

# Self quenching of 1-naphthol.

## Connection between time-resolved and steady-state measurements

Ehud Pines<sup>1</sup>, Graham R. Fleming

*The University of Chicago and The James Franck Institute, Department of Chemistry, Chicago, IL 60637, USA*

Received 5 December 1993; in final form 7 March 1994

---

### Abstract

The photochemistry of 1-naphthol following its electronic excitation in aqueous solution was investigated by a single-photon counting apparatus. It was found that following the proton dissociation the excited naphtholate anion decays non-exponentially with a  $t^{-1/2}$  dependence over time. This we attribute to a self-quenching reaction of the naphtholate anion by its geminate proton. The quenching rate on contact is  $3.5 \times 10^{10} \text{ s}^{-1}$ . We also found that some of the protons interact adiabatically with a geminate recombination rate in  $\text{D}_2\text{O}$  of  $8 \times 10^9 \text{ s}^{-1}$ . The time-dependent escape probability of the naphtholate ion-pair was sampled by carrying out the experiment in presence of a proton scavenger. We show that the leading term in the ultimate scavenging probability is given by the time integral of the homogeneous scavenging rate of the isolated pair at relatively long times following its creation.

---

### 1. Introduction

The probability that an ion-pair avoids self neutralization is a classic problem in chemical reactivity [1,2]. A related problem is the branching between self neutralization and scavenging in the presence of a scavenger [3–7]. Photoacids provide an efficient means for rapidly creating ion-pairs in the excited state [8–12]. The photochemistry and photophysics of 1-naphthol, which is considered a model photoacid [13–24], have been extensively studied over the past 40 years following the original observations of Förster and Weller [22,23]. Two features dominate the kinetic behaviour of the excited 1-naphthol molecule and reduce its quantum yield in aqueous solutions. One feature is an extremely fast proton transfer to water [15,16,19,21]:  $\text{R}^*\text{OH} \rightarrow \text{R}^*\text{O}^- + \text{H}^+$  ( $k_d \approx 2.5 \times 10^{10} \text{ s}^{-1}$ ) which is

among the fastest intermolecular proton transfer reactions known to date. The second feature is the very efficient quenching of the naphtholate anion in strongly acidic media [14–16,23]. We propose that in addition to the bimolecular quenching reaction a geminate proton–anion self-quenching reaction takes place following the proton dissociation from 1-naphthol. This pseudo-nonradiative decay route decreases both the quantum yield and the lifetime of the naphtholate anion. We have found out that a short transient which follows a  $t^{-1/2}$  dependence at relatively long times ( $t > 100$  ps) is apparent in the otherwise monoexponential decay of the naphtholate anion ( $\approx 8$  ns) following its generation by the 1-naphthol dissociation. We also have found out that the otherwise mono-exponentially decaying population of the dissociating 1-naphthol acid exhibits at relatively long times ( $t > 2$  ns) a slowly decaying tail with a  $t^{-3/2}$  dependence over time, similar to that found in reversible geminate recombination

<sup>1</sup> Present address: The Ben Gurion University, Department of Chemistry, Beer Sheba 84105, Israel.

reactions [25,26]. In order to verify our findings, we have devised a unique method which unveils the geminate self-quenching nature of the short transient which is apparent on the naphtholate anion fluorescence decay. We have been able to show both analytically and experimentally that following dissociation the evolving time-dependent escape probability of the isolated naphtholate–proton ion-pair may be sampled with the aid of a suitable scavenger, where the ultimate escape probability of the pair in the presence of each scavenger concentration corresponds to a point on the time-resolved escape probability of the isolated geminate pair. By taking a series of such points, we were able to stop the “internal clock” of the self-quenching reaction each time at a different elapsed time and to reconstruct from the steady-state quantum yield measurements the time-resolved fluorescence decay profile of the naphtholate ion-pair in the absence of the scavenger. In doing so, we also show for the first time that for a general case of pair scavenging the leading term in the ultimate scavenging probability [6] is given by just analytically integrating over time the homogeneous scavenging rate of an isolated pair at relatively long times where its escape probability assumes a  $t^{-1/2}$  dependence.

## 2. Experimental

1-naphthol (Puriss, >99%, Fluka) was recrystallized from 10 vol% ethanol–water mixtures to yield colorless-white feather-like crystals. The fluorescence maxima of the anion and the acid were at 475 and 378 nm. The excitation wavelength was at 303 nm which is an isosbestic point [14]. The data was collected away from the peaks at 350 and 480–510 nm to minimize the overlap between the two fluorescence bands. Water was Baker HPLC reagent and D<sub>2</sub>O was MSD isotopes 99.9%. Potassium acetate was Baker AR and used without further purification. Acetic acid was Aldrich 99.7+ % ACS reagent. The time-resolved fluorescence intensities were collected by a time-correlated single-proton counting system described in detail elsewhere [27]. The instrument response function was 55–70 ps full width at half maximum. The resolution was varied between 5.4 and 107 ps/channel. Typical concentration of 1-naphthol was  $5 \times 10^{-5}$  M. Between  $2 \times 10^5$  and  $10^6$  counts were collected in the peak channel. The

anion fluorescence background at the acid band at 350 nm was subtracted from the data by the following method. Following data collection at 350 nm the pH of the sample was changed to 12.5. The residual fluorescence light emerging from the anion band at 475 nm was then collected over the same sampling time at 350 nm, normalized according to the relative peak reading at 475 nm and subtracted from the previous data record. Solutions containing 1-naphthol were at  $\text{pH } 6.0 \pm 0.5$  and solution containing the naphtholate anion were at  $\text{pH } 12.5$ . All measurements were taken at the magic angle and were repeated at least 10 times with similar results. Measurements were carried out at room temperature ( $23 \pm 1^\circ\text{C}$ ). Steady-state fluorescence spectra were measured with a Spex Fluorolog spectrofluorimeter.

