Wide-Band, Time-Resolved Photoacoustic Study of Electron-Transfer Reactions: Photoexcited Magnesium Porphyrin and Quinones

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Wide-band, time-resolved, pulsed photoacoustics has been employed to study the electron-transfer reaction between a triplet magnesium porphyrin and various quinones in polar and nonpolar solvents. The reaction rate constants are near encounter limited. The yield of triplet state is 70% in both solvents. The yield of ions is 85% in the former and zero in the latter, in agreement with spin dephasing time and escape times from the Coulomb wells in the two solvents. In methanol the plot of measured heat output versus quinone redox potential is linear. This implies that the entropy of electron transfer is constant through the series, but it may not be negligible.

Introduction

The photoacoustic (PA) technique has long been used to measure light absorption in weakly absorbing and opaque media where other techniques are difficult to apply. The theory and some applications of this method have been thoroughly reviewed.[1] It has been shown that time-resolved photoacoustic measurements can provide data on both the energetics and kinetics of chemical processes in solutions. The technique has successfully been applied to a variety of chemical systems.[2-4] The method is based on the absorption of light in solution from a pulsed or a modulated light source. That part of the absorbed photon energy which is dissipated as heat causes an expansion of the compressible medium in the light path which in turn produces a pressure wave that travels away from the illuminated region and is intercepted by an acoustic detector. If the absorption of light by a solute is followed by photophysical and/or photochemical processes with the evolution or absorption of heat or a change in volume, these changes and their time dependence are reflected in the shape of the photoacoustic signal and can thus be determined by convolutions.

We use wide-band as opposed to resonant detectors and the appropriate convolutions to enhance this methodology. We describe the electron-transfer reaction between the triplet state of a porphyrin, Mg mesoporphyrin IX dimethyl ester (MgmP-dME), and various quinones. The electron-transfer rate constants and the heat stored in the long-lived cation and anion formed in the process were measured in the polar solvent methanol and in the nonpolar solvent toluene. These reactions are of particular interest since similar reactants are models of photosynthetic systems.

Methodology

The theory of the photoacoustic method has been amply reviewed by Patel and Tam[1] and by Tam.[5] Theoretical aspects and applications to chemical reactions have been described.[2-4] The main points are briefly outlined here.

In time-resolved photoacoustics a pulse of light, usually from a laser source, is absorbed by the molecules of interest in solution. The absorbed photon energy is degraded to heat, sometimes in several steps, which cause an expansion of the compressible medium in the laser path. The disturbance created by this sudden expansion can be described by a wave equation. The pressure wave, resulting from the expansion and propagating with the velocity of sound v toward the detector, is given by the time derivative of the wave function, φ:[6]

$$p(x,t) = -\rho\, \partial\varphi(x,t)/\partial t = \rho v g'(x - vt) \qquad (1)$$

where p is the pressure measured at a distance x from the disturbance at time t, ρ is the density of the solution, and g' is the time derivative of the shape function of the beam. The velocity of sound is much larger than the rate of diffusion of heat or of matter in the medium. If a thin planar laser beam is used, a planar pressure wave results which propagates at right angles to the laser beam toward the piezoelectric detector. A planar wave does not decrease in intensity with distance as does the customary cylindrical beam, and the use of a spatially well defined laser beam increases the time resolution of the experiment. The thinner and more defined is the laser beam, the sharper is the pressure pulse profile and the better the time resolution. However, multiphoton effects limit the maximum pulse energy. Thus there is an optimum beam width for a given time resolution.

For an instantaneous degradation of the absorbed photons to heat, an infinitely thin, planar laser beam produces a pressure

$$\delta P = \delta E \cdot B \qquad (2)$$

where δE is the light energy absorbed and the constant B is determined by the volume expansivity, the compressibility of the medium, its density, and its heat capacity. The actual pressure, P, is the convolution of δP over all points located at different distances from the detector. This convolution and effects such as the attenuation of the laser beam in the solution or deviation from planarity of the pressure wave are reproduced by using a reference solution of a compound that releases the energy of the photons absorbed instantaneously, i.e. within the time resolution of the experiment. Since it is the rate of heat release that affects the wave function (eq 1), one convolves P with the derivative of the heat release function, $h'(t)$. For the reference solution, $h_0(t)$ is a step function, i.e. $h_0'(t)$ is the delta function $\delta(t)$ and one obtains:

