Communications to the Editor

Salt Effect in Photoacid Quantum Yield Measurements: A Demonstration of the Geminate Recombination Role in Deprotonation Reactions

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Photoacid are an important class of chemical compounds that upon photoexcitation undergo rapid deprotonation in their electronic excited state.[1-6] The steady-state fluorescence spectrum of these compounds exhibits two fluorescence bands in aqueous solutions. One band belongs to the acid form and the other, red shifted, belongs to the base form. The time-resolved fluorescence spectrum of the photoacids shows that as deprotonation occurs the directly excited acid band decays and the indirectly formed base band builds up. Thus, the deprotonation rates can be found either directly by the time-resolved techniques or indirectly by considering the relative quantum yields of the two fluorescent bands.

Table I summarizes the measurements made on several such molecules by both the direct and indirect techniques. In all cases the deprotonation lifetimes measured directly by picosecond time-resolved spectroscopy (PTRS) are significantly shorter than the corresponding lifetimes found by relative quantum yield (RQY) experiments. This discrepancy has been overlooked as it seemed obvious that the more sophisticated direct measurements should yield the better time-resolved results.

We have recently suggested[7] that the two experimental methods are complementary rather than in contradiction to each other. We have proposed that a reversible geminate recombination process is responsible for this discrepancy. This process gradually slows down the initial proton dissociation rate which assumes at long times a $t^{-3/2}$ time dependence.[8-11] Thus, the PTRS has provided the initial deprotonation rates where the RQY yielded the average, geminate-recombination-effected rates.

Here we report a simple demonstration of this idea. Moderate concentrations of strong electrolytes ($NaNO_3$, KNO_3) were used in order to screen the coulombic interaction and to reduce the geminate recombination probability in the deprotonation reaction of HPTS (Table I). The HPTS unscreened anion is expected to exhibit a large recombination effect due to its 4-fold ionic charge.

Table I. Deprotonation Lifetimes of Some Photoacids

photoacid	charge after dep.	dep. lifetimes by PTRS (ps)	dep. lifetimes by RQY (ps)
HPTS[a]	−4	110 ± 10[d] 55 ± 30[e]	250[f] 480 ± 30[g]
HNDS[b]	−3	80 ± 10[h]	260 ± 20[i]
HNMS[c]	−2	980 ± 200[j]	1300 ± 70[g]

[a] 8-Hydroxypyrene-1,3,6-trisulfonate. [b] 2-Naphthol-6,8-disulfonate. [c] 2-Naphthol-6-sulfonate. [d] References 7, 12, 13. [e] Reference 14. [f] Reference 16. [g] Reference 15. [h] Reference 13. [i] Reference 17. [j] Reference 18.

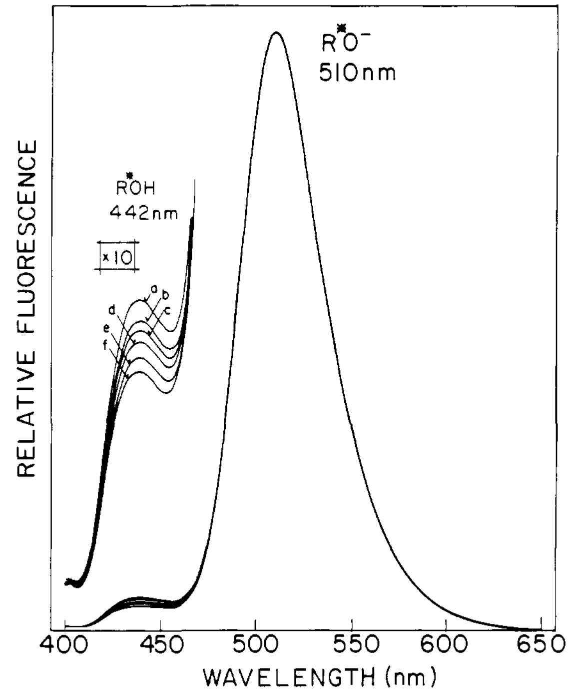

Figure 1. A typical constant intensity excitation experiment of 20 μM HPTS in $NaNO_3$ aqueous solutions, T = 20 °C, λ_{ex} = 353 nm. The fluorescence intensity was normalized to the base band at 510 nm. From top to bottom: (a) 0, (b) 10, (c) 20, (d) 40, (e) 90, (f) 260 mM $NaNO_3$.

The HPTS was already investigated by PTRS and its dissociation profile was found to be nonexponential in agreement with the proposed mechanism for the geminate recombination process.[7-11] Indeed, RQY measurements of the HPTS had predicted much longer deprotonation lifetimes than those that were found by PTRS methods (Table I).

Figure 1 shows typical constant illumination fluorescence spectra of aqueous solutions of HPTS at pH = 5.5 with various concentrations of $NaNO_3$. As the concentration of the strong electrolyte is raised the initial 1:20 intensity ratio between the acid band at 442 nm and the base band at 510 nm becomes larger.

