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Excited State Adduct Formation between Excited Substituted Quinolinium Cations and Specific Inorganic Anions

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Abstract: Fluorescence enhancement of quinolinium, *N*-ethylquinolinium and pseudoisocyanine cations in the Hammett acidity region of $HClO_4$ and H_2SO_4 is shown to be due to the anions of these acids, ClO_4^- and HSO_4^-, whereas other acids and their anions act as strong quenchers. We propose that excited state adducts are formed specifically with ClO_4^- or HSO_4^- whose quantum yields are larger than those of the corresponding uncomplexed cations. Rate constants for a proposed kinetic mechanism are determined from steady-state and pulse experiments. For quinolinium ions a (second) excited state pK_a^* may not be invoked in the Hammett acidity region.

Introduction

In earlier work[1] we measured the relatively low rate constants of proton transfer to a number of cyanine cations acting as carbon acids with pK_a values between 4 and 8 in their electronic ground states. Simple Förster cycle calculations predict these cyanines to be considerably stronger acids in their electronic excited state than in their ground state. In this paper we show that addition of high concentrations of $HClO_4$ or H_2SO_4 leads indeed to a strong increase of fluorescence in the Hammett acidity region without any shift in fluorescence or absorption wavelength. Surprisingly, this observed fluorescence enhancement also occurs with the anions of these acids, i.e., perchlorate or bisulfate ions at low acidities. A similar fluorescence enhancement is observed in the fragment of pseudoisocyanine (1,1-diethyl 2,2-cyanine chloride), namely, *N*-ethylquinolinium ion, whose quaternized nitrogen cannot accept a proton. Thus we are led to conclude that the excited states of these cations interact specifically with the anions of the above acids to form strongly fluorescent ionic adducts. This interpretation may be extended to the dramatic fluorescence enhandement observed for simple quinolinium cations in concentrated $HClO_4$ or H_2SO_4 which has been attributed to a (second) excited state pK_a^* in the Hammett acidity region.[2] However, since $NaClO_4$ (or $KHSO_4$) is shown in this work to produce a similar enhancement, an excited-state pK_a^* may not be invoked in the Hammett acidity region for the quinolinium ion. On the other hand, a number of other strong acids (e.g., HCl) and their anions are efficient quenchers in solvents of high dielectric constant at room temperature.

We present a mechanism that interprets this novel fluorescence behavior in terms of excited-state adduct formation involving the specific anions ClO_4^- or HSO_4^-. One may visualize the strongly fluorescent excited-state adduct as an excited cation which is "protected" from quenching H_2O molecules through complex formation with a specific anion. Adduct formation may be accompanied by a (partial) substitution of the solvation sphere around the cation by the entering ClO_4^- or HSO_4^-. Thus some but not all water molecules may be displaced in the inner cation solvation sphere resulting in the observed fluorescence enhancement without any fluorescence wavelength shift:

$$\begin{tikzcd}[column sep=large]
(A_s^+)^* + S_s^- \arrow[r, shift left, "k_r"] \arrow[d, "I"', "k_f,\ k_{nf}"] & (A^+S^-)_s^* \arrow[l, shift left, "k_d"] \arrow[dl, "k'_f,\ k'_{nf}"] \\
A_s^+ + S_s^- &
\end{tikzcd}$$

where A_s^+, $(A_s^+)^*$, S_s^-, and $(A^+S^-)_s^*$ are solvated quinolinium (derivative) cations, their solvated excited singlet states, solvated anions, and solvated ionic adducts in the excited state, respectively; k_r and k_d are adduct association and dissociation rate constants, respectively; I is the intensity of the exciting light; k_f and k_f' are fluorescence rate constants of the singlet cation and its ionic adduct, respectively.

We have omitted complex formation in the ground state, since no noticeable shift in absorption frequency or optical density is observed upon addition of the specific anions at room temperature under present conditions. Neither charge transfer nor exciplex formation is indicated. Transient measurements of fluorescence decay and steady-state measurements provide values for the rate constants.