$$P_{\mathrm{ref}}(t) = E \cdot B \cdot R(t) * h_0'(t) = E \cdot B \cdot R(t) * \delta(t) = E \cdot B \cdot R(t) \qquad (3)$$

where $R(t)$ is the detector response function and the asterisk denotes the convolution integral. For the solution of interest, the sample, a part of the absorbed light energy δE might be stored temporarily in reaction intermediates. This energy will be released within the illuminated volume during the progress of the reaction with a time function $h(t)$. The pressure measured in this case is

$$P_{\mathrm{sample}}(t) = P_{\mathrm{ref}}(t) * h'(t) \qquad (4)$$

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For a first-order process the heat formation function is the complement of an expoential $1 - e^{-kt}$ and therefore $h'(t) = ke^{-kt}$.

For an excited state reaction sequence the photoacoustic measurements will record the heat released in all reaction steps. The amplitude of the pressure pulse can be separated into three fractions:[2,7]

$$P_{\text{sample}}(t) = A_f{\cdot}P_{\text{ref}}(t) + A_m{\cdot}P_{\text{ref}}(t)*h'(t) + A_s{\cdot}0 \qquad (5)$$

where A_f is the fraction of heat released immediately, i.e. within the resolving time of the measurement, upon absorption of light. Hence the convolution of the first term reduces to P_{ref} itself (see eq 3). A_m is the fraction of heat released over the measured time span (eq 4), and A_s is the heat stored in the products for a time long in comparison with the time of the measurement. The time derivative of $h(t)$ for this term tends to zero. A_s does not, therefore, contribute to the measurable response, $P_{\text{sample}}(t)$. If the excited state loses some of its energy by emission, say fluorescence, this fraction of the total energy is A_{fl}, and it is also not measured by $P_{\text{sample}}(t)$. The sum of the fractions equals unity when normalized to $P_{\text{ref}}(t)$:

$$A_f + A_m + A_s + A_{fl} = 1 \qquad (6)$$

For an electron-transfer reaction between the excited triplet state of a porphyrin, ^{3}P, and a quinone, Q, in solution:

$$^1\text{P} \rightarrow {}^3\text{P} + h_f; \quad {}^3\text{P} + \text{Q} \rightarrow \text{P}^+ + \text{Q}^- + h_m;$$
$$\text{P}^+ + \text{Q}^- \rightarrow \text{P} + \text{Q} + h_s \qquad (7)$$

The initial singlet ^{1}P to triplet ^{3}P intersystem crossing is a rapid process. The heat released in this step appears together with any nonradiative deactivation of the singlet state ^{1}P in the fraction A_f in eq 5. By an appropriate choice of electron acceptor concentrations it is possible to adjust the rate of the bimolecular electron transfer between the triplet, ^{3}P, and quinone, Q, so that it falls within the range measurable by our instrumentation. The fraction of the heat released in this reaction together with any radiationless deactivation of ^{3}P is given by A_m. The heat stored for a comparatively long time in the ions P^+ and Q^- until released in their slow recombination step is represented by A_s. Since we have normalized the calculation, it is convenient to express the heats as energies per quanta or molecule in electronvolts: ν, that of the absorbed light; ν_s, that of the singlet state; ν_t, that of the triplet state, and $\nu_\pm$ that of the separated ions.

For the above reaction scheme the coefficients are given by

$$\begin{aligned} A_f &= [\nu - \nu_s + \eta_t(\nu_s - \nu_t) + (1 - \eta_t - \eta_{fl})\nu_s]/\nu \\ &= [\nu - \eta_t\nu_t - \eta_{fl}\nu_s]/\nu \qquad (8) \end{aligned}$$

$$\begin{aligned} A_m &= \eta_t[\eta_\pm(\nu_t - \nu_\pm) + (1 - \eta_\pm)\nu_t]/\nu \\ &= \eta_t[\nu_t - \eta_\pm\nu_\pm]/\nu \qquad (9) \end{aligned}$$

$$A_s = \eta_t\eta_\pm\nu_\pm/\nu \qquad (10)$$

$$A_{fl} = \eta_{fl}\nu_s/\nu \qquad (11)$$

The quantities η_i are the yields or efficiencies of the respective processes.

