comparison of the theories to experimental data leads to new insight on the mechanism of ultrafast et reactions, especially in the inverted regime.

## EXPERIMENTAL METHODS

The laser source for these experiments is an amplified 70 fs, 792 nm dye laser that has been described previously<sup>11</sup>. The amplified pulses ( $0.5\ \mu\text{J}$ , 8.2 kHz repetition rate) are split into separate pump (90%) and probe (10%) pulses which follow different optical paths of variable relative lengths before passing through a focusing lens (typically 10 cm) and

crossing in the sample (spot size  $100\mu\text{m}$ ). The pump induced absorption change of the probe pulse in the sample is detected with a boxcar averager. The instrument response function, obtained by measuring the optical Kerr effect in water, is 100 fs (FWHM).

All solvents used were of spectroscopic grade and were further distilled over calcium hydride to reduce water impurities, if necessary. Betaine-30 was purchased from Aldrich and used without further purification. Static absorption spectra were taken and found to be in good agreement with previously reported spectra<sup>9</sup>. The methods used for probing with continuum light will be discussed in a subsequent paper.

## RESULTS

We have made transient pump-probe measurements on betaine-30 in various solvents, and as a function of temperature in limited cases. Most of the measurements have been made with identical pump-probe wavelengths,  $\lambda_{\text{pump}} = \lambda_{\text{probe}} = 792\text{nm}$ , the wavelength of our  $\approx 70\text{fs}$  laser. A few measurements were made with different probe wavelengths, using wavelength selected "continuum light" as a probe.

The pump-probe transients were analyzed by a convolute-and-compare algorithm using a multi-exponential model decay and the instrument response function, see Table 1. Each of the measurements in Table 1 corresponds to the average of several separate experiments. The uncertainty in the fitting parameters is about 15%.

The main goal of these experiments is to measure the rate of ground state recovery, i.e.,  $k_{\text{et}}$ . The basic notion is to deplete the  $D^+A^-$  population with the pump (excitation) pulse causing a "transient bleach", which recovers with a rate,  $k_{\text{et}}$ .

For the betaine-30 in non-polar solvents such as benzene, the laser wavelength is near the CT absorption maximum, see Table 1. The observed transient optical density signal in non-polar solvents, e.g. benzene in Figure 2a, shows the expected bleach followed



by a single exponential recovery. The transient data in non-polar solvents shows, in certain cases, an unresolvably rapid ( $<50\text{fs}$ ) component which we attribute to a coherent artifact. This component of the transient can be ignored in the determination of  $k_{\text{et}}$ . Some of the transients in non-polar solvents show a residual bleach of  $<5\%$  at long times, i.e.  $>10\text{ps}$ . This residual, unrecovered signal may be due to a small yield of DA triplets or perhaps to biphotonic destruction of the compound. (At high laser fluences we observe a permanent bleach of the CT absorption.)

The transient pump-probe signal for betaine in polar solvents is more complicated than in non-polar examples. The absorption maximum of betaine-30 in these environments is shifted to the blue of  $792\text{nm}$ . Thus, the pump and probe light is at the red edge of the CT spectrum, which makes this experiment especially sensitive to temporal evolution of the band-shape, as solvation and vibrational relaxation occurs.

Consider, for example, the transient absorption signal of betaine-30 in acetone (Figure 2b). The sign reversal is apparently associated with a relaxation phenomenon. We attribute the early decay to ground state bleach recovery ( $\tau = 0.65\text{ ps}$ ) and the later signal of opposite sign (transient absorption) to a relaxation effect, such as a rapid red shift of the absorption band due to the local deposition of heat from the et process followed by cooling.

For the intermediate polar solvents, triacetin, ethyl acetate, and methyl acetate the contribution from the apparent relaxation effect is small enough that accurate values for  $k_{\text{et}}$  can be obtained from the transient absorption signals. However, for the most polar solvents, acetone, benzonitrile, propylene carbonate, and acetonitrile the apparent relaxation effect is so significant that the  $\tau_1$  values should only be used as a rough estimate of  $k_{\text{et}}$ .

More reliable measurements of  $k_{\text{et}}$  in polar solvents can be made by probing at shorter wavelengths near the band maximum. Preliminary data of this type are shown for

acetone in Figure 3. The signal shows a bleach recovery with no noticeable relaxation induced sign reversal. The recovery time from these data (Figure 3) is  $1.2 \pm 0.4$  ps. The discrepancy between this value and the  $0.65 \pm 0.2$  ps recovery time measured with a 792 nm probe attests to the fact that the  $\tau_1$  in Table 1 for the most polar solvents is only an order-of-magnitude estimate for  $k_{et}$ .

Figure 4 portrays the effect of temperature on the transient pump-probe signal of betaine-30 in triacetin (GTA). The inverse of average bleach recovery time constants are given in Table 2. The ground state recovery time  $\tau_1$  changes by roughly a factor of 2 in this temperature range.

We have also studied the effect of pump light intensity on the transient pump-probe signal. A variation of the pump intensity over a factor of 10 produces no detectable change in the dynamics. The dynamics are also unaffected by the relative polarization of the pump and probe beams.