Stern–Volmer experiments *in the absence* of $NaClO_4$ show that methanol and ethanol are stronger quenchers of cation fluorescence than H_2O molecules. The presence of $NaClO_4$ significantly lowers the quenching rate constants of methanol and ethanol due to the "protection" by ClO_4^- through excited-state adduct formation with the cation. Thus, in a wider sense, the observed fluorescence changes are a manifestation of a general solvent substitution effect.

Experimental Section

Reagent grade *N*-ethylquinolinium iodide and quinoline were purchased from K and K Laboratories, Inc., and Matheson Coleman and Bell, respectively. Pseudoisocyanine chloride (1,1′-diethyl-2,2′-cyanine) was kindly provided by Dr. E. Daltrozzo. High-resolution

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† In partial fulfillment for the Ph.D. degree, 1975.

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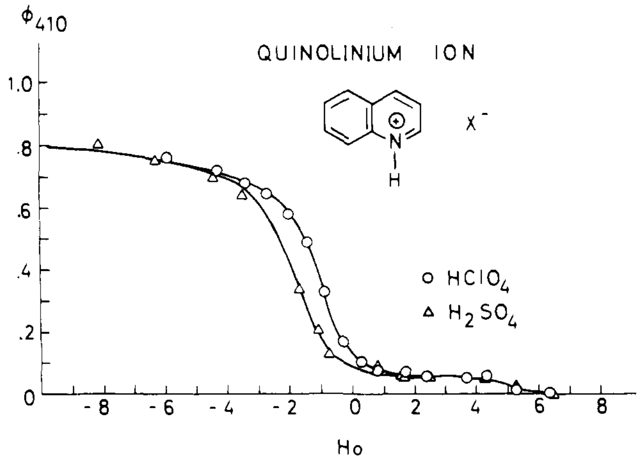

Figure 1. Fluorescence quantum yield at 410 nm vs. Hammett acidity function H_0 of $HClO_4$ and H_2SO_4 for quinolinium cations in aqueous solution at 23 °C.

absorption and emission spectra and melting and boiling point determinations showed no detectable impurities. The high quantum yields exclude impurities responsible for the emission behavior. Stock solutions were vacuum filtered through 0.8 Matricel filter papers. Concentrations, calculated from known extinction coefficients, were at or below 5.0×10^{-5} M unless otherwise indicated. Oxygen was removed by bubbling purified nitrogen through the solutions for 1 h. Experiments were performed within a few hours from initial preparation of solutions. pH measurements were carried out with a Beckman Expandomatic pH meter. For concentrated acid solutions the corrected Hammett acidity function (H_0) tables of Jorgenson and Harter[3] for sulfuric acid and of Yates and Wai[4] for perchloric acids were used.[5] Absorption spectra were measured on a Beckman DK2A, ACTA M6, or Cary 17 spectrometer. Emission spectra were recorded on an American Instrument Co. spectrofluorimeter at 23 ± 1 °C. A 1-cm square precision-bore Pyrex cell was used for all emission measurements where the position of the cell was identical in all cases. All samples were excited at 345 nm. The emission intensities were monitored at 410, 420, and 425 nm for quinolinium, *N*-ethylquinolinium cations, and pseudoisocyanine dications, respectively. In some instances a fluorescence attachment with cutoff filters to the Beckman DK2A was used. Identical results were obtained from both instruments. The method of Parker and Rees[6] for the determination of relative fluorescence quantum yields was employed with quinine bisulfate in 0.1 N sulfuric acid solution ($\phi = 0.55$) as the standard. The uncertainty in quantum yield determinations is ±10% except at very low emission intensities, where it is larger.

