knowledge the original suggestion of the two-buret method by Craig Petro and Edward Mitchell.

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(36) We estimate a $\Delta H_{1,1} = -11.4$ kcal/mol as the value to be expected for this compound in the absence of steric effects from a linear plot of $\Delta H_{1,1}$ for the other compounds vs. their gas-phase basicities, ΔG_i (gas).[35]

Hydrogen Bond Strengths from Solvent-Dependent Lifetimes of Rose Bengal Dye

Laurence E. Cramer and Kenneth G. Spears*

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received June 2, 1977*

Abstract: We report fluorescence lifetimes for rose bengal in a number of protic and aprotic solvents. The technique for obtaining these lifetimes uses time correlated photon counting with tunable dye laser excitation. The lifetimes ranged from 77 ps in CF_3CH_2OH to ~2.5 ns in the aprotic solvents. We propose a linear correlation of the logarithm of the singlet–triplet decay lifetime, ln τ_{NR}, with the ΔH of hydrogen bonding of solvent to the oxygen anion site of rose bengal. Such a correlation might result from the linear relationship between the logarithm of the nonradiative lifetime, ln τ_{NR}, and the difference between singlet and triplet solvation energies. In this model the observed trend is that stronger hydrogen bonding molecules have larger rates of singlet to triplet intersystem crossing. The correlation is tested with the data available on relative hydrogen bond strengths to several bases. By using ln τ_{NR}, of rose bengal, one can order the relative hydrogen bond strengths for proton donors with very high precision. Absolute enthalpies for different proton donors can be found by obtaining the ΔH of hydrogen bonding for any two donors with the base of interest. In general, the hydrogen bond order of a series of proton donors is independent of base. In addition, the strongest hydrogen bond in a series of RXH molecules is formed by a molecule having the strongest XH bond. The picosecond lifetimes of rose bengal in various solvents are given in parentheses: CF_3CH_2OH (77), H_2O, (118), $C_6H_5CH_2OH$ (473), HOC_2H_4OH (481), CH_3OH (543), HOC_3H_6OH (566), $HC(O)NH_2$ (686), 1-C_3H_7OH (739), C_2H_5OH (739), 1-C_4H_9OH (773), 2-C_3H_7OH (975), $HC(O)NHCH_3$ (1020), 2-C_4H_9OH (1040), $(CH_3)_3COH$ (1240), CH_3CN (2380), CH_3COCH_3 (2570), $HC(O)N(CH_3)_2$ (2190).

Introduction

The fluorescence lifetimes of organic dye molecules can be sensitive to solvent environment for a variety of reasons. Several laboratories have recently found that halogen-substituted xanthene dyes have solvent-dependent lifetimes.[1,2] For one of these dyes, erythrosin B, the singlet state is coupled to a lower triplet state and the sum of fluorescence and triplet yield has been shown to be near unity.[3,4] Rose bengal is a tetraiodo-substituted xanthene dye, similar to erythrosin B, with the structure shown in Figure 1. The peak of the absorption spectra is near 558 nm and is slightly solvent dependent. Fluorescence lifetimes and reorientation times for rose bengal have been measured by one group of workers[2] in H_2O, CH_3OH, C_2H_5OH, and 2-C_3H_7OH. We have found different values for the lifetime in these solvents and will discuss possible reasons later in this paper.

Although many of the details of our laser system have been described previously,[5,6,7] we have not provided a complete description of the techniques necessary for performing short lifetime measurements in solution. Therefore, we have included a complete outline of our experimental technique.

Experimental Section

Tunable Dye Laser. An 8-W Ar^+ laser is used to pump a three mirror dye laser cavity. The jet stream solvent is ethylene glycol. For this series of experiments the laser dye Rhodamine 560 (from Exciton

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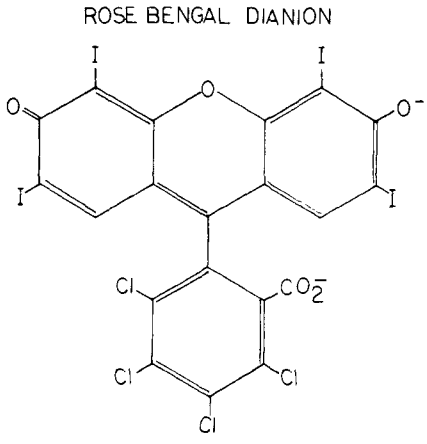

Figure 1. Structure of the rose bengal dye molecule.

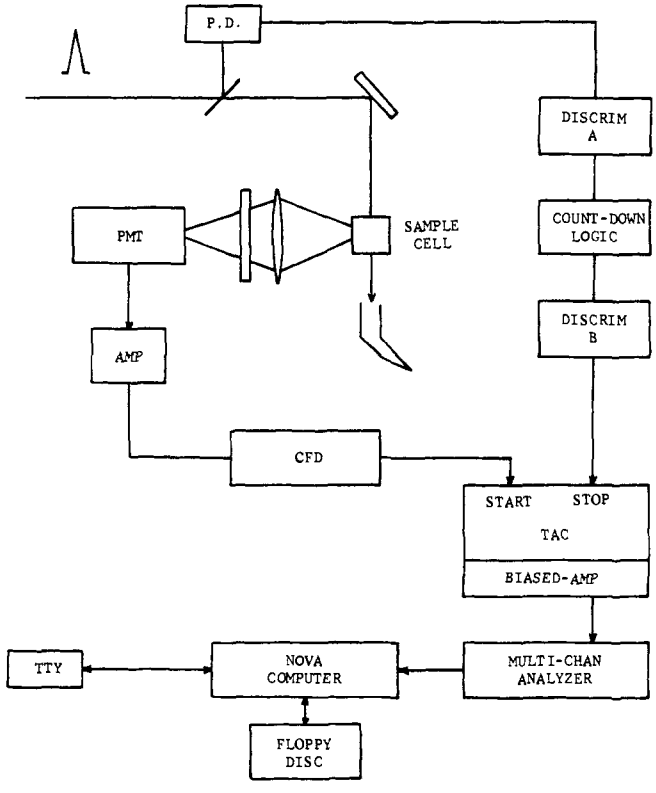

Figure 2. Schematic diagram of the timing electronics used in time-correlated single photon counting.