## DISCUSSION

The electron transfer rates of betaine-30 in various solvents are listed in Table 2 along with other useful information. These are the first data, to our knowledge, on et in the inverted regime between a strongly coupled ( $V_{el} \approx 2900 \text{ cm}^{-1}$ )<sup>12</sup> donor-acceptor system. There are a number of interesting qualitative effects that are worth noting before we begin a quantitative comparison to theory. Foremost, the rates are extraordinarily similar despite a large variation in solvent polarity, solvent relaxation time, and temperature.

Some anticipated trends are observed, but the effects are milder than expected, based on previous measurements on ultrafast et in the barrierless regime<sup>1,6</sup>. We begin analysis of the dependence of  $k_{et}$  on  $\tau_s$ , by comparing et rates in solvents of similar polarity, so that energetic effects due to solvent polarity are minimized. An especially

appropriate measure of solvent polarity is the popular  $E_T(30)$  scale, which is nothing more than the energy of the absorption maximum of betaine-30 (expressed in kcal/mol)<sup>9</sup>.

Limiting the comparison to solvents of similar  $E_T(30)$ , a mild correlation between  $k_{et}$  and  $1/\langle\tau_s\rangle$  is observed. This effect is obviously not the  $k_{et} \cong 1/\langle\tau_s\rangle$  that has been observed for barrierless and normal regime et reactions<sup>1,6</sup>. Furthermore, the rate of electron transfer tends to be greater than the solvation rate,  $1/\langle\tau_s\rangle$ , and is, in some cases, much greater.

There is also a mild increase in the et rate as solvent polarity is increased. At first glance, this is opposite to our expectations for a charge separation reaction in the inverted regime because, as the solvent polarity increases, the driving force,  $\Delta G^0$ , should become more exothermic. This should drive the system further into the inverted regime. However, using Kjaer and Ulstrup's estimates of  $\lambda$  and  $\Delta G^0$  for the related compound betaine-26, it can be shown that the Marcus barrier,  $\Delta G^\ddagger$ , which is a function of  $\lambda$  and  $\Delta G^0$ , apparently decreases as the solvent polarity increases, see Table 3. A more extensive analysis of this surprising effect will be reported in a subsequent paper.

Finally, there is a mild decrease in  $k_{et}$  ( $E_A = 380 \text{ cm}^{-1}$ ) as the temperature is lowered in Table 2, but the effect is much smaller than would be expected from Marcus' theory, see below.

#### $k_{et}$ according to a classical model for the vibrational modes

Sumi and Marcus recently gave a theoretical treatment for the effect of intramolecular vibrations and solvent diffusion on the et rate<sup>7</sup>. The vibrational coordinates are treated classically. Essentially all the information required to predict  $k_{et,SM}$  from the Sumi and Marcus model has been estimated by Kjaer and Ulstrup, employing a bandshape analysis of the CT absorption band<sup>10</sup>. Unfortunately, the latter analyzed betaine-26 rather

than betaine-30, but these compounds are similar enough that the estimates are suitable at this level of comparison.

The Kjaer and Ulstrup analysis can be reformulated to give the contribution to the total reorganization energy,  $\lambda$ , namely a low frequency (classical,  $\lambda_{\text{class}}$ ) component and a high frequency (quantum mechanical,  $\lambda_{\text{QM}}$ ) component. In addition, their analysis yields an effective frequency of the the quantum mechanical mode,  $\nu_{\text{QM}}$ . The value in a few representative polar solvents are shown in Table 3. By extrapolating the data for polar solvents in Figure 3 of Kjaer and Ulstrup to the "gas phase intercept" it is possible to apportion  $\lambda_{\text{class}}$  to solvent and vibrational contributions ( $\lambda_{\text{class,vib}} = 150\text{cm}^{-1}$ ), as shown in Table 3. We estimate that the appropriate frequency for the low frequency contribution to the vibrational reorganization energy is  $50\text{cm}^{-1}$ , a typical low frequency vibrational mode (although the conclusions of this paper are unchanged if a frequency as large as  $200\text{cm}^{-1}$  were assumed to be the appropriate frequency instead). The additional quantities we need are the electronic matrix element,  $V_{\text{el}}$ , which is estimated from the Marcus-Hush expression<sup>12</sup>, and the average solvation time  $\langle \tau_s \rangle$  which is available from transient Stokes shift measurements<sup>13</sup> or, alternatively, dielectric relaxation data<sup>14</sup> (using a standard procedure for calculating  $\langle \tau_s \rangle$ ).

Using the parameters in Table 3 it is easy to show that  $k_{\text{et}}$  is predicted to be in regime of Sumi/Marcus in which the reactant concentration decays as a single exponential (with  $\Delta G^*/k_{\text{B}}T \gg 1$ ). The expression for  $k_{\text{et}}$  in this limit may be found in eqn 8.8 of reference 7.

The predicted rates are many orders of magnitude slower than the observed rates! In addition, the predicted activation energy ( $\Delta G_{\text{SM}}^\ddagger$ ) in triacetin is much bigger than the observed activation energy ( $E_{\text{A}} = 380\text{cm}^{-1}$ ) near room temperature i.e. a factor of about 6-9. Apparently, the deficiency of the Sumi and Marcus theoretical expressions for our

purposes here can be largely attributed to the classical treatment of the vibrational modes. High frequency accepting modes are known to play an important role in the inverted regime<sup>15,16</sup>.