Lifetimes were determined with a 100-kW pulsed nitrogen laser (3371 Å) whose pulse width was 10 ns. The emission, at right angles to the excitation, was passed through a 0.5-m Bausch and Lomb monochromator at the maximum emission wavelength. The longer lifetimes were determined with a PAR Model 160 Boxcar Integrator. For short lifetimes (<15 ns) the resulting signal was photographed from a Hewlett-Packard Model 183 oscilloscope and analyzed according to the phase plane method of Demas and Adamson.[7] The uncertainty in lifetimes is ±15%. Subsequent measurements on a 1-MW pulsed nitrogen laser (Lambda Physik) with a shorter pulse width of 2.8 ns verified all lifetime measurements within experimental error.

Results

Fluorescence titrations of quinolinium ions were carried out with $HClO_4$ and H_2SO_4 (Figure 1), $NaClO_4$ at pH ≃3 (Figure 2), and $KHSO_4$ in 1.44 M H_2SO_4 at $H_0 \approx -0.5$ (Figure 3). At constant absorption the quantum yield at 410 nm increases from 0.06 to 0.8 as a function of increasing acid concentrations (Figure 1). When the quantum yields in the perchloric acid and sodium perchlorate solutions are plotted vs. molar concentrations rather than H_0 (Figure 2) the two titration curves are almost identical except at low concentrations. The latter deviation may be partially due to experimental scatter in measuring low emission intensities. Furthermore, owing to the ground-state pK_a (= 5.1)[8] of the quinolinium cation, ϕ_{410} approaches zero at pH ≥6.6 (Figure 1) or at zero perchloric acid concentration (Figure 2), since the conjugate quinoline base does not fluoresce. Similarly, a plot of ϕ_{410} vs. molar concentrations of sulfuric acid or potassium bisulfate leads to practically identical curves (Figure 3). A similar set of fluorescence titrations was carried out with *N*-ethylquinolinium cations in $HClO_4$ and H_2SO_4 (Figure 4), $NaClO_4$ at pH 5.6 (Figure 5), and $KHSO_2$ in 1.44 M H_2SO_4 (Figure 6). The titration curves of *N*-ethylquinolinium cations with H_2SO_4 (Figures 4 and 6) show a minimum in ϕ_{420} which is due to quenching by SO_4^{2-}. With perchloric acid no such minimum exists. Fluorimetric titrations of pseudoisocyanine dications (ϕ_{425}) with $HClO_4$ and H_2SO_4 as a function of H_0 are shown in Figure 7. ϕ_{425} also increases as a function of $NaClO_4$ in 0.79 M $HClO_4$ (Figure 8). However, ϕ_{425} is relatively constant at constant ClO_4^- (6 M), although $HClO_4$ increases strongly (Figure 8). A Stern–Volmer plot (Figure 9) shows fluorescence quenching of *N*-ethylquinolinium ions in aqueous solution through addition of ethanol and methanol as quenchers in the absence and presence of $NaClO_4$. It is seen that quenching by ethanol and methanol is least strong in the presence of $NaClO_4$.

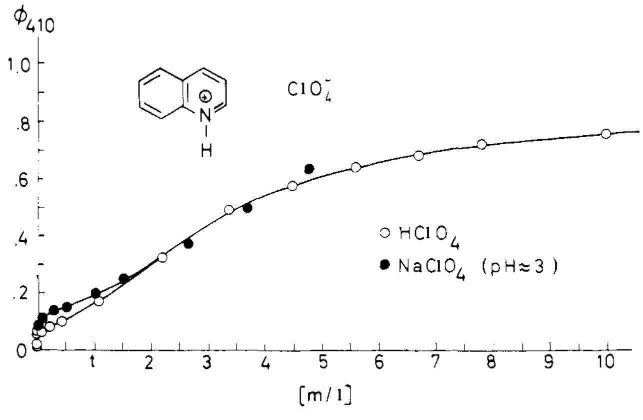

Figure 2. Fluorescence quantum yield at 410 nm vs. molar concentration of $HClO_4$ and $NaClO_4$ at pH ≃3 for quinolinium cations in aqueous solution at 23 °C.