## 3. Results

Fig. 1 shows the time decay of the naphtholate anion following the dissociation of the excited 1-naphthol at  $\text{pH } 6.0$  and the same decay following the direct excitation of the naphtholate anion at  $\text{pH } 12.5$ . The two fluorescence decays were first normalized and then tail matched for display. The fluorescence decay of the anion at  $\text{pH } 12.5$  is mono-exponential with a lifetime of  $7.95 \pm 0.05$  ns. The fluorescence decay at  $\text{pH } 6.0$  is non-exponential exhibiting a short initial transient

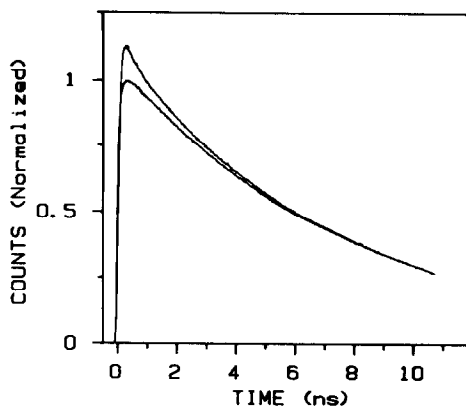


Fig. 1. Time-resolved decay of the naphtholate anion following excitation at 303 nm. Top: indirect excitation at  $\text{pH } 6.0$ . Bottom: direct excitation at  $\text{pH } 12.5$ . The single photon counting decay curves ( $2 \times 10^5$  counts in the peak channel) were normalized and tail matched.

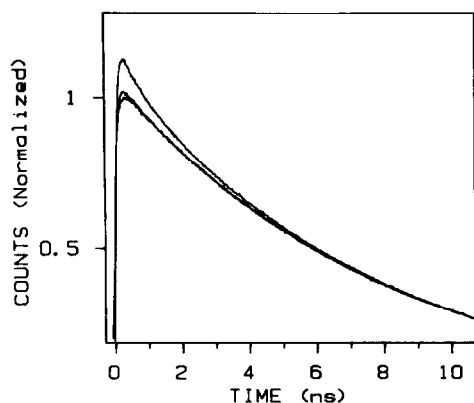


Fig. 2. Same as Fig. 1 with an additional fluorescence decay curve taken at pH 6.0 in presence of 50 mM potassium acetate (middle curve).

before becoming almost purely exponential. The final portion of the decay has an identical lifetime to that of the directly excited anion at pH 12.5. Fitting the decay profile to a single exponential decay over a limited time range produced a time range dependent lifetime starting at  $\approx 7.0$  ns over the first 2 ns of the decay and ending at  $\approx 7.8$  ns when an extended time range of 25 ns was fitted (not shown). Fitting the decay curve with more than one exponent revealed that it contains very rapidly decaying components starting at  $\approx 40$  ps. Judging from the relative amplitudes of these multi-exponential fits, the fast transient carries  $40 \pm 10\%$  of the total decaying population amplitude.

Fig. 2 shows the same data as in Fig. 1 with the additional decay profile of the naphtholate anion in

buffer acetate 50 mM at pH 6.0. The fluorescence decay now is almost identical with the decay of the directly excited anion at pH 12.5. Some residual short transient is present at the very beginning of the decay profile. The average lifetime of the naphtholate decay excluding the first nanosecond is  $7.8$  ns. Judging from the amplitudes of a multiexponential fit the residual short transient consists of  $15 \pm 5\%$  of the decaying population.

Fig. 3 shows steady-state fluorescence measurements of 1-naphthol in aqueous solutions containing various concentrations of acetate buffer at  $\text{pH } 6.0 \pm 0.5$ . Starting from the indirectly excited naphtholate anion at pH 6.0 the quantum yield increases progressively as a function of the acetate anion concentration approaching the quantum yield found for the directly excited anion at pH 12.5. Judging from the peak heights the quantum yield between the indirectly and directly excited naphtholate anion is  $0.63 \pm 0.03$ . In  $\text{D}_2\text{O}$  this value was found to be  $0.64 \pm 0.03$ .

The fluorescence decay of the 1-naphthol acid in  $\text{D}_2\text{O}$  is shown in Figs. 4a and 4b. The decay is non-exponential at longer times. Multi-exponential fit of the decay reveals that it contains a dominant  $133 \pm 15$  ps decay component and also contributions from more slowly decaying components starting at  $\approx 600$  ps. The major decaying component was  $36 \pm 5$  ps in  $\text{H}_2\text{O}$  with slower components starting at  $\approx 250$  ps (not shown). However, even with four exponents the fit was poor at early times indicating that the decay profile is highly non-exponential in nature.

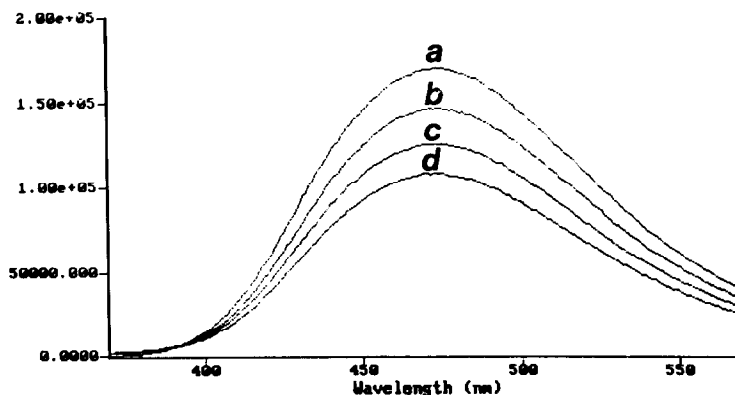


Fig. 3. Steady-state fluorescence emission spectra of the naphtholate anion excited at  $\text{pH } 6.0 \pm 0.5$  in presence of various concentrations of acetate anion. From top to bottom: (a) directly excited naphtholate anion at  $\text{pH } 12.5$ ; (b–d) indirectly excited (following dissociation) naphtholate anion at  $\text{pH } 6.0 \pm 0.5$ , (b) 600 mM, (c) 40 mM, (d) 0 mM acetate anion. The concentration of the naphtholate anion was kept constant.