### quantum mechanical treatment of the vibrational modes

Jortner and Bixon recently reported a modification of the outer sphere et model<sup>3</sup> to incorporate high frequency accepting modes. An explicit expression was given for  $k_{et}^{0n}$ , which corresponds to a sum over parallel vibronic channels,

$$k_{et,JB}^{0n} = k_{NA}^{0n} / (1 + \mathcal{H}_A^{(n)}) \quad (3)$$

where  $n$  refers to the quantum level of the high frequency accepting mode in the product state (in our case  $D^+ A^-$ ).  $k_{NA}^{0n}$  is the nonadiabatic rate constant for each vibronic channel, i.e.

$$k_{NA}^{0n} = A_{NA} |\langle 0 | n \rangle|^2 \exp \left[ - \frac{(\Delta G_n^0 + \lambda_{solv})^2}{4 \lambda_{solv} k_B T} \right] \quad (4)$$

where  $A_{NA}$  is given as

$$A_{NA} = \frac{2 \pi V^2}{\hbar (4 \pi \lambda_{solv, JB} k_B T)^{\dagger}} \quad (5)$$

and  $\Delta G_n^0$  is the modified driving force for each channel.

$$\Delta G_n^0 = \Delta G^0 + n h \nu_{QM} \quad (6)$$

the remaining term is the adiabaticity parameter,

$$\mathcal{H}_A^{(n)} = \frac{4 \pi V^2 \langle \tau \rangle_s}{\hbar \lambda_{solv, JB}} |\langle 0 | n \rangle|^2 \quad (7)$$

which is  $\gg 1$  if a particular channel is electronically adiabatic.

The Jortner/Bixon model only considers high frequency, quantum mechanical vibrational modes. We, therefore, assumed that all of the (low frequency) reorganization energy is associated with the solvent, i.e.  $\lambda_{solv, JB} \cong \lambda_{class}$ . We will return to this point

below.

The Jortner/Bixon approach requires two more additional pieces of information than the Sumi/Marcus theory, namely the frequency,  $\nu_{QM}$ , and displacement,  $\Delta_{QM}$ , of the high frequency mode, which has also been determined by Kjaer and Ulstrup.

As expected from previous application of theory in the inverted regime, models that include high frequency accepting modes predict rates that are orders-of-magnitude more rapid than the classical vibrational mode model, see Table 3. For the betaines a close examination of eqn 4 reveals that most of the rate is carried by a two vibronic channels ( $n=4$  and  $5$ ) both of which have a small effective barrier. These two particular channels are almost in the barrierless regime and are solvent controlled, i.e.,  $k_{et} \cong 1/\langle \tau_s \rangle$ . The Jortner/Bixon predictions are much closer to the experimental results than the purely classical model. This dramatic effect is a strong indication of the importance of high frequency accepting modes in the product state.

The analysis here employs only a single high frequency mode. A multimode approach would undoubtedly lead to several channels each with a small activation energy. Consequently, the Jortner/Bixon prediction for betaine is effectively leading to a barrierless  $et$  rate, with  $k_{et} \cong 1/\langle \tau_s \rangle$ . In fact, this result is general, i.e.,  $et$  reactions in the inverted regime with very large  $V_{el}$  and moderate vibrational displacements of high frequency modes, should exhibit  $k_{et} \cong 1/\langle \tau_s \rangle$ . Physically, however,  $k_{et,JD}$  should not exceed  $1/\tau_s$  since the solvent coordinate is the accepting mode for at least some of the reaction energy, i.e., for each vibronic channel the energy deposited in the solvent coordinate is  $\Delta G^0 + nh\nu_{QM}$ .

It is fascinating that  $k_{et,obs}$  in slowly relaxing solvent, for example triacetin, is orders-of-magnitude faster than  $k_{et,JB}$ . Indeed, in these environments  $k_{et} \gg 1/\langle \tau_s \rangle$ . This strongly implies that besides the solvent, there must be an additional "energy bath"

that alleviates the energy mismatch ( $\Delta G^0 + nh\nu_{QM}$ ) in these environments. The correlation time of this (hypothetical) bath is apparently much less than  $\langle \tau_s \rangle$  in these environments.

### beyond the Jortner/Bixon and Sumi/Marcus models

We have very little information on the physical nature of the additional bath modes. It may be that this bath involves low frequency vibrational modes of betaine—30. If this turns out to be the case, and the relaxation time of this mode,  $\tau_{\text{bath}} \ll 1/k_{\text{et}}$ , then one can envision a hybrid of the Jortner/Bixon and Sumi/Marcus models. We now briefly consider such a model. The basic idea is to use Jortner/Bixon theory to find the most efficient, non-adiabatic channel (n), where n refers to the quantum number of the final product vibrational level. After this level is identified, Sumi and Marcus theory can be used to calculate the rate using  $\lambda_{\text{vib,class}}$  as the vibrational reorganization energy. Although this procedure is a crude approximation, it does lead to interesting insight on the betaine kinetics.

To consider this further we need to summarize the basic Sumi/Marcus theory. The model involves a two-dimensional free energy surface,  $G(X,q)$ , spanned by the solvent coordinate, X, and the vibrational, nuclear coordinate, q. The coordinate X diffuses under the influence of the potential, with a diffusion constant, D, that can be related to  $\langle \tau_s \rangle$ . During the diffusion, the reactant changes into product (et) with a probability rate constant,  $k(X)$ . In terms of the probability distribution function,  $P(X)$ , the key equation is

$$\frac{\delta P}{\delta t} = D \frac{\delta^2 P}{\delta X^2} + \frac{D}{k_B T} \frac{\delta}{\delta X} \left[ P \frac{\delta V}{\delta X} \right] - k(X)P \quad (8)$$

which can be solved in different limits by a variety of methods.