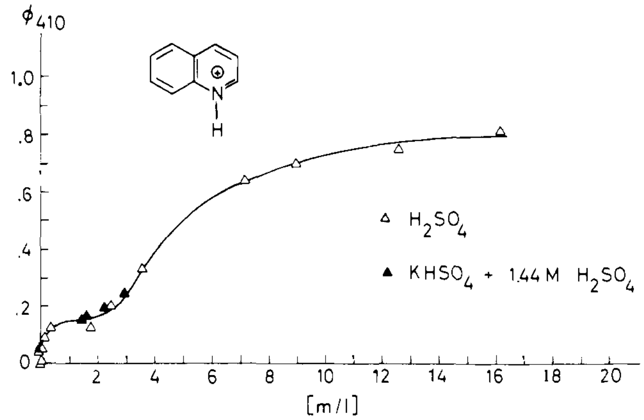

Figure 3. Fluorescence quantum yield at 410 nm vs. molar concentration of H_2SO_4 and $KHSO_4$ + 1.44 M H_2SO_4 for quinolinium cations in aqueous solution at 23 °C.

Lifetimes of the singlet states of quinolinium, *N*-ethylquinolinium, and pseudoisocyanine dications under various conditions are given in Table I. They show single exponential decays. Within a series all lifetimes increase with increasing electrolyte concentrations. The quantum yields of quinolinium, *N*-ethylquinolinium, and pseudoisocyanine cations were in-

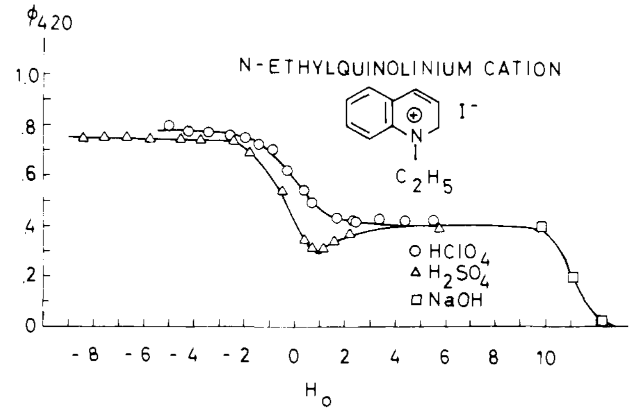

Figure 4. Fluorescence quantum yield at 420 nm vs. Hammett acidity function H_0 of $HClO_4$ and H_2SO_4 for N-ethylquinolinium iodide in aqueous solution at 23 °C.

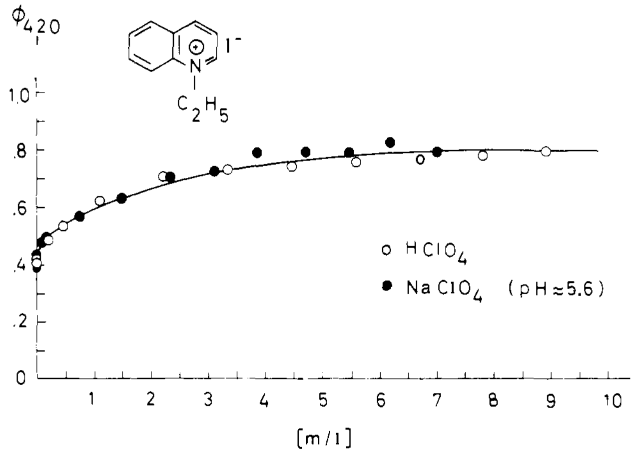

Figure 5. Fluorescence quantum yield at 420 nm vs. molar concentration of $HClO_4$ and $NaClO_4$ (pH ≃5.6) for N-ethylquinolinium iodide in aqueous solution at 23 °C.

dependent of their concentrations in the concentration range used in this study (0.5-5 × 10^{-5} M).