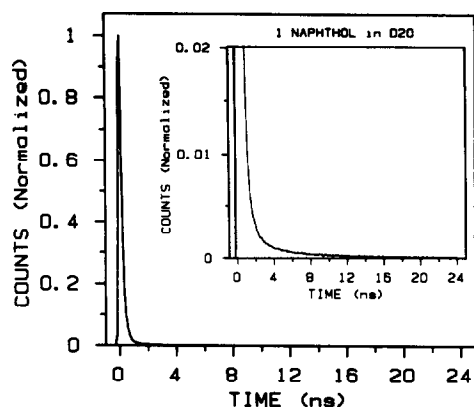


Fig. 4. (a) Fluorescence decay of 1-naphthol in D<sub>2</sub>O. The single-photon counting decay ( $10^6$  counts in the peak channel) is shown after background subtraction and was normalized. (b, insert) Vertical scale expansion of (a) ( $\times 50$ ). The fluorescence curve at long times is not exponential and has a slowly decaying tail.

Table 1 summarizes the major kinetic parameters of excited 1-naphthol as measured by us and by several other investigators. A comparison between these results show that in general our measurements reproduce the previously reported kinetic values.

Table 1  
Kinetic parameters for electronically excited 1-naphthol

Compd.	Temp. (K)	$\tau_d^a$	$\tau_f'^b$ (ns)	$\tau_f'^c$ (ns)	$\phi_{sp}(\text{pH } 6.0)/\phi_{direct}(\text{pH } 12.5)^d$	Ref.
1-ROH	296 $\pm$ 1	36 $\pm$ 5 <sup>e</sup>	direct ex.	indirect ex.		
	295 $\pm$ 1	40	7.95 $\pm$ 0.05	6.9–7.9 <sup>f</sup>	0.63 $\pm$ 0.03	this work [21]
	300	35 $\pm$ 4 <sup>g</sup>	8.1	7.1–7.9 <sup>h</sup>	0.65 $\pm$ 0.03	[19]
	296	33 <sup>i</sup>	8.0	7.5 $\pm$ 0.4	0.66	[15]
	298		8.0 $\pm$ 0.2		0.68	[14]
1-ROD	296 $\pm$ 1	133 $\pm$ 15 <sup>e</sup>	23.2 $\pm$ 0.1	19–23 <sup>h</sup>	0.64 $\pm$ 0.03	this work
	300	85 $\pm$ 10 <sup>g</sup>	23.6 $\pm$ 1.1		0.61 $\pm$ 0.03	[19]
	298	100 <sup>i</sup>	20.0 $\pm$ 1.0	17.2 $\pm$ 1.0	0.66 $\pm$ 0.05	[16]

<sup>a</sup> Fluorescence lifetime of 1-naphthol in H<sub>2</sub>O or D<sub>2</sub>O.

<sup>b</sup> Fluorescence lifetime of the naphtholate anion at pH 12.5  $\pm$  0.5.

<sup>c</sup> Fluorescence lifetime of the naphtholate anion at pH 6.0  $\pm$  0.5.

<sup>d</sup> Ratio between the quantum yield of the naphtholate anion at pH 6.0 (following dissociation) and pH 12.5 (direct excitation).

<sup>e</sup> The fastest component in a multi-exponential fit.

<sup>f</sup> Average lifetime fitted over different sections of the decay profile. See text for details.

<sup>g</sup> Measured by fitting the rise time of the anion taken by a streak camera.

<sup>h</sup> Lifetime altered by various concentrations of NaCl.

<sup>i</sup> From computer best fit analysis of both steady-state and time-resolved measurements. The actual time-resolved decay profiles shown are somewhat slower than the computer simulated decay profiles.

## 4. Discussion

### 4.1. Recombination probability of an isolated reactive pair

The dynamics of an isolated reactive pair is usually treated with the Debye–Smoluchowski equation [28–30], which assumes a diffusive flux of reactants towards the reaction centre [1,6,30,31]. To account for chemical reactivity on contact, a radiative boundary condition at the contact is usually used [32]. In that approach one assumes that the reaction rate on the reaction surface is proportional, in turn, to the diffusive flux at that surface, the proportionality constant being the chemical reaction rate on the contact,  $k_r$ ,

$$D \left( \frac{\partial \rho(r, t)}{\partial r} + \frac{\rho(r, t)}{k_B T} \frac{\partial V(r)}{\partial r} \right)_{r=a} = k_r \rho(a, t). \quad (1)$$

In this expression the reaction space is assumed to be spherically symmetric,  $D$  is the mutual diffusion coefficient of the reactive pairs,  $\rho$  is the relative density of particle B around A,  $V$  is their interaction potential which is assumed to be Coulombic, and  $a$  is the pair separation at “contact” where the chemical reaction takes place.  $k_r$  is the chemical reaction constant on

contact and has units of length/time. The boundary and initial conditions for isolated pairs generated at the initial separation,  $a$ , are given by [31]

$$4\pi r^2 \rho(r, 0) = \delta(r - a), \quad (2a)$$

$$\lim_{r \rightarrow \infty} \rho(r, t) = 0, \quad (2b)$$

where  $\delta$  is the delta function and we assume that the pair is generated at the contact where it either recombines or separates by diffusion. At any given time following the initial generation, the pair population is distributed between recombined pairs and separated pairs. The probability of finding a pair still separated at time  $t$  after generation may be found by summing up all separation distance probabilities, i.e. [31]