$k(X)$  in the Sumi/Marcus theory is given by

$$k(X) = \nu_q \exp \left[ - \frac{\Delta G^* (X)}{k_B T} \right] \quad (9)$$

where  $k(X)$  is the  $X$  dependent rate,  $\nu_q$  is the frequency factor for the et along  $q$ , as discussed below, and  $\Delta G^*(X)$  is the solvent coordinate dependent activation energy given as

$$\Delta G^*(X) = \frac{1}{4\lambda_{\text{vib}}} \left[ (2\lambda_{\text{solv}})^{\frac{1}{2}} X - (\lambda_{\text{vib}} + \lambda_{\text{solv}} + \Delta G^0) \right]^2 \quad (10)$$

where  $\lambda_{\text{solv}}$  is the solvent reorganization energy, and  $\lambda_{\text{vib}}$  is the vibrational reorganization energy.

If we take the point of view of a hybrid Jortner/Bixon and Sumi/Marcus treatment, then  $\lambda_{\text{vib}}$  in eqn 10 should be identified with  $\lambda_{\text{vib,class}}$ . In contrast, the effect of the high frequency reorganization energy,  $\lambda_{\text{vib,QM}}$ , should be treated quantum mechanically, as in the Jortner/Bixon theory. Accordingly,  $\Delta G^0$  in eqn 10 should be replaced by

$$\Delta G_n^0 = \Delta G^0 + nh\nu_{\text{QM}} \quad (11)$$

where  $n$  is the number of vibrational quanta in the specific channel. The vibrational frequency factor  $\nu_q$  is given by eqn 12, which includes a dressed matrix element

$$V_n^2 = V_{\text{el}}^2 | \langle 0 | n \rangle |^2,$$

$$\nu_q = \left[ \frac{V_n^2}{h} \right] \left[ \frac{\pi}{\lambda_{\text{vib}} k_B T} \right]^{\frac{1}{2}} \quad (12)$$

For Betaine-30 the moderate  $| \langle 0 | 7 \rangle |^2$  Frank Condon factor leads to ultrafast vibronic et through the  $n=7$  channel by maintaining a large preexponential factor in  $k(X)$ .

$$k(X) = \nu_q \exp(-\Delta G_n^*(X)/k_B T) \approx 10^{11} \exp(-\Delta G_n^*(X)/k_B T) \quad (13)$$

There is a small activation energy  $\Delta G_n^*(X_t) \approx 2k_B T$  at the value of the reaction coordinate ( $X = (2\lambda_{\text{solv}})^{\frac{1}{2}}$ , or  $X_t = 0$ ) that corresponds to the region prepared by the laser excitation at  $t=0$ . A small, fractional variation in  $h\nu_{\text{QM}}$  would lead to  $\Delta G_n^*(X_t) \approx 0$ ; this is probably close to the actual situation because betaine undoubtedly has a number of displaced modes which are not included in this analysis. Therefore, the hybrid model predicts that  $k(X_t=0) \approx 10^{11}$ , if additional vibrational enhancements are included.



In slowly relaxing solvents the rate of et of laser prepared solution should be much faster than the rate of solvent diffusion such that the reaction is in the "no diffusion limit" of Sumi/Marcus. Thus, for a slow solvent such as GTA, the rate should be on the order of  $10^{11} \text{ sec}^{-1}$ , and  $k_{et}(X_t=0) \gg 1/\tau_s$ . This hybrid is in better agreement with experiment than either of the models alone.

## CONCLUSIONS AND SUMMARY

Transient pump-probe measurements have been made on Betaine-30, the solvent polarity probe. The transient data has been analyzed to measure  $k_{et}$ , the electron transfer rate constant, in polar solvents for this inverted regime et. The observed rate constant,  $k_{et}$ , in various polar solvents is over a factor of  $10^5$  bigger than is predicted by the standard, classical, implementation of Marcus theory, using Kjaer and Ulstrup's estimates of the necessary parameters. In contrast, a quantum treatment of the vibrational modes by Jortner and Bixon, predicts that the rate should be approximately  $k_{et,JB} \cong \frac{1}{\langle \tau_s \rangle}$ . This is close to the experimental results ( $\cong 10^{12} \text{ sec}^{-1}$ ) in typical polar aprotic solvents. However, in highly viscous, slowly relaxing solvents,  $k_{et,JB} \ll k_{et,obs}$ . This is taken as evidence that the accepting mode for the et in these environments is not the "conventional" solvent coordinate. It is shown that a hybrid of the Jortner/Bixon and Sumi/Marcus theories can physically account for the results. The kinetic behavior of Betaine-30 in slowly relaxing solvents is shown to be in the "diffusionless limit" of the hybrid, generalized Sumi-Marcus/Jortner-Bixon picture.