Chemical) was used at a concentration of approximately 10^{-4} M. Rhodamine 560 (also called Rhodamine 110 by Eastman), at this concentration, gives a continuous tuning range of 540–580 nm. Lasing at a selected wavelength is accomplished by means of a birefringent tuning element with resultant line widths of ~0.1 nm.

The dye laser is acoustooptically mode locked to yield a pulse train consisting of subnanosecond (<0.5 ns rise time) pulses separated by 10-ns intervals. The cavity output mirror is coated to give 4% transmittance over the wavelength range of the dye.

The average output power is a function of the gain of the dye. At 575 nm, the wavelength used under the conditions of this experiment, the average mode-locked output power was 20 mW.

Timing Electronics. A schematic diagram of the timing apparatus is shown in Figure 2. The key component in the single photon counting apparatus is the time to amplitude converter (TAC). We normally invert the TAC inputs, so that a pulse corresponding to a detected photon starts the TAC, and the delayed output from a photodiode monitor of the excitation pulse train stops the TAC. The TAC output is a voltage proportional to the time difference between the start and stop inputs. Each output of the TAC is stored in a multichannel analyzer (MCA) which orders each count according to its voltage and thereby produces a display of intensity vs. time delay. The TAC start pulse is generated by the response of the photomultiplier (PMT) to a detected photon. As shown in Figure 2 the output of the PMT is typically amplified and passed through a constant fraction discriminator (CFD) before triggering the TAC. The reference stop pulse signal is generated by the response of a PIN photodiode (H-P 4203) to a portion of the 100-MHz pulsed laser beam. The photodiode is operated at −100 V bias to provide a rise time of ~1 ns at ~0.5 V amplitude. This output triggers a fast discriminator which then drives the countdown logic gate. The logic gate reduces the frequency of the signal to 50 MHz because the TAC has a minimum reset time of ~10 ns. A second discriminator and a variable coaxial delay system complete the stop channel to the TAC. For high-precision work, the dynode output of the PMT can be used to strobe the TAC into the MCA only when the PMT output pulse is within a selected amplitude range of a single channel analyzer. This technique along with the use of the CFD reduces the time walk in the pulse timing so that, for a very short laser pulse duration, the observed pulse width on the MCA is determined by the transit time dispersion of the PMT. For our RCA C31034 PMT we find 0.8-ns fwhm as the narrowest possible measured pulse width. The MCA is a Northern Scientific Model 906 and the data are filed on a magnetic floppy disk via an interface to a Data General Nova 2/10 minicomputer.

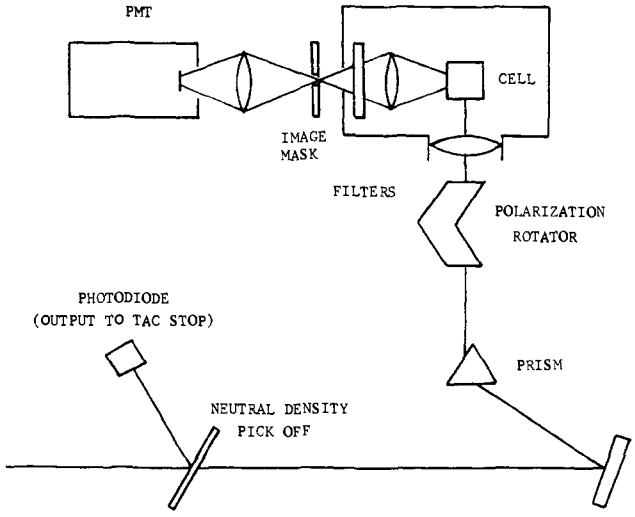

Figure 3. Schematic diagram of the experimental arrangement.

For lifetimes ≲0.5 ns, a deconvolution of the fluorescence response is essential to obtain the decay parameters. There is no fundamental limit to such a deconvolution and it can be used to study arbitrary response profiles. The most significant advantage is that decay profiles are *essentially noise free and the measurement precision is only limited by photon counting statistics.* Later sections will illustrate these points with data from rose bengal.

Optical System. It has been shown[2] that for the case of rose bengal in solution, molecular reorientation is taking place on the time scale of the observed fluorescent lifetime. If a sample is excited with a polarization selected light source, the resultant fluorescence is a function of the exponential fluorescent decay time and the mean molecular reorientation time. The effect of molecular reorientation may be removed,[8] in a polarization resolved experiment, by exciting the sample with the polarization of the incoming laser rotated to 54.4° from the vertical and collecting the fluorescence at a right angle through a vertically oriented polarizer. Rotation of the polarized laser beam is conveniently accomplished by the use of an internal reflection double Fresnel rhomb fixed in a rotation mount. The rhomb is wavelength independent and is particularly suitable for tunable lasers.