$$P_s(t) = 4\pi \int_0^\infty \rho(r, t) r^2 dr, \quad (3)$$

where  $P_s(t)$  is the survival probability of the separated pair at time  $t$  after generation. The total probability of finding the pair either separated or recombined is unity assuming infinite lifetimes of the reactants,

$$P_s(t) + P_r(t) = 1, \quad (4)$$

where  $P_r(t)$  is the recombination probability of the pair. Eq. (4) implies that  $P_s(t)$  and  $1 - P_r(t)$  have the same functional dependence on time. The functional form of  $P_r(t)$  at long times may be guessed since the reaction rate at long times follows the decrease in the relative concentration of the reactants which is given by the reciprocal of their time-dependent separation volume. The separation volume in turn depends on the dimensionality of the diffusion space,  $d$ ,

$$\rho(a, t) \propto t^{-d/2}, \quad (5)$$

in three dimensions one has [25]

$$R(t) \propto \rho(a, t) \propto t^{-3/2}, \quad (6)$$

where  $R(t)$  is the time-dependent recombination rate.

The well-known result for the overall recombination probability at long times ( $t \gg \Delta t$ ) is found by integrating  $R(t)$  over time, i.e.

$$P_r(t) \propto \int_{\Delta t}^t t^{-3/2} dt \propto t^{-1/2} + C, \quad (7)$$

where  $C$  is a constant.

Following the analytic derivation by Hong and Noolandi [31] one can rewrite their analytic solution for the long time behavior of  $P_r(t)$  and  $P_s(t)$  in the form of

$$P_r(t) = P_r(\infty) - Kt^{-1/2}, \quad (8a)$$

$$P_s(t) = P_s(\infty) + Kt^{-1/2}, \quad (8b)$$

where  $K$  is a constant having the units of  $s^{1/2}$ .  $P_r(\infty)$  and  $P_s(\infty)$  are the ultimate recombination and escape probabilities which may be found by steady-state measurements. At any given time  $P_r(t) + P_s(t) = P_r(\infty) + P_s(\infty) = 1$ .

In our case  $P_s(t)$  is given by [31]

$$P_s(t) = P_s(\infty) \left[ 1 + \frac{P_s(\infty) a^2 k_r}{D(\pi D)^{1/2}} \exp\left(\frac{R_c}{a}\right) t^{-1/2} \right], \quad (9)$$

with

$$K = P_s^2(\infty) \frac{a^2 k_r}{D(\pi D)^{1/2}} \exp\left(\frac{R_c}{a}\right). \quad (10)$$

$R_c$  is the Onsager length which scales the Coulombic interaction between unit charges,

$$R_c = \frac{e^2}{\epsilon_0 k_B T}, \quad (11)$$

where  $e$  is the electron charge,  $\epsilon_0$  the static dielectric constant and  $k_B T$  the Boltzmann factor.

The absolute quantum yield (AQY) of a separated pair having a fluorescence lifetime,  $\tau'_f$ , is the total sum over time of the exponentially decaying population  $P_s(t)$  multiplied by the emission rate  $k_f$ , where  $(\tau'_f)^{-1} = k'_f$ , and  $k'_f = k_f + k_{nr}$  is the overall decay constant of the excited state [33]

$$\phi_{sp} = k_f \int_0^\infty P_s(t) \exp(-k'_f t) dt. \quad (12)$$

$\phi_{sp}$  is the AQY of the separated pairs (in our case  $R^*O^-$ ). In order to calculate  $\phi_{sp}$  we use as a first approximation the long time approximation for  $P_s(t)$  (Eq. (8b)). Although this analytic approximation of  $P_s(t)$  becomes progressively poorer at shorter times than  $R_c^2/D$  [31] we tactically integrate from time zero as the short time contribution to the total quantum yield is negligible. We get

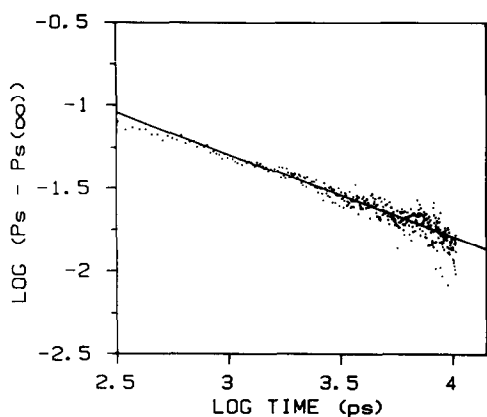


Fig. 5. Log-log plot of  $P_s(t) - P_s(\infty)$  as function time. The slope of the full line is  $-0.5$ . The experimental data are taken from the indirectly excited naphtholate anion shown in Fig. 1.

$$\phi_{sp} = k_f \int_0^{\infty} [P_s(\infty) + Kt^{-1/2}] \exp(-k'_f t) dt, \quad (13)$$

or

$$\begin{aligned} \phi_{sp} = & k_f \int_0^{\infty} P_s(\infty) \exp(-k'_f t) dt \\ & + k_f K \int_0^{\infty} t^{-1/2} \exp(-k'_f t) dt. \end{aligned} \quad (14)$$

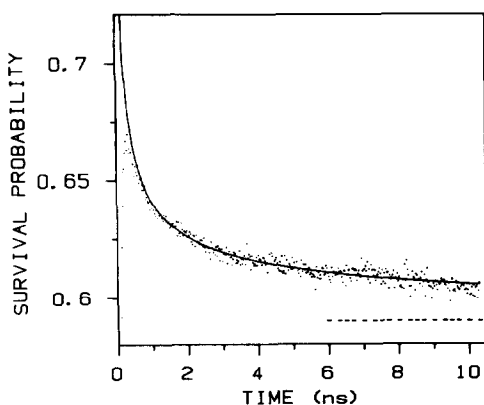


Fig. 6. The survival probability of the indirectly excited (after dissociation) naphtholate anion. The data are taken from Fig. 1. Full line: long time solution for the escape probability given by Eq. (8b) with  $K = 1.6 \times 10^{-6} \text{ s}^{1/2}$  and  $P_s(\infty) = 0.595$ . The ultimate escape probability  $P_s(\infty)$  is shown as a broken horizontal line.