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**Table 1. Multi-exponential Fit Parameters for the Transient Pump-Probe Signal of Betaine-30 in Various Solvents.<sup>a</sup>**

Solvent	$\tau_1$ (ps)	$A_1$	$\tau_2$ (ps)	$A_2$	$\lambda_{\text{max. CT band}} (\text{\AA})$
propylene carbonate	1.1	0.69 <sup>b</sup>	5.8	-0.31 <sup>b</sup>	621
acetonitrile	0.5	0.67	2.0	-0.33	630
acetone	0.7	0.65	2.3	-0.35	687
benzonitrile	3.6	0.55	4.7	-0.45	690
GTA <sup>c</sup>	3.4	0.92	>30	-0.08	697
methyl acetate	1.3	0.84	8.0	-0.16	725
ethyl acetate	1.5	0.83	7.0	-0.17	761
butyl acetate	2.0	1.0			784
metadichlorobenzene	4.3	1.0			784
benzene	2.7	1.0			840
toluene	3.2	1.0			855

<sup>a</sup> Temperature = 293°K.

<sup>b</sup>  $A_1$  and  $A_2$  are the amplitudes of each exponential in the model decay function, see text.

<sup>c</sup> GTA = triacetin.

**Table 2.** Electron Transfer Rates of Betaine-30 Correlated with Solvent Dynamics<sup>a</sup>

Solvent	$k_{et}$ ( $10^{12}\text{sec}^{-1}$ )	$1/\langle\tau_s\rangle$ ( $10^{12}\text{sec}^{-1}$ )	$E_T(30)$ (kcalmol <sup>-1</sup> )
propylene carbonate	0.91	0.29	46.6
acetonitrile	2.0	2.0	46.0
acetone	1.4	1.2	42.2
benzonitrile	0.27	0.21	42.0
GTA, 263 <sup>o</sup> K <sup>b</sup>	0.22	$10^{-4}$	44.0
GTA, 293 <sup>o</sup> K <sup>c</sup>	0.29	0.01	41.5
GTA, 347 <sup>o</sup> K	0.44	—	36.7
methyl acetate	0.77	0.60	40.0
ethyl acetate	0.67	0.38	38.1
butyl acetate	0.5	0.15	—
metadichlorobenzene	0.23	—	37.0
benzene	0.37	—	34.5
toluene	0.31	—	33.9

<sup>a</sup> The et rate constants were measured at 293<sup>o</sup>K, except where otherwise indicated.

<sup>b</sup> Calculated from the dielectric data of reference 14.

<sup>c</sup>  $\langle\tau_s\rangle$  for GTA at 293<sup>o</sup>K was estimated by the single wavelength method<sup>13</sup> using transient fluorescence data at 480nm with Coumarin 153.

Table 3. Parameters, Calculated Rate Constants, and Observed Rate Constants in Selected Solvents.

Solvent	$\Delta G^\circ$	$\lambda_{\text{class}}$	$\lambda_{\text{sol}}$	$\lambda_{\text{QM}}$	$\nu_{\text{QM}}$	$\frac{1}{\langle \tau_s \rangle}$	$k_{\text{et,SM}}$	$k_{\text{et,JB}}$	$k_{\text{et,obs}}$
	—————(10 <sup>3</sup> cm <sup>-1</sup> )—————					—————(10 <sup>12</sup> sec <sup>-1</sup> )—————			
acetonitrile	9.6	3.3	3.2	0.85	1.7	2.1	10 <sup>-3</sup>	1.6	2.0
acetone	9.5	2.7	2.5	0.72	1.6	1.49	10 <sup>-5</sup>	0.84	1.4
benzonitrile	9.7	2.4	2.3	0.66	1.6	0.19	10 <sup>-8</sup>	0.11	0.27
GTA, 263 <sup>o</sup> K	9.6	3.0	2.8	0.78	1.7	10 <sup>-4</sup>	10 <sup>-9</sup>	10 <sup>-4</sup>	0.22
GTA, 293 <sup>o</sup> K	9.7	2.4	2.4	0.66	1.6	10 <sup>-2</sup>	10 <sup>-9</sup>	10 <sup>-2</sup>	0.29

<sup>a</sup> For GTA at 263<sup>o</sup>K, an interpolation between the estimated parameters<sup>10</sup> for betaine-26 in acetonitrile and benzonitrile was made, in order to predict the behavior in a solvent whose polarity lies between the polarities of those two. For GTA at 293<sup>o</sup>K, the parameters for benzonitrile were employed.

<sup>b</sup>  $\lambda_{\text{solv}}$  and  $\lambda_{\text{class}}$  differ by  $\lambda_{\text{class,vib}} = 150\text{cm}^{-1}$ , see text.

## FIGURE CAPTIONS:

- Figure 1. Free energy surfaces for the ground and first excited electronic states of Betaine-26 in acetonitrile as a function of the classical degree of freedom which includes solvent polarization and low frequency solute degrees of freedom. The dashed lines represent vibrationally excited levels of each electronic state. Betaine-30 is the solute whose electron transfer dynamics are reported in this communication.
- Figure 2. Transient absorption ( $\Delta OD$ ) of Betaine-30 in (a) benzene and (b) acetone with  $\lambda_{\text{pump}} = \lambda_{\text{probe}} = 792\text{nm}$ . The actual data (points) have been fit by a convolution procedure which is described in the text.
- Figure 3. Transient absorption ( $\Delta OD$ ) of Betaine-30 in acetone with  $\lambda_{\text{pump}} = 792\text{nm}$  and  $\lambda_{\text{probe}} = 700\text{nm}$ . see text for details. The actual data (points) have been fit by a convolution procedure which is described in the text.
- Figure 4. Transient absorption ( $\Delta OD$ ) of Betaine-30 in triacetin (GTA) at (a)  $74^\circ\text{C}$ , (b)  $20^\circ\text{C}$  and (c)  $-10^\circ\text{C}$ . Triacetin's average solvation time is three orders of magnitude faster in (a) than (c), yet the observed electron transfer dynamics differ by only a factor of 2. The actual data (points) have been fit by a convolution procedure which is described in the text.