The complete experimental setup is shown schematically in Figure 3. An aluminized neutral density filter (1.0 ND) reduces the intensity of the beam and acts as a pickoff for the 100-MHz photodiode, used to generate the TAC stop signal. The laser beam is next passed through a prism to disperse cavity superradiance before it is directed through the Fresnel rhomb and focused (15 cm fl) into the sample cell. The power of the laser just before being focused into the cell is typically 1–2 mW. The results are independent of focusing and a sharp image

is useful for the collection optical train. The sample cell is a standard 1-cm square fluorescence cuvette and is housed in a light-tight box with a baffled entrance port.

The fluorescence is collected at a right angle and a small region from the center of the cuvette is selected by means of a masked, intermediate focus, relay lens system. In addition, the sample cuvette is tipped ~20° about the collection axis so that the return reflection of the exciting laser (~4% of the initial intensity) is directed away from the image volume. A colored filter system is used to reject light scattered at the excitation wavelength, and an aperture combined with a neutral density filter is used to attenuate the fluorescence signal. We use a 2-63 Corning filter and a neutral density of ~2.0 for fluorescence detection. For excitation profile detection we use a Corning 4-64 filter with a neutral density of ~2.0.

Sample Preparation. The rose bengal was obtained from Eastman Kodak (certified grade). An attempt at purification was made by using thin layer chromatography (TLC) techniques. Eastman no. 13179 silica TLC plates were used in a solvent system consisting of a 35/65% mixture of ethanol and acetone, respectively. The plate was baked for 15 min at 100 °C before being spotted wih a concentrated (in CH_3OH) rose bengal solution. The separation revealed five components. The dominant component of the separation was assumed to be the purified dye. A low concentration impurity (I), having the shortest retention time, preceded the rose bengal. Two impurity components (II and III) directly following the rose bengal (greater retention time) were in the largest concentration. A small concentration of a fourth impurity (IV) followed at a much greater retention time. Impurity component III was peach colored, and all the others were similar to the color of rose bengal. We obtained the fluorescence lifetimes of the impurity components, in selected solvents, in order to investigate possible effects of these impurities on the observed lifetimes of rose bengal. As a check on our purification scheme, the fluorescence excitation spectra of the unpurified dye, the chromatographically purified dye, and the peach-colored impurity component (III) were measured in 2-propanol. The fluorescence spectra were measured with a Hitachi Perkin-Elmer fluorescence spectrophotometer MPF-2A. The results of these investigations are discussed in a later section.

Sample preparation, for a fluorescence measurement, consisted of cutting out a portion of the mylar chromatographic sheet containing the dye and immersing it into the desired solvent for study. After dissolution of the dye into the solvent, the plate was removed and the dye concentration was adjusted to be within the range of 10^{-5}–10^{-6} M. Finally, the sample was usually degassed (saturated with N_2) and centrifuged before being transferred to the fluorescence cuvette for the lifetime measurements. The degassing step was found to be unnecessary when tested for C_2H_5OH, although it was still done for those solvents yielding longer lifetimes. The centrifugation step was necessary to reduce the amount of scattered light from the sample caused by excess particulate in solution.

The solvents used in this study were obtained from manufacturers supplying high-purity solvent with low water content. The solvents were generally used as received after testing for the absence of fluorescing impurities.

For measurements at a basic pH, we prepared saturated solutions of NaOH in CH_3OH, C_2H_5OH, 1-C_3H_7OH, 2-C_3H_7OH, and 1-C_4H_9OH. Dye solutions were made basic by removing 10% of the solution and replacing it with stock base solution.

Lifetime Procedure. In performing deconvolution studies, it is necessary to have an accurate record of both the fluorescence response function and the instantaneous response or scattered light function. The additional critical requirements of instrument stability and wavelength-insensitive response of the photomultiplier have been previously discussed.[5] The TAC bias must also be adjusted to provide a relatively flat differential nonlinearity. Small nonlinearities can be corrected in our calculation but large effects (~10%) cannot.

As a matter of procedure, a scattered light response function is obtained at the wavelength of excitation, followed by the fluorescence response function and a second scattered light function. The "front and back" scattered light records serve as a check of instrument stability. In general, we find that after thermal equilibration of the dye laser, records of scattered light functions separated in time over several hours are identical to within statistical counting error. The data collection rates are much lower than the 100-MHz excitation rate and are limited by the C31034 photomultiplier tube and MCA data accepting rate. Typical counting rates used in these experiments range from 10^4 to 6×10^4 Hz with corresponding times of 3 min to 30 s for collecting a scattered light profile that contains a peak of 20 000 counts and a flat background of 20 counts. For a scattering medium, we have obtained satisfactory results from dilute solutions of water and powdered coffee creamer. Blanks were prepared by dissolving clean pieces of the TLC plates into the various solvents. These solvent blanks were then tested to ensure the absence of background fluorescence.

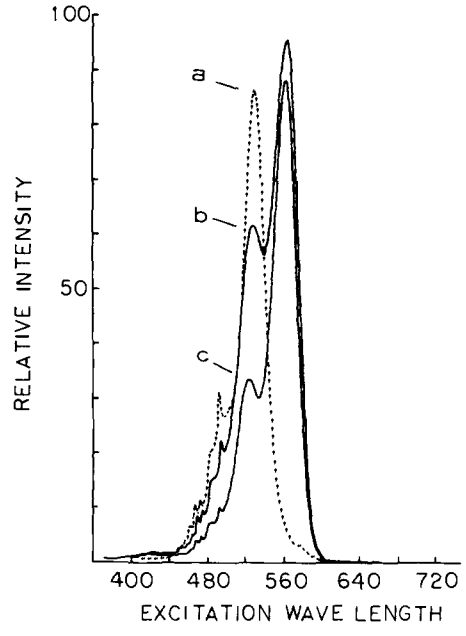

Figure 4. Fluorescence excitation spectra of impure (b) and purified (c) forms of rose bengal dye with the fluorescence excitation spectra of the peach-colored impurity (a). The labels point toward the top of the impurity peak.