The first term in (14) is just  $(k_f/k'_f)P_s(\infty)$  while the second term is given by

$$k_f K \int_0^{\infty} t^{-1/2} \exp(-k'_f t) dt = k_f K (k'_f)^{-1/2} \Gamma(1/2), \quad (15)$$

where  $\Gamma$  is the gamma function,  $\Gamma(1/2) = \pi^{1/2}$ . Substituting (14) we get

$$\phi_{sp} = \frac{k_f}{k'_f} P_s(\infty) + k_f K \left( \frac{\pi}{k'_f} \right)^{1/2}. \quad (16)$$

We now make use of the fact that in the case of direct excitation of the naphtholate anion the AQY is given by

$$\phi'_{sp} = k_f/k'_f, \quad (17)$$

where  $\phi'_{sp}$  is the AQY in the case of direct excitation. Dividing by  $\phi'_{sp}$  and rewriting for  $P_s(\infty)$  we finally have

$$P_s(\infty) = \phi_{sp}/\phi'_{sp} - K(\pi k'_f)^{1/2}. \quad (18)$$

Thus  $P_s(\infty)$  may be estimated from the steady-state measurement of  $\phi_{sp}/\phi'_{sp}$  and knowledge of  $k'_f$ .  $K$  may also be independently estimated by fitting the time resolved measurements to Eq. (8).

Fig. 5 shows a log-log plot of  $P_s - P_s(\infty)$  assuming that  $P_s(\infty) = 0.595$  and taking  $\phi_{sp}/\phi'_{sp}$  as 0.64. This gives  $K = 1.6 \times 10^{-6} \text{ s}^{1/2}$ . The slope of the line shown is  $-0.5$  and the decay profile of the naphtholate anion approaches it from below. The asymptotic long time slope is reached by  $\approx 500$  ps after the proton dissociation. The survival probability was reconstructed from the amplitude of the fluorescence curve by multiplying it by  $\exp(k'_f t)$  and assuming the calculated value (Eq. (8b)) of  $P_s = 0.62$  at 4 ns after the proton dissociation. Fig. 6 clearly shows that most of the quenching reaction occurs within the risetime of the naphtholate anion, i.e. within the first 100 ps following the proton dissociation. The fluorescence decay curve of the naphtholate anion is fit very well by Eq. (8b), shown in Fig. 6 as a solid line. Substituting the value of  $K = 1.6 \times 10^{-6} \text{ s}^{1/2}$  into Eq. (10) and setting  $P_s(\infty) = 0.595$ ,  $a = 6 \times 10^{-8} \text{ cm}$ ,  $D = 10^{-4} \text{ cm}^2 \text{ s}^{-1}$  and  $|R_c| = 7.1 \times 10^{-8} \text{ cm}$ , we get for the self-quenching constant of 1-naphthol

$$k_r = 0.068 \text{ (}\dot{\text{A}}/\text{ps)}, \quad (19)$$

which may be converted to the more common units of a first-order reaction rate ( $\text{s}^{-1}$ ) according to

$$k_{\tau} (\text{s}^{-1}) = \frac{4\pi a^2 k_{\tau}}{v(a)} \times 10^{12} \text{ s}^{-1} \quad (20)$$

$$= \frac{3k_{\tau}}{a (\text{\AA})} \times 10^{12} = 3.4 \times 10^{10} \text{ s}^{-1}, \quad (21)$$

where  $v(a)$  is the reaction volume with radius  $a$ . It follows that the self-quenching rate on contact is very high ( $29 \text{ ps}^{-1}$ ). This is in accordance with our experimental finding that most of the quenching reaction occurs within the first 100 ps following the proton dissociation. This high rate of quenching may be explained by the close proximity of one of the suggested quenching sites to the hydroxyl 1 position, i.e. the adjacent 8 position on the aromatic ring. The other proposed quenching site is the 5 position [16,34].

#### 4.2. The ultimate escape probability of an isolated pair in the presence of a scavenger

Fig. 7 shows the dependence of the fluorescence quantum yield of the naphtholate anion at  $\text{pH} = 6.0 \pm 0.5$  on the concentration of added acetate ion. The relative quantum yield  $\phi_{\text{sc}}/\phi_{\text{sp}}$  increases as the square root of the acetate concentration where  $\phi_{\text{sc}}$  is the fluorescence quantum yield of the naphtholate anion in the presence of the scavenger. We attribute

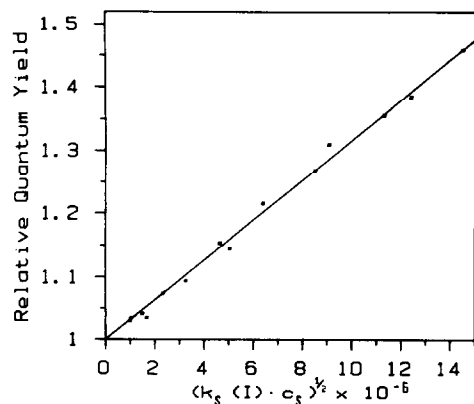


Fig. 7. Relative peak intensities of the indirectly excited naphtholate anion in presence of acetate ion (data taken from fluorescence decays similar to those shown in Fig. 3) as compared to the peak intensity of the indirectly excited anion with no acetate present. The relative intensities are plotted against  $(k_s(I)c_s)^{1/2}$ . From the slope of the line shown  $K$  may be estimated to be  $1.15 \times 10^{-6} \text{ s}^{1/2}$ .

this effect to the proton scavenging reaction by the acetate anion ( $\text{Ac}^-$ ) which is diffusion controlled [9]. We further assume that  $k_s$  depends on the ionic strength according to the Brønsted kinetic salt effect with numerical values suggested by Weller [9],

$$\log k_s(I) = \log k_s(I=0) - \frac{1.02 I^{1/2}}{1 + 2 I^{1/2}}, \quad (22)$$

where  $I$  is the ionic strength which in our case of a 1:1 electrolyte is equal to the concentration of the electrolyte.