Experimental Methods

The apparatus used for the time-resolved photoacoustic measurements consists of a laser pulse of about 10 ns fwhm from a tunable dye laser (Rhodamine 6G) driven by a Xe–Cl excimer laser (Lambda Physik E-50) which excites the solutions of MgmPdME or Sudan black, the reference. The laser beam, after expansion in a telescope, was shaped and positioned by a succession of three horizontal slits to a planar geometry. It then passed through the thermostated solution cell in a plane parallel to the detector surface. The pulse energy was 10–30 μJ at 580 nm on an area of 0.1 cm^2. This is well within the linear range ensuring no multiphoton effects. The detector is an adaptation of one described by Patel and Tam.[1] A piezoelectric polyvinylidene membrane of 28 μm thickness (Kynar Piezo Film) was tightly held in a stainless steel covered housing. The pressure wave, after passing the metal cover, activates the membrane, which has a broad-band frequency response. The resulting voltage signal is fed into an Amptek A250 (rise time 5 ns) preamplifier and thence into a Stanford Research Systems 560 amplifier. The latter limits the present measurements to a bandwidth of 1 MHz. The signal is then channelled into a Tektronix RTD710 digitizer which is interfaced to a Hewlett Packard 340 computer for data analysis, storage, and display. Because of reflections from surfaces in the detector and from the cell walls a rather complex signal is produced after the first, main peak. To obtain acceptable results for the required fractions A_f, A_m, and A_s and the rate constant k by convoluting P_{ref} with $h'(t)$ (eq 5) it was most important to maintain rigidly the laser beam–solution cell–detector geometry since slight movements would affect the complex signal and thus reduce the signal-to-noise ratio.

The data were analyzed by convoluting the instrument response function $P_{\text{ref}}(t)$ with the derivative of the heat release functions $h'(t)$ by an iterative procedure.[4] The whole range of A_f, A_m, and k values was explored, and the best fit with the observed signal $P_{\text{sample}}(t)$ was judged by the minimal value of the least-squares deviations (LSQ).[8] As mentioned above, the missing energy after the above parameters were fitted represents the sum of both the residual heat stored in the system, A_s, and the emitted light energy, A_{fl}. If the fluorescence quantum yield and wavelength are known, the value of A_s can be obtained.

MgmPdME was obtained from Porphyrin Products (Logan Utah), Sudan black was a Geigy Co. product, and the solvents methanol and toluene were of HPLC grade. Aliquots of 0.07 to 0.1 mL of 2.5 × 10^{-2} M quinone solutions were added to the cell with a 0.1 mL Hamilton syringe to attain the required quinone concentrations of 0.3 to 1.2 × 10^{-3} M. The solutions were freed of O_2 by bubbling for 20 min with nitrogen (Matheson prepurified 99.999%) saturated with the solvent. The photoacoustic signal was measured in the absence of quenchers in oxygen free solution and at increasing quinone concentrations, [Q], ranging from 3 × 10^{-4} to 12 × 10^{-4} M. The following quinones were used: benzoquinone (BQ), 2,6-dichlorobenzoquinone (Cl_2BQ), 1,4-naphthoquinone (NQ), 2,6-methoxybenzoquinone (MeO_2BQ), and duroquinone (DQ).

Results

Solutions of MgmPdME in methanol and in toluene were illuminated at 580 nm. The fluorescence yield of MgmPdME was determined as $\eta = 0.13$ from a comparison with the fluorescence intensity of ZnOEP for which a yield of $\eta_{fl} = 0.04$ was assumed similar to the value for Zn mesoporphyrin in 2-propanol quoted by Gradyushko and Tsvirko.[9]

Figure 1 shows the power of the convolution method used. In Figure 1a the comparatively slow electron transfer from ^{3}MgmPdME to 4.35 × 10^{-4} M duroquinone (DQ) in toluene distorts considerably the instrument response P_{ref}. The convolution is able to recover the appropriate time constant $(1/k)$ of 1.1 μs and the heat losses originating in the triplet state, A_m, to fit the experimental data. Figure 1b shows a similar experiment at a higher DQ concentration, 1.3 × 10^{-3} M, where the electron transfer takes place more rapidly, i.e. $\tau = 0.34$ μs. Although the signal of $P_{\text{sample}}(t)$ differs less from $P_{\text{ref}}(t)$, this method is able to retrieve the experimental parameters as seen from the least-squares (LSQ) fit and the (five times magnified) residuals. In both cases a value of 0.15 is obtained for A_s plus A_{fl} which is close to $A_{fl} = 0.13$ (see eq 11). The quenching rate constants were determined