For all of the lifetimes measured here, the TAC–MCA combination was set to give a time/channel resolution of 17.43 ps over 256 channels. This time range was calibrated using delay cables, which had been previously calibrated from an MCA/TAC measurement of the precise time interval defined by the scattered light from the 100-MHz mode-locked laser.

The deconvolution calculations are performed on our Nova 2/10 minicomputer with a Fortran program based upon the Marquardt algorithm.[9] The program uses a reduced χ_r^2 statistic to judge the goodness of fit. We find that a χ_r^2 of ≤ 1.2 is usually an excellent calculational fit, as expected from the theory of χ_r^2. For a single exponential fluorescence decay the program fits the data to the general form

$$f(t) = Ae^{-t/\tau} + B$$

A is the preexponential factor and τ the observed lifetime. B is the variable background, both flat and exponential (if needed for longer lifetimes). We visually examine the quality of the fit by displaying the signed percentage differences between the calculation and the data. Random variations within statistical counting uncertainties are obtained for those data with $\chi_r^2 \leq 1.2$.

Results

We found that the observed lifetimes strongly depend on the solvent. The results of our lifetime measurements for rose bengal in the various solvents are shown in Table I with results of Fleming et al.[4] and values for solvent dielectric constant and dipole moment. The lifetimes reported by Fleming et al.,[4] with the exception of water, are somewhat larger than our results. We feel that a possible explanation for this discrepancy can be found in our examination of the dye impurity effects. No changes in fluorescence lifetimes were observed for those solvents that were tested by OH^- addition.

In Figure 4 the fluorescence excitation spectra are shown for the unpurified and the "purified" form of rose bengal and the peach-colored impurity (III). The solvent was 2-propanol. As can be seen from the figure, the unpurified form of rose

Table I. Fluorescence Lifetimes of Rose Bengal[a]

Solvent[a]	Fluorescence lifetime,[b] ps	Standard deviation,[c] ps	No. of expts	Other results[a]	Dielectric constant	Dipole moment, D	Nonradiative lifetime,[g] ps
1. CF_3CH_2OH	77[d]	4	3				78
2. $H_2O(D_2O^f)$	118	5	7	95	78.5	1.82	120
3. $C_6H_5CH_2OH$	473	2	3		13.1	1.66	507
4. HOC_2H_4OH	481[e]	3	3		37.7	2.28	517
5. CH_3OH	543	9	3	655	32.7	1.71	589
6. HOC_3H_6OH	566	7	3		35.0	2.50	616
7. $HC(O)NH_2$	686	9	3		111.0	3.37	761
8. C_2H_5OH	739	3	5	820	24.5	1.73	827
9. 1-C_3H_7OH	739	5	5		20.3	1.75	827
10. 1-C_4H_9OH	773	7	2		17.5	1.75	869
11. 2-C_3H_7OH	975	2	2	1015	19.9	1.66	1134
12. $HC(O)N(CH_3)H$	1020	14	3		182	3.86	1196
13. 2-C_4H_9OH	1040[e]	3	4		16.6	1.66	1223
14. $(CH_3)_3COH$	1240	3	4		12.5	1.66	1506
15. CH_3CN	2380	22	3		37.5	3.44	3604
16. $HC(O)N(CH_3)_2$	2190	18	2		36.7	3.86	3685
17. CH_3COCH_3	2570	64	2		20.7	2.72	4073

[a] Values for ϵ and μ taken from the recommended values of either J. A. Riddick and W. B. Bunger, "Organic Solvents, Physical Properties and Methods of Purification", 3rd ed, A. Weissberger, Ed., Wiley-Interscience, New York, N.Y., 1970, or A. L. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, Calif., 1963. Values of lifetimes reported under other results are taken from ref 4. The listed formulas follow: (1) 2,2,2-trifluoroethanol, (2) water, (3) benzyl alcohol, (4) ethylene glycol, (5) methanol, (6) propylene glycol, (7) formamide, (8) ethanol, (9) 1-propanol, (10) 1-butanol, (11) 2-propanol, (12) *N*-methylformamide, (13) 2-butanol, (14) *tert*-butyl alcohol, (15) acetonitrile, (16) *N,N*-dimethylformamide, (17) acetone. [b] Values reported for fluorescence lifetimes are those obtained under the same experimental conditions over a period of several days. Unless otherwise noted these values are largely determined from calculations yielding χ_r^2 of <1.2 with no χ_r^2 values greater than 2. [c] Standard deviations reported here represent precision for a given set of experimental conditions. An absolute accuracy of 1.5% can be assumed based upon long-term reproducibility (see text). [d] Values for fluorescence lifetimes taken from calculations yielding χ_r^2 of 4–5 but without systematic deviations. Additional work is being done to refine this value. [e] Only values of χ_r^2 between 1.5 and 2.5 were obtained but no systematic deviations were present. [f] Our initial measurements on D_2O yield a lifetime nearly identical with that of H_2O. Work is continuing to refine the value for D_2O. [g] See text for explanation of calculation. This lifetime is for singlet–triplet intersystem crossing.