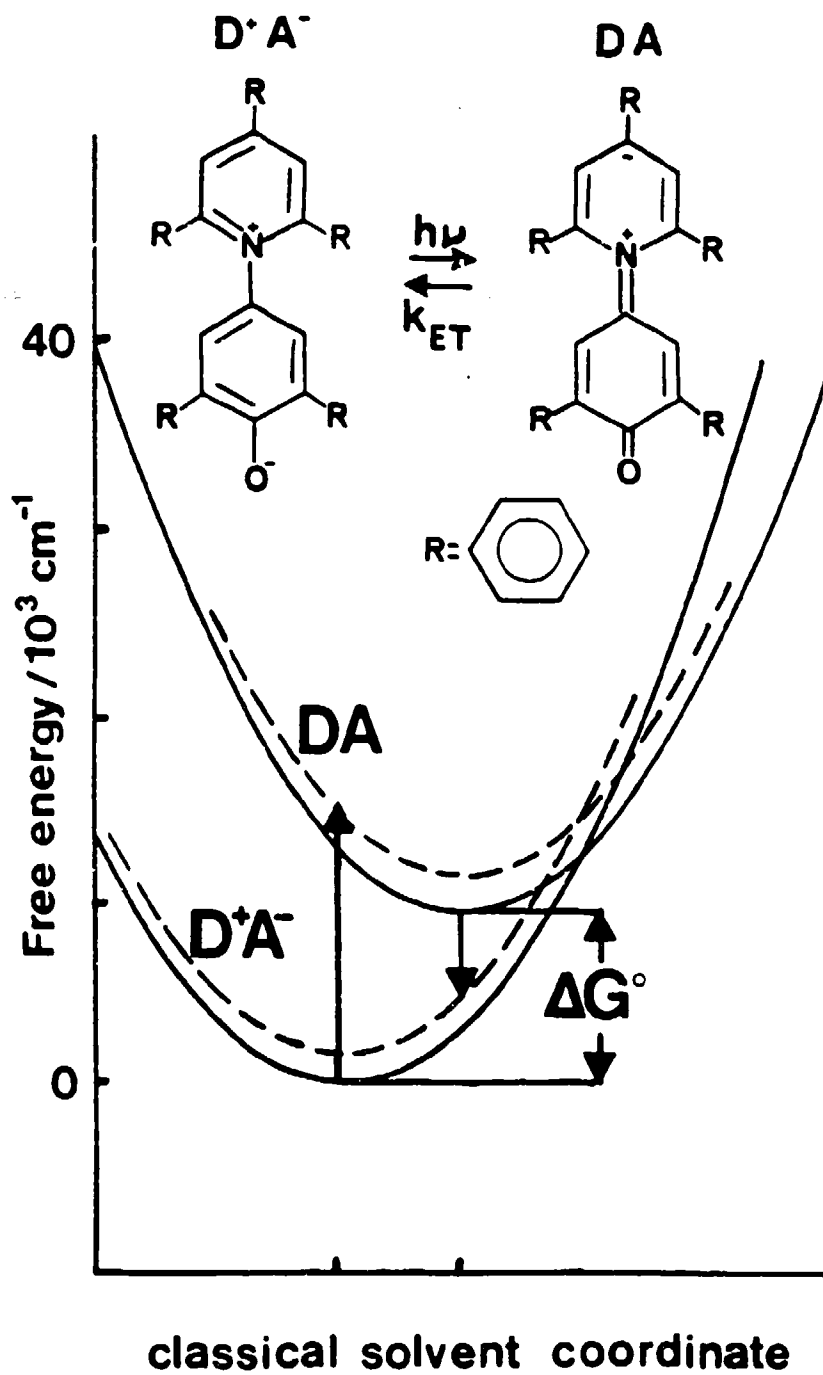


FIGURE 1



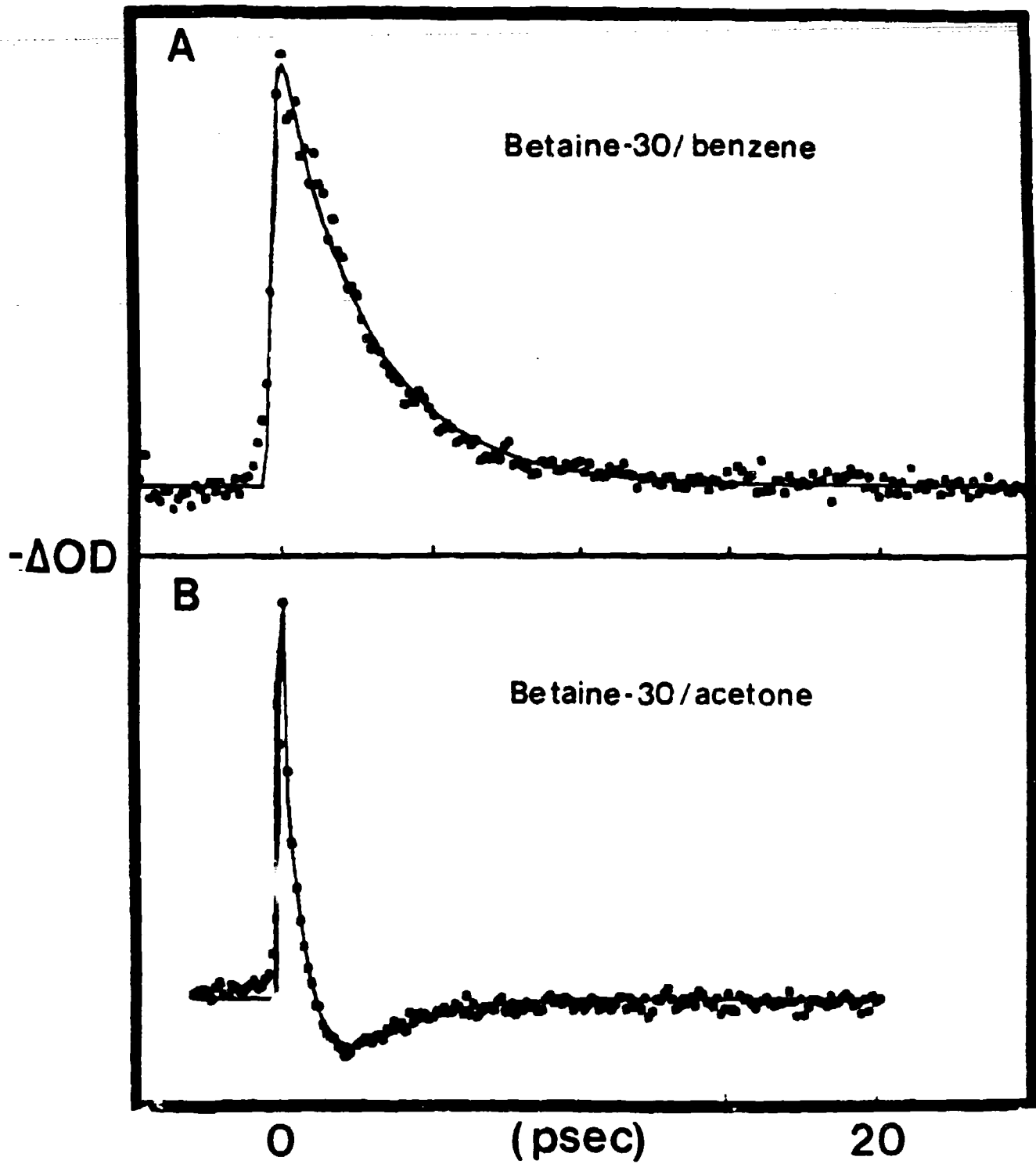