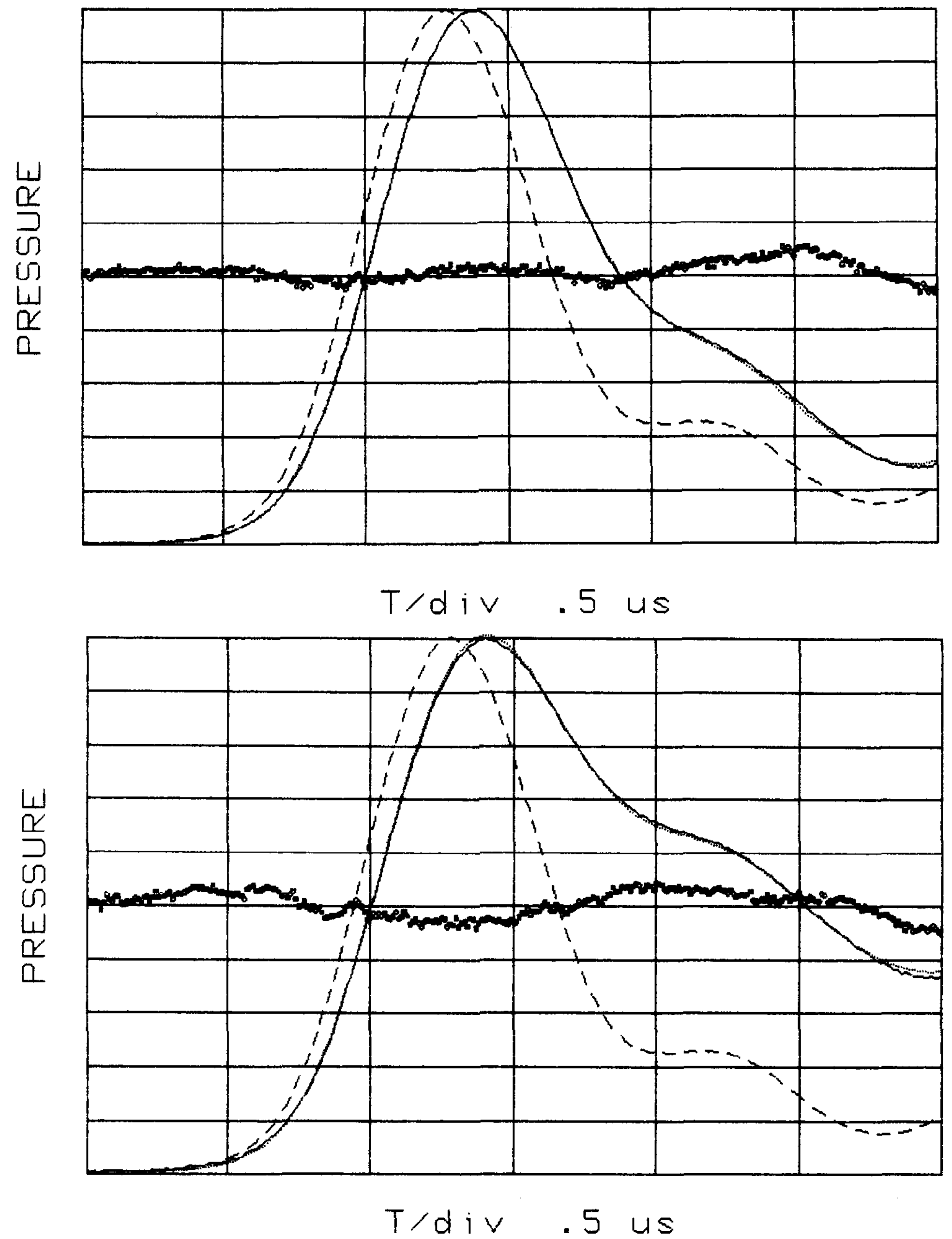

Figure 1. (a, top) Plot of the reaction of ^{3}MgmPdME with 4.35×10^{-4} M duroquinone in toluene. The solid line is the data, the dashed line the reference (sudan black), the fine dotted line the fit, and the squares the residuals on a 5-fold vertical expansion with 0 at center. The data are normalized to the pulse amplitude for ease of viewing. The fit parameters are $A_f = 0.26$, $A_m = 0.59$, $A_s + A_{fl} = 0.15$, and $\tau = 1.1$ μs. (b, bottom) Same as a, with 1.3×10^{-3} M duroquinone. The fit parameters are $A_f = 0.30$, $A_m = 0.55$, $A_s + A_{fl} = 0.15$, and $\tau = 0.34$ μs.

from $1/\tau - 1/\tau_0$ vs [Q]. Since τ_0 lies in the millisecond region while the measured lifetimes were in the micro- and submicrosecond domain, the $1/\tau_0$ term in the above Stern–Volmer equation is safely omitted. The quenching rate constants together with the polarographic half-wave reduction potentials (measured in dimethylformamide)[10,11] are given in Table I together with the fast, A_f, the measurable, A_m, and the combined slow, A_s, and fluorescence, A_{fl}, fractions of the signal (eq 8–11). Data for methanol and for toluene solutions are presented. The above convolution procedure fits A_f, A_m, and $k = 1/\tau$. The residual energy, not measured, is $A_s + A_{fl}$. The value of A_s is obtained by subtracting A_{fl}. When the values of A_s are plotted against the reduction potentials of the quinones a linear relation, within the experimental error, is obtained (Figure 2). The reduction potentials, measured as polarographic half-wave potentials, are dependent on the solvent. However, differences in a single solvent can be assumed to be significant.