Discussion

Evidence for excited-state adduct formation is provided by the identical fluorescence enhancement of N-ethylquinolinium ions by $HClO_4$ and $NaClO_4$ (at pH 5.6) (Figures 4 and 5) and, correspondingly, by H_2SO_4 and $KHSO_4$ (in 1.44 M H_2SO_4) (Figure 6). The N atom in N-ethylquinolinium cannot be protonated since it is quaternized. Ring protonation is unlikely since it would reduce π-electron delocalization contrary to spectral evidence. Nonparticipation of the proton and the direct involvement of the perchlorate and bisulfate ions are indicated. There is a minimum in quantum yield of N-ethylquinolinium in the H_2SO_4 system at $H_0 \simeq 1$ (Figure 4) which is a consequence of SO_4^{2-} quenching whose quenching constant is diffusion controlled. The SO_4^{2-} concentration reaches a maximum at $H_0 \simeq 1.0$ in H_2SO_4 on account of the second pK_a of H_2SO_4. A corresponding minimum is obscured in the quinolinium system probably because of the larger scatter of the intensity measurements at very low ϕ ($\simeq 0.06$).

The fluorescence quantum yield ϕ_{425} of the dication of pseudoisocyanine, which contains two N-ethylquinolinium fragments connected by a methylene group, shows a similar increase with $HClO_4$ or H_2SO_4 as that of the N-ethylquinolinium ion (Figure 7) indicating a similar mechanism. The direct involvement of ClO_4^- in excited adduct formation is again indicated by the increase of ϕ_{425} as a function of $NaClO_4$ in the presence of 0.79 M $HClO_4$. The latter high $HClO_4$ concentration had to be chosen because of the low pK_a of pseudoisocyanine[8] ($pK_a = 4.01$ in 0.2 M KNO_3 at 25 °C). In order to show that the fluorescence increase is not due to an effective H_0 increase, a titration was carried out at a constant total ClO_4^- concentration of 6.0 M but *strongly* increasing $HClO_4$. No appreciable increase in fluorescence occurred (Figure 8). This finding shows that the quantum yield is determined primarily by ClO_4^- (or HSO_4^-) and not by H^+.

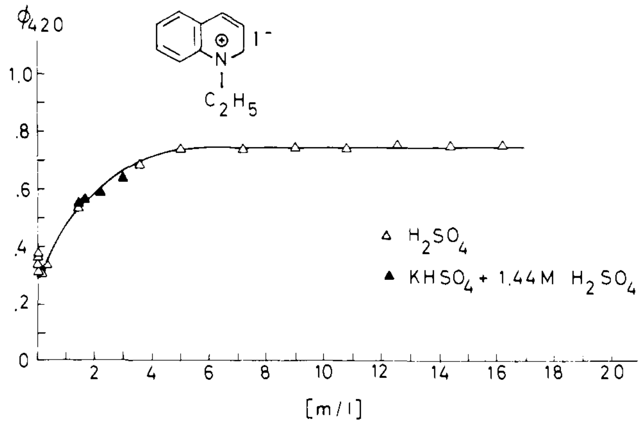

Figure 6. Fluorescence quantum yield at 420 nm vs. molar concentration of H_2SO_4 and $KHSO_4$ + 1.44 M H_2SO_4 for N-ethylquinolinium iodide in aqueous solution at 23 °C.

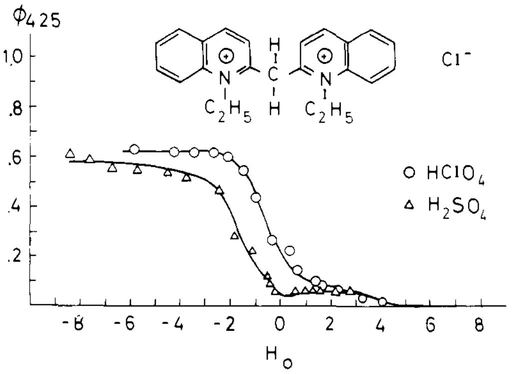

Figure 7. Fluorescence quantum yield at 425 nm vs. Hammett acidity function H_0 of $HClO_4$ and H_2SO_4 for pseudoisocyanine chloride in aqueous solution at 23 °C.