FIGURE 2

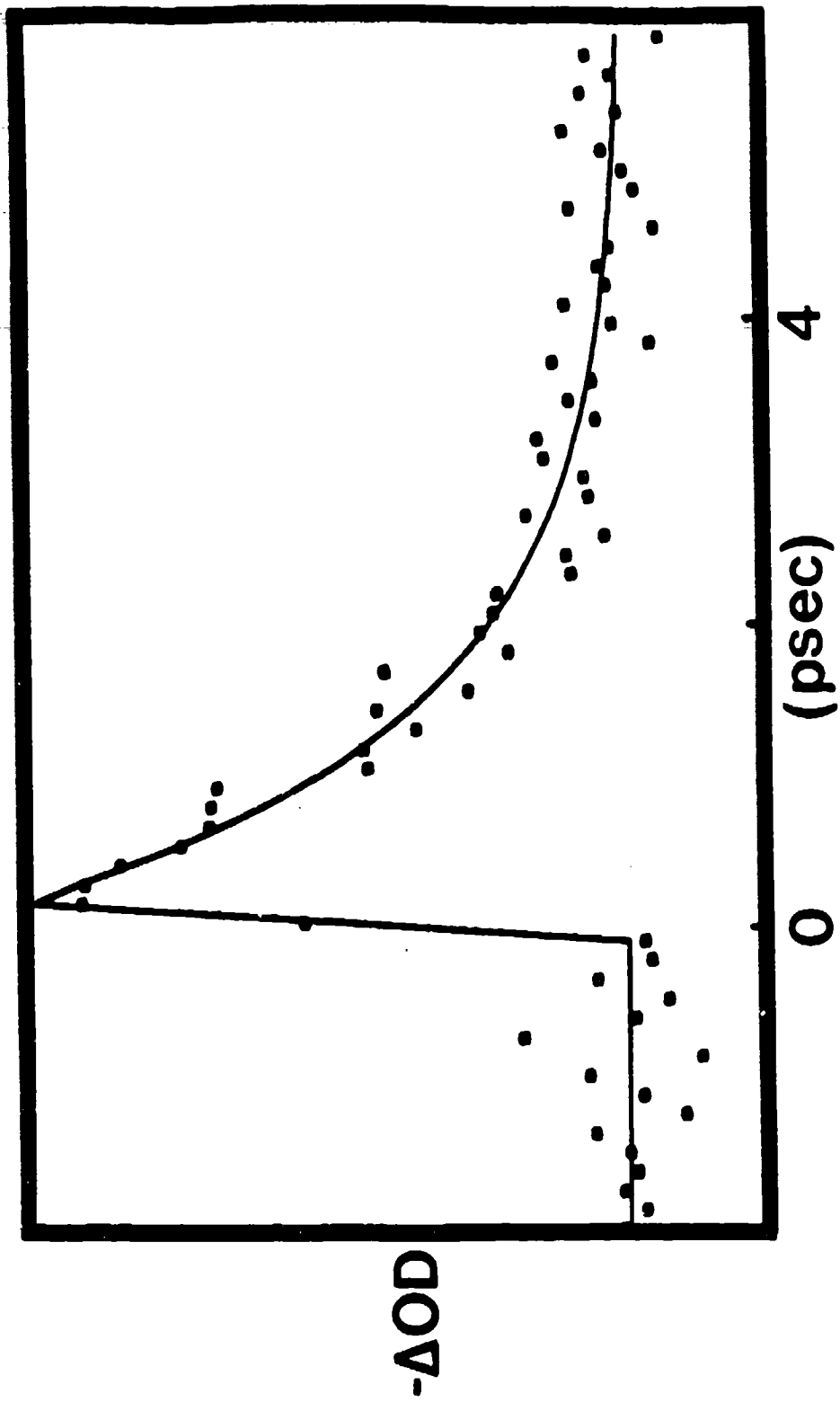


FIGURE 3