Discussion

The standard free energy for the transfer of an electron from an excited donor, D*, to an acceptor, A, in solution is:

$$\Delta G^\circ = E^\circ(\mathrm{D/D^+}) - E^\circ(\mathrm{A^-/A}) - E_0 \qquad (12)$$

where $E^\circ(\mathrm{D/D^+})$ and $E^\circ(\mathrm{A^-/A})$ are the oxidation potential of the donor and the reduction potental of the acceptor, respectively. They are often approximated by the corresponding polarographic half-wave potentials.[12] $\mathrm{E_0}$ is the electronic excitation energy of the donor. The commonly used "electrostatic correction term"[12] can be ignored since the measured enthalpic effects occur on a microsecond time scale and the escape of the geminate ion pair occurs in a few nanoseconds. Thus our enthalpic measurements refer to the ionically equilibrated solution. It has been found experimentally that for a variety of acceptors with $-\Delta G^\circ < 0.4$ eV the electron-transfer rate is diffusion limited.[12] This relation

TABLE I: Photoacoustic Data for Reaction of Photoexcited MgmPdME with Quinones[a]

quinone	solvent	A_f	A_m	$A_s + A_{fl}$	$10^{-9}k_q$	E_{red}, mV (SCE)
Cl_2Bq	methanol	0.28	0.42	0.29	10.8	–30
BQ	methanol	0.28	0.35	0.37	8.9	–383
NQ	methanol	0.20	0.35	0.45	10.8	–555
$(MeO)_4BQ$	methanol	0.22	0.37	0.41	7.8	–535
DQ	methanol	0.23	0.29	0.48	8.9	–738
Cl_2BQ	toluene	0.29	0.59	0.11	9.0	
BQ	toluene	0.30	0.60	0.11	7.6	
DQ	toluene	0.31	0.53	0.13	2.2	

[a] The error in the data is ±10%. The potentials are from ref 10 except for $(MeO)_4BQ$, which is from ref 11.