The total quantum yield of the HPTS as well as the quantum yield of the acid and base forms when present alone in the solution is known to be close to unity.[16] At pH = 5.5 practically all the HPTS in the ground state is present in its acidic form (pK°_{HPTS} = 7.7). At the same time this pH is high enough so the bimolecular (as opposed to geminate) protonation of the anion is negligible during the lifetime of the excited state (~6 ns). With

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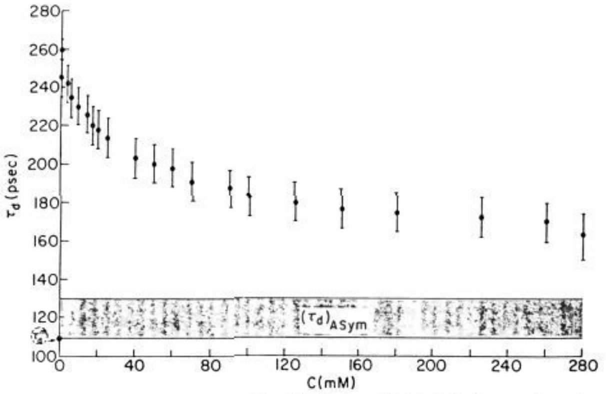

Figure 2. Average deprotonation lifetimes of HPTS (τ_d) as a function of $NaNO_3$ concentration. $\tau_d{}^m$ is the initial deprotonation lifetime found by direct measurements and $(\tau_d)_{asymp}$ is the theoretical lower limit for τ_d attainable by the salt effect.

these conditions the relative fluorescence efficiencies of the acid and base bands are directly proportional to the average deprotonation lifetime of the acid.[16,17,19]

$$\tau_d = \tau_f^{R^*OH}(\phi_{R^*OH}/\phi_{R^*O^-}) \tag{1}$$

$\tau_d = (k_d)^{-1}$ is the average lifetime of the reaction

$$R^*OH \xrightarrow{k_d} R^*O^- + H^+$$

$\tau_f^{R^*OH}$ is the radiative lifetime of the excited acid (R^*OH) in the absence of proton dissociation, and ϕ_{R^*OH} and $\phi_{R^*O^-}$ are the absolute quantum yields of the acid and base forms, respectively. τ_d can be shown to be of a form of

$$\tau_d = \tau_d{}^m + \tau_d{}^{gem} \tag{2}$$

$\tau_d{}^m$ is the pure dissociation lifetime of the molecule, which depends on the chemical properties of both the molecule and the solvent, and $\tau_d{}^{gem}$ is the geminate recombination contribution to the total dissociation lifetime, which is mainly dependent on the electrostatic interaction between the ion pair. In the asymptotic event where all the coulombic interaction is screened there is still a slight probability for a geminate encounter between the ions. For HPTS this asymptotic value is equal to $1.08\tau_d{}^m$; Introducing the value found by PTRS at 20 °C of $\tau_d{}^m = 110 \pm 10$ ps[3,7,12] one gets for the minimum deprotonation lifetime of HPTS attainable by total coulombic screening $(\tau_d{}^{HPTS})_{asym} = 120 \pm 10$ ps.[20]

Figure 2 shows τ_d calculated according to eq 1 as a function of the $NaNO_3$ concentration. The data were extracted from at least 20 independent experiments such as portrayed in Figure 1.

The asymptotic value of τ_d is clearly approached as the concentration of $NaNO_3$ is raised. However, at roughly 0.2 M $NaNO_3$ τ_d seems to level off at a value of 170 ± 10 ps. At these electrolyte concentrations the activity of the aqueous solution is significantly lowered and $\tau_d{}^m$ starts to increase with the $NaNO_3$ concentration.[13] Thus, at this range of concentrations (0.2–0.3 M $NaNO_3$) the decrease in $\tau_d{}^{gem}$ is cancelled out by the increase in $\tau_d{}^m$ and hence their sum, τ_d, remains practically constant. Further increase in the electrolyte concentration will eventually cause an increase in τ_d.[13] (At 4 M $NaNO_3$ $\tau_d{}^m$ was measured by PTRS to be 300 ± 30 ps.[20]) At the concentration range where $\tau_d{}^m$ is a constant and τ_d is well characterized (0–0.1 M $NaNO_3$), a quantitative analysis of the screening effect is possible. This analysis is the subject of a subsequent paper.[20]

Preliminary PTRS results of the HPTS/$NaNO_3$ system point to the same conclusion, i.e., the addition of the salt enhances the average dissociation rate of the photoacid.[22]

In summary, we present here for the first time clear evidence that reversible proton geminate recombination processes affect macroscopic observables such as the relative fluorescence quantum yields of photoacids. By doing so, we resolve the long-standing discrepancy between direct and indirect measurements of dissociation lifetimes of photoacids.

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Transesterification in the Gas Phase: Transfer of a Solvent Molecule from Reactant to Product Ions

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Ion molecule reactions in the gas phase differ significantly from those in solution due to the absence of solvation effects. Recently, attempts have been made to bridge this difference by comparing the gas-phase reactivity of single ions and those complexed to one or more "solvent" molecules. In particular, equilibrium studies of these systems have resulted in significant advances in our understanding of the energetics of ion-solvent interactions.[1] The dynamic effects, however, are less well understood.[2] For example, S_N2 reactions of solvated ions have been studied, but the major reaction products are unsolvated.[3] In this paper, we report one of the first examples of a nucleophilic displacement in which the solvent molecule is efficiently transferred from the reactant to the product ion.[4]

We have investigated a series of reactions of alkoxide–alcohol dimers with selected alkyl formates using Fourier transform ion cyclotron resonance (FT-ICR) spectrometry.[5] As shown in Table

$$RO^- \cdot\cdot HOR + H\overset{O}{\overset{\|}{C}}OR' \longrightarrow ROH \cdot\cdot {}^-OR' + H\overset{O}{\overset{\|}{C}}OR \tag{1}$$

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(5) Experiments were performed with an IonSpec FTMS2000 mass spectrometer attached to a home-built vacuum system. Ions were trapped in a 1-in. cubic cell placed between the poles of an electromagnet operating at 10–12 kg. Ions were typically trapped for 1 s with the total gas pressures being ca. 10^{-6} Torr. All alkoxide ions except for unlabeled methoxide were generated from electron impact on the corresponding alkyl nitrites. Unlabeled methoxide was formed from electron impact on dimethyl peroxide. All reactant ions were isolated by standard notched ejection techniques. Reactions of the isolated ions with the neutral formates followed good pseudo-first-order kinetics.

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