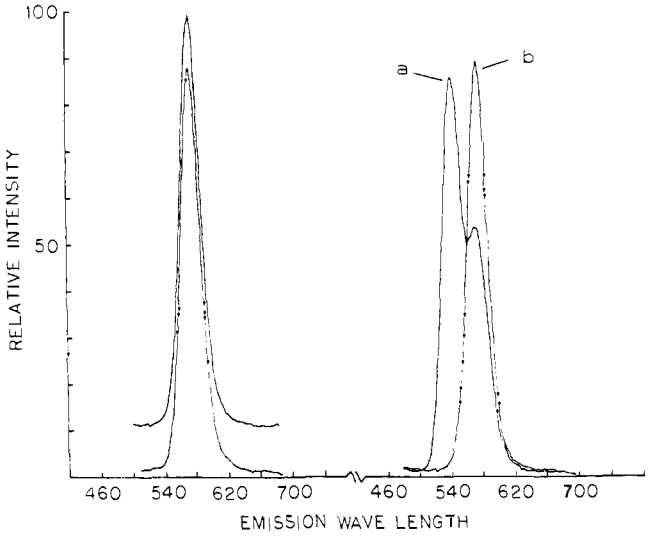

Figure 5. Fluorescence emission spectra of rose bengal dye in 2-propanol. The left half of the figure shows the pure and impure (as received from the manufacturer) forms of the dye, when excited at 575 nm. The base lines are shifted to show the overlap. The right half of the figure shows the unpurified form of the dye when excited (a) at 530 nm and (b) at 575 nm.

bengal shows a peak of fluorescent intensity when excited at 530 nm. The excitation spectrum of the purified form of rose bengal shows a great reduction of this peak (note that our purification technique was *not* sufficient to completely remove this peak). The spectrum of the impurity has a similar peak at 530 nm. The fluorescence spectra of the purified and unpurified forms of the dye, as shown in Figure 5, are identical when excited at the wavelength 575 nm, which lies outside of the absorption band of the impurity. This wavelength corresponds to the excitation wavelength used in our lifetime experiments. Figure 5 also shows the fluorescence spectrum of the impure dye excited at 575 nm compared with excitation at 530 nm.

Impurity III may be the impurity remaining in our "purified" rose bengal (Figure 4) or we may not have separated all impurities absorbing at 530 nm by a simple TLC method. The observed lifetime of this impurity component (III) has a value of 1 ns in H_2O, 2 ns in methanol, and 2.3 ns in ethanol. The other impurities had fluorescence lifetimes similar to that of rose bengal. Since the fluorescence maximum of this impurity (III) is at or very near the wavelength of excitation used by Fleming et al.[4] (530 nm from a doubled Nd^{3+} glass laser), we suggest, that if their purification technique was not complete, that addition of the longer lived component to their fluorescence response data could have resulted in a fitted lifetime that is too long. The noise in their technique is sufficient so that a long-lived emission present in small amounts could distort the decay curve without being easily detected as a second exponential. For a solvent such as H_2O our 118-ps lifetime approximately agrees with Fleming et al.[4] The 118-ps decay is much shorter than the impurity and therefore the impurity would appear to be more like a flat background. We found that if we run an unpurified sample in ethanol while exciting at 540 nm, a poor fit ($\chi_4^2 = 2.8$) is obtained, with an apparent lifetime of 835 ps. This is similar to the reported value of Fleming et al.[4] With an impure sample and a technique that has low amplitude precision, the apparent lifetime would appear to depend on the impurity concentration and the excitation wavelength.

The precision of our measurements has been tested over many independent samples and experimental setups. For example, four measurements for rose bengal in C_2H_5OH over 2 days on the same experimental arrangement gave an average value of 740 ps with a standard deviation of ±3 ps. For 11 separate measurements (having $\chi_r^2 \leq 1.2$), obtained over a

5-month period with completely different optical and laser alignments, we find a mean lifetime, for ethanol, of 730 ps with a standard deviation ±11 ps. From these results we feel that measurements with a $\chi_r^2 < 1.2$ made over several days with the same experimental arrangement can be considered precise to a standard deviation of <1% ($\tau \gtrsim 250$ ps). The absolute accuracy of the time/channel calibration factor is within 0.5% so that the accuracy of our lifetimes over many different arrangements is probably equivalent to our long-term precision of 1.5% (based on ethanol over 5 months). For lifetimes near 100 ps our precision is reduced. For example, 13 independent runs for H_2O give a mean and standard deviation of 115 ± 7 ps. The precision of our deconvolution is clearly reduced to 6% near 100 ps and precision similar to this can be maintained to ~50 ps which defines a practical limit of ~1/15 fwhm for precise deconvolution. However, there is no question that a 20-ps decay could be differentiated from a 50-ps decay. Figure 6 shows a typical excitation shape with fluorescence decays of 114 and 543 ps from the solvents H_2O and CH_3OH, respectively.

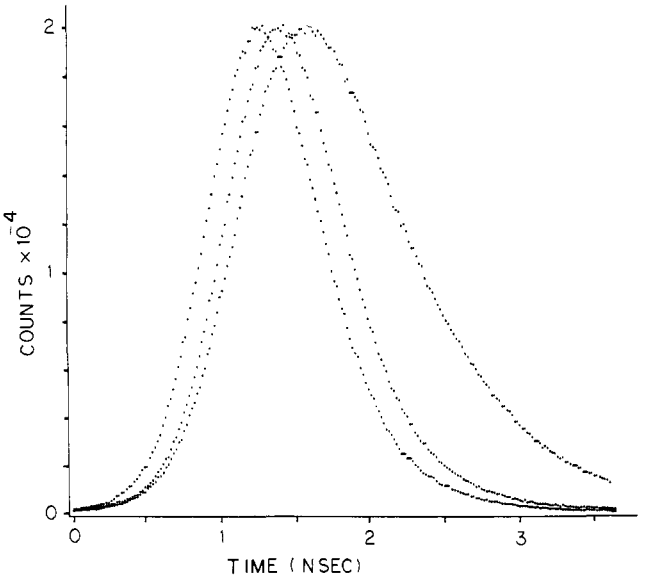

Figure 6. MCA display of the excitation pulse shape shown with two fluorescence response functions. The fastest rising curve is the excitation pulse, the second fastest rising shape is from rose bengal in water (τ = 114 ps), and the third fastest rising shape is from rose bengal in methanol (τ = 543 ps).