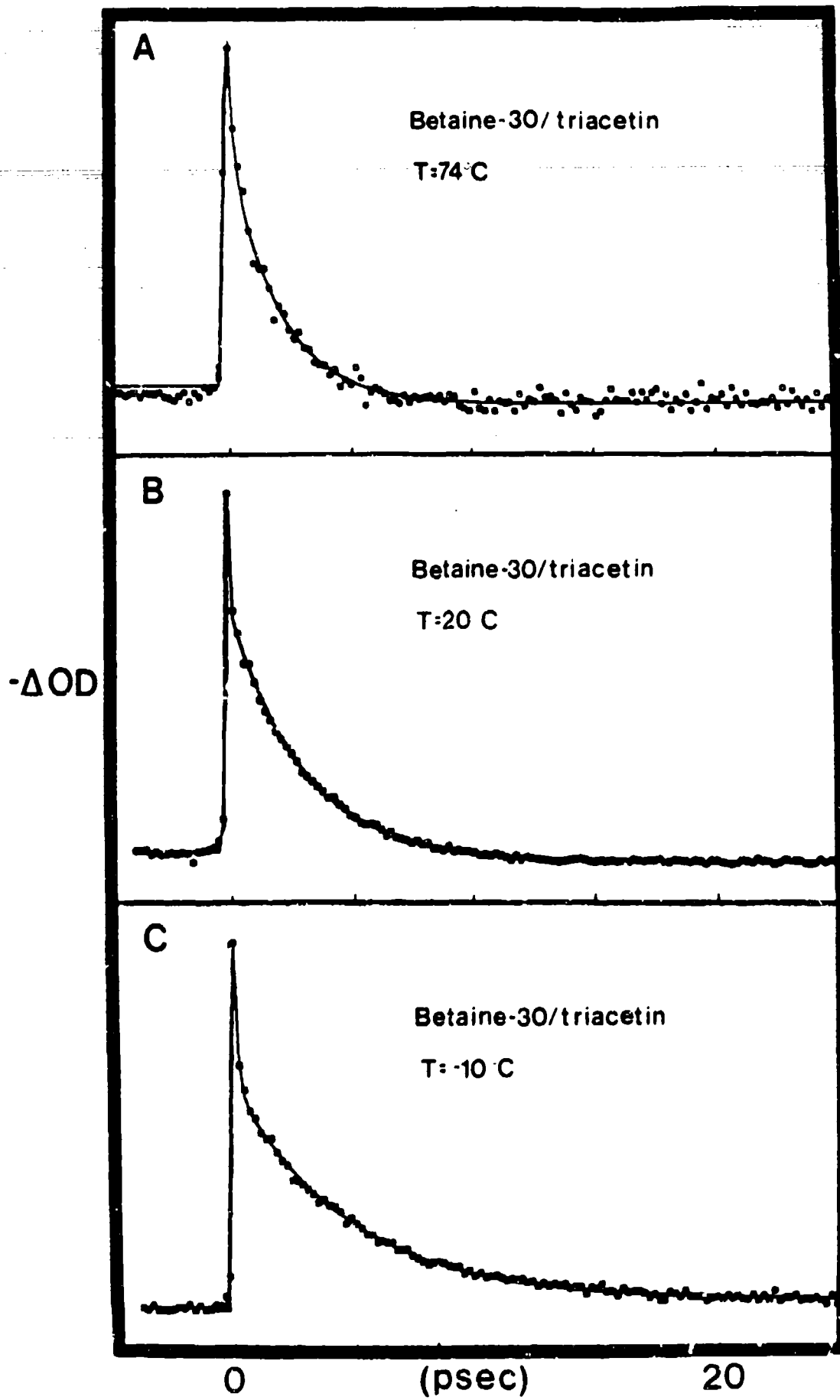


FIGURE 4

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