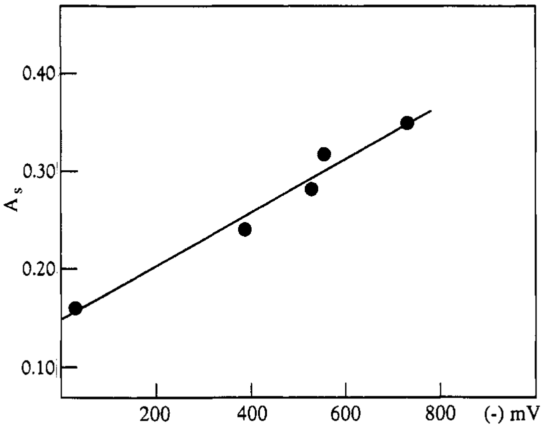

Figure 2. Plot of the fraction of the residual excitation energy, A_s, as a function of quinone reduction potential (vs SCE).

holds for the reaction in methanol. The oxidation potential of MgmPdME is approximated by the value of Mg octaethyl porphyrin in butyronitrile, 0.54 V,[13] or (potentiometrically) in methanol, 0.43 V,[14] and those of the quinones are in DMF (Table I). The k_q values obtained fall in the diffusion-limited range with the possible exception of DQ in toluene.

The A_f values allow us to calculate the triplet quantum yield (η_t, eq 8) once the energies of the triplet (1.77 eV) and the singlet states (2.14 eV)[15] as well as the fluorescence quantum yield (η_{fl} = 0.13) are known. The value obtained is $\eta_t = 0.71 \pm 0.05$ for both methanol and toluene. This may be compared to 0.62 for Mg mesoporphyrin at low temperature.[15] The values in the fifth column in Table I contain both the fraction of energy stored in the ion pair P^+ and Q^-, $\eta_\tau\eta_\pm\nu_\pm/\nu$, and the fraction of energy emitted as fluorescence, $\eta_{fl}\nu_s/\nu$, 0.13. The bimolecular back reaction between the two ions is a slow process, in the millisecond time range at the low concentrations formed by the weak laser pulse.

It is found that A_s depends linearly on the reduction potential of the quinone used (see Figure 2). The less negative the latter, i.e. the better an electron acceptor is the quinone, the lower the energy stored by P^+ and Q^-. This is understandable in terms of the relative energy levels of Q^- and P^+. For a given donor a better electron acceptor of larger electron affinity (EA) has a lower energy level of Q^- than a poor electron acceptor. The back reaction $P^+ + Q^- \rightarrow P + Q$ releases in this case a smaller amount of energy upon the return of the electron from Q^- to P^+. From the definitions of the fractions A_f, A_m, and A_s it can be expected that a change in the values of A_s will be reflected in A_m. A_m describes the heat release from the reactions in the triplet state, including the formation of P^+ and Q^-, and therefore it should complement the changes in A_s. Although such a trend can be observed in Table I, it is obscured by fluctuations in A_f that describe singlet state reactions. It is interesting to note that in toluene, $A_s + A_{fl}$ has a value of only 0.12 ± 0.03 for all quinones. Since $A_{fl} = 0.13$, A_s is zero within experimental error. In this solvent the escape time from the Coulomb well (~100 μs) is far longer than the spin dephasing time (~10 ns) and the ion yield is extremely small.[16] The energy of the short-lived ion pair appears in the A_m term which approaches the value of $\eta_t\nu_t/\nu = 0.58$, i.e. all of the triplet energy is released as heat.

For the exothermic ion recombination both the free energy, $\Delta G = E°_{Q^-} - E°_{P^+}$, and ΔH are negative quantities. The sign convention comes from $\nu_\pm = \Delta H = \Delta G + T\Delta S$. Equation 10 can be written as:

$$A_s = \eta_t\eta_\pm\nu_\pm/\nu = \eta_t\eta_\pm(E_Q{}^\circ - E_P{}^\circ + T\Delta S)/\nu \qquad (13)$$

The $T\Delta S$ term is to be interpreted generally and could include other photoacoustic contributions such as electrostriction. Evaluation of this term is in progress as it requires redox and photoacoustic measurements under the same conditions. The slope of this relation depends only on the product of the yields of triplets and of ions, as long as the ΔS term itself is not a function of the redox potential of the quinone—a reasonable assumption. The plot of the relevant data in Figure 2 shows that the value of the slope times ν (2.15 eV) is 0.60. Since this is equal to $\eta_t\eta_\pm$ (see eq 13), the value of $\eta_\pm$ is 0.85 ± 0.05. This is consistent with the "escape" yield of a triplet geminate ion pair in this low viscosity, high dielectric constant solvent.[16]

Data on yields of photochemical reactions are difficult to obtain. For example, in flash photolysis one requires absolute extinction coefficients of the short-lived species. Photoacoustic measurements provide the yields of the ions formed directly and unambiguously.

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