Discussion

Possible Model. The fluorescence lifetime of rose bengal obviously depends on the solvent. An examination of the data listed in Table I indicates that this solvent dependence is not a function of either dielectric constant or dipole moment. There is a strong dependence on whether the solvent is aprotic or protic. All aprotic solvents that we have measured give nearly the same long lifetime of ~2.5 ns. Among the alcohols one could consider methanol as the primary R′R″R‴COH alcohol and note that lifetimes increase with increasing alkylation of the COH group. The length of an alkyl chain is not important but the classification of the -OH group as a primary secondary or tertiary substituted alcohol appears to be very important. Organic chemistry has similarly correlated alkyl group substitution with the relative "acidity" of the ROH group.[10] It is interesting to note that gas-phase proton transfer studies on organic compounds have been done by many workers[11-13] and they find the opposite correlation of acidity. That is, CH_3O^- holds a proton more tightly than $(CH_3)_3CO^-$ so that $(CH_3)_3CO^-$ is more acidic with respect to proton donation.

We must now answer the question of how a solution phase concept of "acidity" relates to the fluorescence lifetime of rose bengal. It is first relevant to examine the concept of "acidity" and select those facets of the large and active literature that apply to our problem. We note that the lifetime of rose bengal does not change with addition of OH^-. Furthermore, rose bengal is removed as a colored species by addition of H^+. We believe, therefore, that the mechanism of lifetime perturbation is not related to proton transfer. This point is supported by the near unity sum of fluorescence and triplet quantum yield found for the related erythosin B molecule.[3] If a proton transfer quenching mechanism were operative, population of a triplet state would be unlikely. The structure of rose bengal, as shown in Figure 1, illustrates that the dye can be considered as a large $R\text{-}O^-$ molecule. with R as the chromophore. Adding large H^+ concentration changes the chromophore into a UV-absorbing species. We can consider the $R\text{-}O^-$ structure as the base of a strong acid whose basicity will depend on the excited state.

The most probable mechanism for affecting the lifetime of rose bengal as a function of solvent is that solvent interactions change the rate of singlet-triplet intersystem crossing. The mechanism for changing the intersystem crossing rate may be either a solvent-specific change of the singlet-triplet interaction strength or a change of the singlet-triplet energy gap. In the following discussion we explore the consequences of a solvent-dependent singlet-triplet energy gap, E_{ST}, but we do not exclude the possibility of a specific solvent effect on the strength of singlet-triplet coupling.

As is well known in radiationless processes, there is usually an exponential relationship between the radiationless rate and the energy gap because of changes in Franck-Condon factors.[14,15] We can represent the nonradiative intersystem crossing rate, k_{NR}, as

$$k_{NR} \propto e^{-A\Delta E_{ST}} \tag{1}$$

This equation assumes only weak participation of the solvent vibrational motions. Our initial measurements on D_2O yield the same lifetime as H_2O. This is expected if eq 1 holds for rose bengal.

The $\pi^* \leftarrow \pi$ transition will allow the excited singlet state to reduce its charge density of O^- to create an even weaker base while the triplet states should be less affected. Such effects are well known for excited states of naphthols,[16,17] and one could anticipate that the dominant change in energy levels as a function of solvent is due to the different solvation energies. It was previously postulated[4] that the ground state is solvent stabilized the most, the excited state somewhat less, and the triplet state least of all. We use ΔE_G, ΔE_S, and ΔE_T as the unsigned magnitude of solvation energy change for the ground, excited singlet, and triplet state, respectively. In this notation the singlet-triplet energy gap in any solvent is

$$\Delta E_{ST} = \Delta E_{ST}^\circ - \Delta E_S + \Delta E_T \tag{2}$$

There are small shifts in the location of the absorption maxima as a function of solvent and one group of workers has reported[4] a blue shift of 420 cm^{-1} for H_2O compared with 2-propanol. A blue shifts supports the argument that the singlet state is stabilized slightly less than the ground state. These absorption shifts do not directly relate to changes in ΔE_{ST}. We can obtain the dependence of τ_{NR} on solvation energies by substituting eq 2 into eq 1 and we find

$$\Delta E_S - \Delta E_T = -C \ln \tau_{NR} + D \tag{3}$$

where C and D are constants.

We propose to correlate ln τ_{NR} with solvation energy and therefore we must analyze the solvent contributions in greater detail. For example, the ΔE_S and ΔE_T have contributions from solvent reorganization energy and from the energy of solvent hydrogen bonding to rose bengal. It is probable that the elec-