The possibility that fluorescence enhancement of the dication of pseudoisocyanine in $HClO_4$ or H_2SO_4 may be due to an excited-state pK_a^* involving the methine carbon can be dismissed for the following reasons. Proton transfer to the *ground* state of pseudoisocyanine has been shown by temperature-jump experiments to be relatively slow and the Brønsted curve reaches saturation already at k = 729 L/mol·s.[1] Attempts by flash experiments[9] to spectroscopically observe the *excited* conjugate base formed by deprotonation of its *excited* conjugate acid failed owing to the fact that either the rate of deprotonation in the excited state is too slow ($k_{\text{deprotonation}} \ll 10^5\ s^{-1}$) or it does not occur at all. Any perturbation of the (slow) ground-state equilibrium by deactivated conjugate base that would have been formed by such a cyclic process was not observed for similar reasons. Thus an excited pK_a^* process can be excluded under present conditions.

For pseudoisocyanine dications H_+ should be employed instead of H_0 since the conjugate acid has two positive charges. However, the H_+ and H_0 scales turn out to be almost identical for H_2SO_4 and $HClO_4$ where comparisons are available.[5] It is seen directly from Figures 2, 3, 5, 6, and 8 that ClO_4^- and HSO_4^- enhance the fluorescence intensity of quinolinium, N-quinolinium, and pseudoisocyanine cations. This behavior is in contrast to the halides and SO_4^{2-}, which are efficient

Table I. Experimental Lifetimes of the Quinolinium, *N*-Ethylquinolinium, and Pseudoisocyanine Systems in Concentrated Electrolyte Solutions

	quinolinium		*N*-ethylquinolinium		1,1′ diethyl-2,2′-cyanine	
	ϕ_{410}	τ', ns	ϕ_{420}	τ', ns	ϕ_{425}	τ', ns
$HClO_4$[a]	0.76	35	0.79	25	0.62	42
$NaClO_4$[a]	0.72 (pH $\simeq$3)	39	0.79 (pH 5.6)	29		
H_2SO_4[a]	0.80	27	0.74	26	0.60	41
HNO_3 (0.1 M)	0.09 (pH $\simeq$1)	~2			0.06	6

[a] Concentrations are those of the respective high concentration regions (low H_0 values) where ϕ and τ' become essentially constant. The concentrations ($\gtrsim$7 mol/L) may be read off directly from the respective figures.

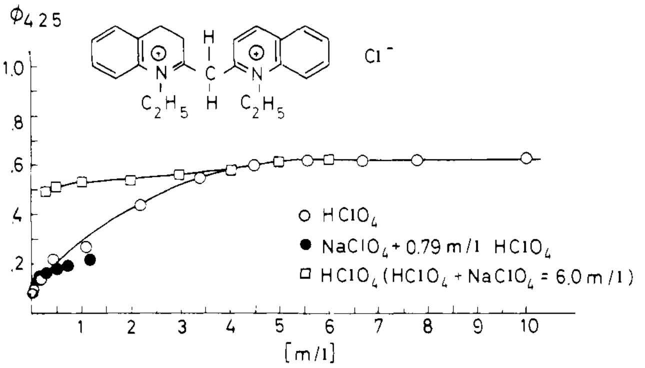

Figure 8. Fluorescence quantum yield at 425 nm vs. molar concentration of $HClO_4$, $NaClO_4$ + 0.79 M $HClO_4$, and $HClO_4$ (at constant perchlorate concentration of 6 M) for pseudoisocyanine chloride in aqueous solution at 23 °C.