The ultimate probability of a pair to escape recombination in the presence of a scavenger ( $P_{\text{sc}}$ ) may be approximated at relatively low concentrations of scavenger by assuming a homogeneous scavenging reaction independent of time or pair separation [6]. In this case the problem of calculating the ultimate escape probability in the presence of a scavenger is analogous to the quantum yield problem, i.e.

$$P_{\text{sc}}(\infty) = k_s c_s \int_0^{\infty} P_s(t) \exp(-k_s c_s t) dt, \quad (23)$$

where the fluorescence lifetime of the pair is assumed to be much longer than  $(k_s c_s)^{-1}$  the effective lifetime of the pair in the presence of the scavenger. In Eq. (23)  $P_{\text{sc}}(\infty)$  is the ultimate escape probability of the pair in the presence of the scavenger and  $P_s(t)$  is given by Eq. (8b) and is, as before, a long time approximation for the time-dependent escape probability of the isolated pair. Substituting for  $P_s(t)$  and solving we get

$$P_{\text{sc}}(\infty) = P_s(\infty) + k_s c_s K (\pi k_s c_s)^{1/2}, \quad (24)$$

which is identical with the solution obtained by Sano and Tachiya [6] by a more elaborate procedure. Defining an effective lifetime of the pair,  $t_{\text{sc}} = (k_s c_s)^{-1}$ , we finally get

$$P_{\text{sc}}(\infty) = P_s(\infty) + K \left( \frac{t_{\text{sc}}}{\pi} \right)^{-1/2}. \quad (25)$$

A comparison with Eq. (8b) reveals that  $P_s(t)$  and  $P_{\text{sc}}(\infty)$  have an identical form up to a factor of  $\pi^{1/2}$  in the time-dependent term. Eq. (25) implies that one could reconstruct the time-dependent profile of  $P_s(t)$  by measuring  $P_{\text{sc}}(\infty)$  at several scavenger concentrations. Eq. (25) may be further simplified if we assume that the self-quenching reaction is fast compared to the

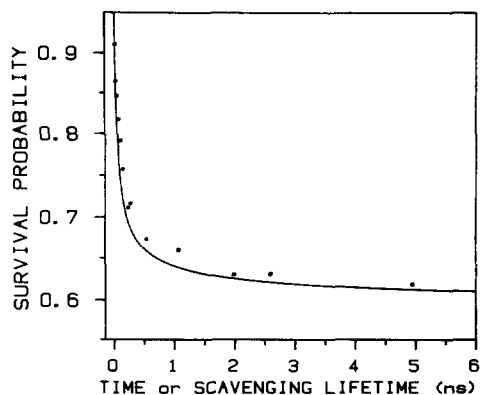


Fig. 8. Reconstruction of the time resolved profile of the indirectly excited naphtholate anion fluorescence decay from the steady-state intensities of the naphtholate ion in the presence of a proton scavenger (acetate ion, Fig. 3). The scavenger concentration was varied between 3 mM to 1 M of acetate anion. For scaling purposes the effective scavenging lifetime was taken as  $(k_s(I)c_s/\pi)^{-1/2}$ . The full line is identical with the one shown as the best fit for the time-resolved fluorescence decay (Fig. 6).

lifetime of the excited state. In this case the relative quantum yields of the anion in the presence of the scavenger roughly equal the relative escape probabilities, i.e.  $P_{sc}(\infty)/P_s(\infty) \approx \phi_{sc}/\phi_{sp}$ . In this case we may rewrite Eq. (25) as

$$\frac{\phi_{sc}}{\phi_{sp}} = 1 + \frac{K}{\phi_{sp}} \left( \frac{t_{sc}}{\pi} \right)^{-1/2}. \quad (26)$$

Eq. (26) corresponds to the full line shown in Fig. 7. From the slope of the line we get  $K = 1.15 \times 10^{-6} \text{ s}^{1/2}$ . We stress the point that this value was found with no free parameters. Taking into account the approximate nature of our approach we consider the agreement between the time-resolved and steady-state data as remarkable.

To illustrate our point further, we plotted the survival probability of the pair found from the steady-state data as a function of  $(t_{sc}/\pi)^{-1/2}$  (Fig. 8). The solid line is identical with the one shown in Fig. 6. It is of interest to note that the steady-state scavenger data is capable of sampling the escape probability of the isolated pair at very short times which in time-resolved measurements are buried within the experimental dissociation lifetime of the proton. It follows that the long time approximation roughly holds in this case down to times on the order of 50 ps, which is the time given by  $R_c^2/D$ .

#### 4.3. Adiabatic proton recombination in 1-naphthol dissociation

The contribution of the adiabatic proton recombination to the total QY of the acid form of 1-naphthol is very small. As shown in Fig. 4 the geminate recombination [25,26,34] contribution to the decay profile of 1-naphthol becomes apparent in  $D_2O$ . Here both the proton dissociation and the fluorescence lifetimes are some three times longer than in  $H_2O$ . As a result one has a much better signal-to-noise ratio at the fluorescence tail of 1-ROD as compared to that of 1-ROH. A log-log plot of Fig. 4 shows that at the tail the fluorescence tends to a  $t^{-3/2}$  dependence on time (Fig. 9). Such a dependence is characteristic of the long time behavior of a reversible geminate recombination reaction [25,26,35].