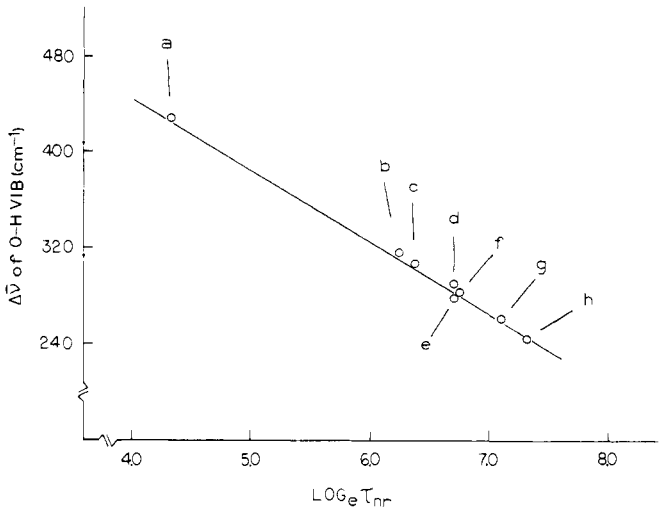

Figure 7. Plot of $\Delta\bar{\nu}$ of OH vibration vs. ln τ_{NR}. Values for $\Delta\bar{\nu}$ are taken from measurements of complexation of the given alcohols with pyridine in non-hydrogen-bonding solvents (ref 20 and 21). Values for τ_{NR} are taken from Table I for the following solvents: a (CF_3CH_2OH), b ($C_6H_5CH_2OH$), c (CH_3OH), d (C_2H_5OH), e (1-C_3H_7OH), f (1-C_4H_9OH), g (2-C_4H_9OH), h ($(CH_3)_3COH$).

tronic structure and geometry of rose bengal are similar for singlet and triplet states (see next paragraph) so that the solvent reorganization energies nearly cancel. Therefore, we can expect that bulk solvent properties and solvent self-interaction energies are unimportant in affecting τ_{NR}. The solvation of nonchromophoric regions of the molecule are expected to be quite similar for triplet and singlet states. Therefore, the chlorinated benzene ring having the carboxylic acid substituent will provide equivalent solvation energies for singlet and triplet states. The solvation of the xanthene chromophore is likely to be larger at the ionic position in the R-O^- structure. As previously mentioned, the electron density at the O^- site can be expected to be strongly reduced in changing from the ground to excited singlet state. We assume that electron density at this site is also likely to be affected when comparing solvating ability of singlet and triplet states. We can therefore conjecture that the largest contribution to the $\Delta E_S - \Delta E_T$ energy difference arises from the solvent binding energy at the O^- site and that the rest of the molecule provides about the same stabilization for singlet and triplet states. As previously stated, the ΔE_T must be less than ΔE_S to show the observed lifetime change. Because solvation energy is controlled by the electronic structure of the molecule, the solvation energy of the triplet is likely to be a constant fraction of the singlet state solvation energy so that we can recast eq 3 into the form

$$\Delta E_S = -B \ln \tau_{NR} + K \quad (4)$$

where B and K are constants.

There is a possibility that solvent reorganization around the excited singlet state of rose bengal could provide a wavelength-dependent delay in the the emission. We have not found such a delay in our lifetimes (no wavelength resolution with a monochromator was attempted) and published work[1] on the related xanthene dye erythrosin B shows no rise time dependent emission. The fluorescence spectrum is a reasonably good mirror image with the absorption spectrum; this is consistent with the absence of reorganization effects and small geometry changes between the ground and the singlet state. Our solvation arguments in the preceding section assume that all solvent reorganization is very small so that reorganization time durations are much less than the excited state lifetime.

Test of a Correlation. In order to understand the observed solvent dependence, we must first determine whether it is reasonable that aprotic solvents with large dielectric constants and dipole moments should be such poor solvators of an R-O^- molecule. Gas-phase solvation of Cl^- and O_2^- has been done by Yamdagni et al.[18] for CH_3CN, CH_3OH, and H_2O. The total ΔH for three ligands about these ions shows that for O_2^- (but not for Cl^-) there is a marked difference between CH_3CN and CH_3OH or H_2O (~12-20% different). A "softer" anion such as O_2^- will bond more strongly to protic solvents than a "harder" anion such as Cl^- and we believe that rose bengal is a "softer" anion. For rose bengal in solution, our conjecture, that the dominant perturbation of solvent on the singlet-triplet energy gap is localized on the O^- site, is consistent with the large difference between aprotic and protic solvents.

To use our correlation of τ_{NR} with solvation energy we must convert our observed lifetimes to nonradiative lifetimes. We have inferred from data on related molecules that the only radiationless path is intersystem crossing so that the observed decay rate, $k_{obsd}(1/\tau_{obsd})$, is equal to the sum of the radiative and nonradiative decay rates. The quantum yield of fluorescence is equal to the ratio of the radiative rate to the observed decay rate. The published data of Fleming et al.[4] give quantum yields for H_2O, CH_3OH, C_2H_5OH, and 2-C_3H_7OH. We are uncertain about the accuracy of these yields because of the previously mentioned possible problem with impuirities. We assume that any impurity effects are least for the solvent with the longest lifetime and use the value of 0.14 for 2-C_3H_7OH,[4] with our observed lifetime of 975 ps, to obtain a radiative decay rate of 1.44×10^8 s^{-1}. We assume that this value is constant for our solvents and note that any actual solvent dependence will only slightly change our calculated τ_{NR}. This is especially true for the shorter lifetimes. The results for τ_{NR} are listed in Table I.

Under the typical conditions of constant pressure it is reasonable to rewrite eq 4 in terms of solvation enthalpy to yield

$$\Delta H_S = -B' \ln \tau_{NR} + K' \quad (5)$$

The best available correlation of bond strengths of protic acids to bases is found in the large literature on hydrogen bond strengths. For rose bengal there are no ΔH measurements of hydrogen bonding so that we cannot *directly* test eq 5.