This dependence is approximately given by [26]

$$\frac{I_f(t)}{I_f(0)} = \frac{K_{eq}}{(4\pi Dt)^{3/2}}, \quad (27)$$

where  $I_f(t)$  and  $I_f(0)$  are the fluorescence intensities at time  $t$  and immediately following delta function excitation of the acid, respectively.  $K_{eq}$  is the equilibrium constant between the bound ROH state and the ion-pair state defined at the contact distance,  $a$ , and has the unit of volume,

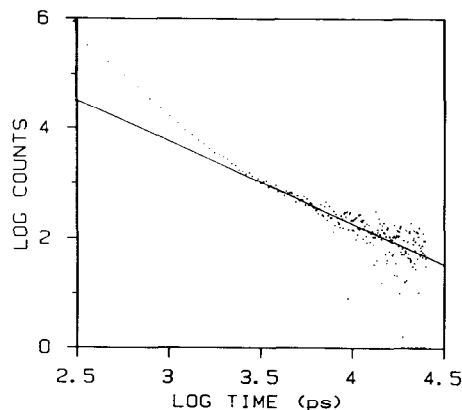


Fig. 9. A log-log plot of the undeconvoluted decay curve shown in Fig. 4a. The experimental fluorescence intensities were multiplied by an exponential factor to correct for the finite lifetime of the naphtholate anion in  $D_2O$   $\tau_f' = 23.2 \text{ ns}$ ;  $I'(t) = I(t) \exp(t/\tau_f')$ . Where  $I'(t)$  is the intensity after correction. The full line shown has a slope of  $-1.5$ .



$$K_{\text{eq}} = \frac{4\pi a^2 k_r^a}{k_d} \exp(R_c/a), \quad (28)$$

where  $k_r^a$  is the adiabatic recombination rate and  $k_d$  is the proton dissociation rate. Rearranging, we get for  $k_r^a$

$$k_r^a = (4\pi)^{1/2} a^{-2} k_d \frac{I_f(t)}{I_f(0)} \exp\left(-\frac{R_c}{a}\right) (Dt)^{3/2}. \quad (29)$$

Substituting for the experimental values  $I_f(t)/I_f(0) \approx 2.5 \times 10^{-5}$  at  $t = 31.6$  ns and  $k_d \approx 7.5 \times 10^9 \text{ s}^{-1}$  and inserting the kinetic parameters  $a = 6 \times 10^{-8}$  cm,  $R_c = 7.1 \times 10^{-8}$  cm,  $D \approx 6.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  we find using Eq. (20)

$$k_r^a \approx 8.2 \times 10^9 \text{ s}^{-1} (\text{D}_2\text{O}).$$

Assuming that the recombination rate at the contact distance obeys a linear free-energy law [10], we can estimate the value of  $k_r^a$  in  $\text{H}_2\text{O}$  by comparing it to the value found for 8-hydroxypyrene 1,3,6-trisulfonate [35], which belongs to the same family of hydroxy photoacids as 1-naphthol and has a similar  $\text{p}K_a^*$  in the excited state (0.5 compared to 0.4 of 1-naphthol). In this case recombination rate in  $\text{H}_2\text{O}$  was larger by a factor of about 2 [26,33]. Applying this factor to 1-naphthol we can estimate  $k_r^a (\text{H}_2\text{O})$

$$k_r^a \approx 1.6 \times 10^{10} \text{ s}^{-1} (\text{H}_2\text{O}).$$

Comparison of this value with the value of  $k_r^q$  reveals that the quenching reaction is about 2.1 times faster than the adiabatic proton recombination. A similar conclusion is reached when one compares the total quenching yield (40% of the total pair population is quenched) with the total yield of the adiabatic proton recombination which we crudely estimate from a multi-exponential analysis of the fluorescence decay of 1-naphthol (see below). Judging from the relative areas of a four-exponential fit, the combined weight of the slowly decaying components is  $\approx 0.15 \pm 0.05$  of the area under the initial 36 ps decaying component. The ratio between the quenching yield and the adiabatic recombination yield is then  $\approx 0.40/0.15 = 2.6 \pm 1$  in a close agreement with our previous estimation. The total proton recombination rate at the contact distance is  $k_r^a + k_r^q = 5.0 \times 10^{10} \text{ s}^{-1}$ , a rate comparable to the diffusion-controlled limit of the bimolecular reaction between the naphtholate anion and the proton  $k_D \approx 5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  [14],

where  $k_D$  is the diffusion-controlled bimolecular rate. For that reason we expect that in strongly acidic media the bimolecular proton recombination rate should approach the diffusion-controlled limit. Assuming no site preference at early times of the pair recombination one may conclude that the measured homogeneous rates of proton quenching and adiabatic recombination should scale as their corresponding  $k_r$ 's, i.e. a ratio of about 2:1 between the homogeneous quenching reaction and the homogeneous adiabatic recombination. This conclusion agrees very well with the bimolecular homogeneous rate constants reported by Harris and Selinger [14],  $k_r^q = (2.8 \pm 0.5) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_r^a = (1.4 \pm 0.3) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , ( $k_r^q/k_r^a = 2.0 \pm 0.4$ ). In combination the two recombination rates approach the diffusion-controlled limit,  $k_r^q + k_r^a = (4.2 \pm 0.8) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . Our values are in less good agreement with those reported by Webb et al [16],  $k_r^q = 3.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_r^a = 6.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . We believe that this reported value of the adiabatic homogeneous recombination rate is too large since even without the additional quenching reaction it exceeds the diffusion-controlled limit. Furthermore, it follows that our analysis agrees very well with the data of Harris and Selinger [14] who considered steady-state relative quantum yields and worked in an environment where the homogeneous quenching was much larger than self quenching, i.e. strongly acidic solutions. Less agreement exists with the analysis of Webb et al. [16] who attempted to optimize both the steady-state and time-resolved data to a single self-consistent set of kinetic parameters, without taking into account the self-quenching reaction which is important in neutral solutions.

## 5. Conclusion

We have shown that the naphtholate anion decays non-exponentially following the proton dissociation reaction from the 1-naphthol molecule. The long time dependence of the decay suggests a self-quenching mechanism of the naphtholate anion. This explains both the shorter lifetime of the naphtholate anion and the decrease in its quantum yield as compared with the corresponding parameters of the directly excited anion. We further suggest that the actual fluorescence lifetime of 1-naphthol is long, so the additional loss of excitation

due to the non-radiative decay of 1-naphthol is small. We have also demonstrated that some of the protons may combine adiabatically in a reversible geminate recombination reaction. We find a ratio of about 2:1 for quenching to adiabatic recombination. This agrees well with steady-state measurements of 1-naphthol in strongly acidic media where both homogeneous quenching and adiabatic recombination were observed with a similar branching ratio. The existence of the self-quenching reaction may be demonstrated by using suitable proton scavengers which diminish the self-quenching reaction. We have also shown that this reaction may be treated analytically for times longer than 100 ps. We also demonstrate that the time-dependent escape probability of the isolated pair may be reconstructed from a set of steady-state measurements taken at various scavenger concentrations.

## Acknowledgement

This work was supported by a grant from the NSF.

## References

- [1] L. Onsager, *J. Chem. Phys.* 2 (1934) 599; *Phys. Rev.* 54 (1938) 554.
- [2] A. Mozumder, *J. Chem. Phys.* 48 (1968) 1659.
- [3] A. Mozumder, *J. Chem. Phys.* 55 (1971) 3026.
- [4] J.L. Magee and A.B. Tayler, *J. Chem. Phys.* 56 (1972) 3061.
- [5] A. Hummel, *J. Chem. Phys.* 49 (1968) 4840.
- [6] H. Sano and M. Tachiya, *J. Chem. Phys.* 71 (1979) 1276.
- [7] S. Raaen and P.C. Hemmer, *J. Chem. Phys.* 76 (1982) 2569.
- [8] J.F. Ireland and P.A.H. Wyatt, *Advan. Phys. Org. Chem.* 12 (1976) 131.
- [9] A. Weller, *Progr. React. Kinetics* 1 (1961) 189.
- [10] E. Pines and G.R. Fleming, *J. Phys. Chem.* 95 (1991) 10448.
- [11] G.W. Robinson, P.J. Thistlethwaite and J. Lee, *J. Phys. Chem.* 90 (1986) 4224.
- [12] E. Pines, D. Huppert and N. Agmon, *J. Chem. Phys.* 88 (1988) 5620.
- [13] J.L. Rosenberg and I. Brinn, *J. Phys. Chem.* 76 (1972) 3558.
- [14] C.M. Harris and B.K. Selinger, *J. Phys. Chem.* 84 (1980) 1366.
- [15] S.P. Webb, S.W. Yeh, L.A. Phillips, M.A. Tolbert and J.H. Clark, *J. Am. Chem. Soc.* 106 (1984) 7286.
- [16] S.P. Webb, S.W. Yeh, L.A. Phillips, M.A. Tolbert and J.H. Clark, *J. Phys. Chem.* 90 (1986) 5154.
- [17] J. Lee, G.W. Robinson, S.P. Webb, L.A. Phillips and J.H. Clark, *J. Am. Chem. Soc.* 108 (1986) 6538.
- [18] R. Krishnan, J. Lee and G.W. Robinson, *J. Phys. Chem.* 94 (1990) 6365;  
R. Krishnan, T.G. Fillingim, J. Lee and G.W. Robinson, *J. Am. Chem. Soc.* 112 (1990) 1353;  
T.G. Fillingim, N. Luo, J. Lee and G.W. Robinson, *J. Phys. Chem.* 94 (1990) 6368.
- [19] H. Shizuka, T. Ogiwara, A. Narita, M. Sumitani and K. Yoshihara, *J. Phys. Chem.* 90 (1986) 6708.
- [20] R. Knochenmuss and S. Leutwyler, *J. Chem. Phys.* 91 (1989) 1268.
- [21] N. Agmon, D. Huppert, A. Masad and E. Pines, *J. Phys. Chem.* 95 (1991) 10407.
- [22] Th. Förster, *Z. Elektrochem.* 54 (1950) 531.
- [23] A. Weller, *Z. Elektrochem.* 56 (1952) 662; *Z. Physik. Chem. (Frankfurt am Main)* 17 (1958) 224.
- [24] G.K. Heidt, *Appl. Spectry.* 30 (1976) 553.
- [25] E. Pines and D. Huppert, *J. Chem. Phys.* 84 (1986) 3576; *Chem. Phys. Letters* 126 (1986) 88.
- [26] D. Huppert, E. Pines and N. Agmon, *J. Opt. Soc. Am. B* 7 (1990) 1545.
- [27] M.C. Chang, S.H. Courtney, A.J. Cross, R.J. Gulotty, J.W. Petrich and G.R. Fleming, *Anal. Instrum.* 14 (1985) 433.
- [28] M. Smoluchowski, *Z. Physik. Chem.* 92 (1917) 129.
- [29] P. Debye, *Trans. Electrochem. Soc.* 82 (1942) 265.
- [30] A. Mozumder, *J. Chem. Phys.* 61 (1974) 780.
- [31] K.M. Hong and J. Noolandi, *J. Chem. Phys.* 68 (1978) 5163.
- [32] F.C. Collins and G.E. Kimball, *J. Colloid. Sci.* 4 (1949) 425.
- [33] E. Pines, D. Huppert and N. Agmon, *J. Phys. Chem.* 95 (1991) 666.
- [34] H. Shizuka, *Accounts Chem. Res.* 18 (1985) 141.
- [35] N. Agmon, E. Pines and D. Huppert, *J. Chem. Phys.* 88 (1988) 5631.