Calorimetric measurements of ΔH for dilute proton donor and base mixtures are usually performed in an inert solvent to remove the effects of solvent reorganization. Much effort has been expended in finding correlations of some physical measurement with the ΔH of hydrogen bonding. Several monographs exist with extensive literature references.[19] In general most workers use some property of the acid, such as the X-H vibration frequency, to correlate many bases with only a few proton donors. The necessity of using inert solvents such as CCl_4 tends to restrict the selection of proton donors. The work by Neerinck and Lamberts[20] with pyridine as the base in CCl_4 has covered the largest range of alcohols. In Figure 7 we plot their observed shift of OH vibration frequency for various alcohols against our values of ln τ_{NR} for the same alcohols. Figure 7 also contains a point for CF_3CH_2OH measured by Sherry and Purcell[21] in hexane, which we assume gives results similar to CCl_4. Figure 7 shows a clear correlation between the $\Delta\bar{\nu}$ of the OH vibration and the ln τ_{NR}. (We also could have plotted the ΔH of hydrogen bonding on the ordinate because for the alcohols there is a linear relation between $\Delta\bar{\nu}$ and ΔH of hydrogen bonding; however, the scatter in the more difficult ΔH measurements is larger than the $\Delta\bar{\nu}$ measurements.) *A successful linear correlation as shown in Figure 7 is only possible if eq 5 is correct and if the relative hydrogen bonding strength of these solvents is substantially independent of base.*

A surprising result of Figure 7 is that the relative hydrogen bond strength for a series of alcohols is independent of whether

the base is rose bengal or pyridine. We have found additional enthalpy data[22] supporting this observation for a smaller number of alcohols with the weaker bases diethyl ether and isopropyl ether. The relative order of hydrogen bond strength for these bases is identical with pyridine which suggests that the order of hydrogen bond strength is substantially independent of the charge density on the base. *Therefore, it is a reasonable conclusion that the electronic nature of the proton donor is controlling the strength of interaction with most bases.* Such a generalization may be incorrect in the limit of a base that is very "soft" or that can have specific covalent interactions with proton donors.[23] For proton donors of the R-X-H type structure (X is O, N, S) we expect that ln τ_{NR} of rose bengal will correlate with the strength of the hydrogen bond to most bases.

The model of a dominant anion site suggests that steric crowding of bulky solvent molecules could reduce the average number of molecules contributing to the hydrogen bond stabilization of the anion. We must therefore note that an implicit assumption of all preceding arguments was that a constant coordination number of solvent exists around the anion site. When steric crowding of solvent is present, the value of ln τ_{NR} still correlates with the *total* solvation energy. However, the relative hydrogen bonding of a sterically crowded molecule cannot be ranked on the same relative scale as uncrowded molecules without compensating for the coordination number.

In summary we find that the correlation of hydrogen bond strength with the logarithm of the rate for singlet-triplet intersystem crossing is an excellent empirical method to probe solvation energies at a single anion site. This correlation is expected if the phenomena involves solvent-dependent changes in the singlet-triplet energy gap. We cannot exclude, however, a specific solvent effect on the single-triplet interaction strength that also involves hydrogen bonding at the anion site. Until the mechanism is proven, the observed correlation must be considered empirical. However, as a probe of hydrogen bond strength for proton-donating substances of dissimilar chemical structure, our correlation has the following advantageous characteristics.

1. The measurements are very precise and are sensitive to small differences in hydrogen bonding.

2. The correlation is insensitive to solvent reorganization energy.

3. The hydrogen bonding effects on the singlet-triplet intersystem crossing of rose bengal are dominated by solvent interaction at a single anion site of rose bengal.

4. The relative ranking of hydrogen bond strengths of protic substances is not very dependent on the specific base and therefore the hydrogen bond strength of all proton donors can be made quantitative by calorimetric measurement of any two proton donors to a given base.

5. Solvents that cannot be studied calorimetrically can be ranked with the rose bengal probe.

Acidity and Hydrogen Bonding. We can further examine the relations between liquid-phase acidity, gas-phase proton transfer, and the nature of hydrogen bonding. As we noted in previous discussion the observed lifetime of rose bengal increases as the liquid-phase "acidity" decreases. The gas-phase proton transfer "acidity" has the opposite order relative to the liquid phase. The gas-phase proton transfer acidity could only be rationalized by assuming that the order of liquid phase "acidities" is due to differences in stabilization of RO^- and H^+ ions while the gas-phase proton transfer acidity corresponds to relative OH bond strengths.[11] Our measurements of relative hydrogen bond strength confirms that the solvating ability of a related series of solvents (such as the alcohols) to an anion is the dominant factor in the observed liquid phase "acidity." Consequently, our correlation of relative hydrogen bond strengths will be most useful either when comparing liquid-phase "acidities" of a similar series of compounds or when comparing the relative solvent stabilization of a given anion or base in a wide variety of chemically different protic solvents. This latter application might allow separation of solvent reorganization effects from the intrinsic energy of solvation.

Our ability to perform high-precision ranking of hydrogen bond strengths presents a challenge to the theoretician on three fronts. The first challenge is to predict the relative hydrogen bond strength for the subtle effects of chemical substitution. The second challenge is to explain why the order of hydrogen bond strength is independent of the base structure (over bases ranging from anions to weak bonding neutrals). A third challenge is to obtain sufficient accuracy to successfully calculate the hydrogen bond strength of chemically different proton donors such as water, formamide, and methanol. With regard to the second point, the gas-phase proton transfer data suggests that CH_3OH forms a stronger hydrogen bond than C_2H_5OH because there is larger electron density on the O atom in CH_3OH thereby yielding a stronger OH bond that is more polarizable. Such a simple electrostatic concept can be tested by high-quality quantum calculations providing charge density maps.

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