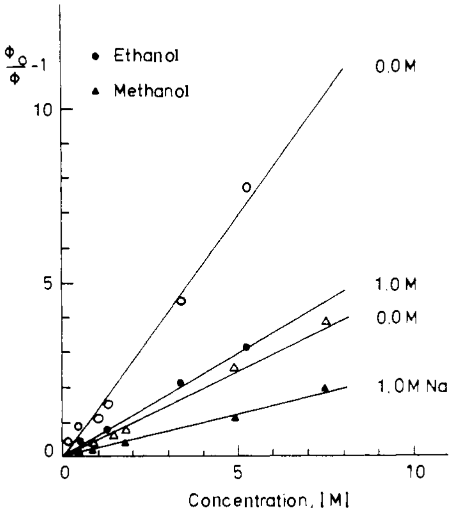

Figure 9. Stern-Volmer plot, concentration axis represents ethanol and methanol concentrations in the absence and presence of 1.0 M $NaClO_4$ in an aqueous solution of *N*-ethylquinolinium iodide at 23 °C. The values of K_{sv} are for methanol, 0.50 (no $NaClO_4$) and 0.25 (1.0 M $NaClO_4$); for ethanol, 1.4 (no $NaClO_4$) and 0.60 (1.0 M $NaClO_4$), τ_0 = 17 ns for *N*-ethylquinolinium ions in aqueous solution without any quenchers.

quenchers, whereas acetate and trichloroacetate quench moderately. KH_2PO_4 and KNO_3 are found to quench at low concentrations and to slightly enhance the emission intensity at higher concentrations (≈3 M, not shown). In all of the above solutions of the cationic forms there is no detectable wavelength shift in emission or absorption as a function of added electrolyte or as a function of increasing cation concentrations at room temperature. For these reasons neither exciplexes nor charge transfer complexes[11] may be formed. Short-lived excited-state adducts are also formed between electronically excited quinolinium ions and ClO_4^- or HSO_4^-. This conclusion is arrived at on the basis of the almost identical fluorescence enhancement of quinolinium ions by $HClO_4$ and $NaClO_4$ (at pH $\simeq$3) (Figure 2) which shows the involvement of the perchlorate ion in the enhancement process. A similar fluorescence enhancement occurs with H_2SO_4 and with HSO_4^-. The latter titration is carried out with $KHSO_4$ in 1.44 M H_2SO_4 (Figure 3) because of the second pK_a of H_2SO_4 (= 1.9). Thus our experiments show that excited-state proton transfer may not be invoked to explain the strong enhancement of fluorescence intensity of quinolinium ions in concentrated $HClO_4$ and H_2SO_4.

We interpret steady-state fluorescence enhancement and the measured lifetimes on the basis of the above excited-state adduct mechanism. For the perchlorate system the straightforward steady-state solution is

$$\phi_t = (k_f + k_f'\tau'_s k_r[S_s^-])/(k_r[S_s^-] + k_f + k_{nf} - k_d\tau'_s k_r[S_s^-]) \qquad (1)$$

where τ'_s is the fluorescence lifetime of $(A^+S^-)_s{}^*$ ($\tau'_s = 1/(k_d + k_f' + k'_{nf})$ as measured in the saturation region at low H_0 values (Table I). Equation 1 is obtained by setting the rates of $(A_s^+)^*$ and $(A^+S^-)_s{}^*$ formation equal to zero, solving for the steady-state concentrations of $(A_s^+)^*$ and $(A^+S^-)_s{}^*$, and substituting the latter expressions into the expressions for the respective rates of emission: $I_f = k_f(A_s^+)^*$ and $I_f' = k_f'(A^+S^-)_s{}^*$. The fluorescence quantum yields are defined as $\phi = I_f/I$ and $\phi' = I_f'/I$, respectively. The total quantum yield is the sum $\phi_t = \phi + \phi'$ (eq 1), since fluorescence from the two excited species shows no discernible wavelength difference.

The total quantum yield for the H_2SO_4 system contains the additional quenching term k_{SO_4}-$[SO_4^{2-}]$ in the denominator. To obtain the best fit for the values of k_r, k_d, and k_{nf} (eq 1) we used a nonlinear least-squares computer program.[10] Experimental input parameters in our computer calculations were ϕ_t, $(S^-)_s$, k_f, k_f', and τ'_s. The value for k_f is obtained in the low acidity region (high H_0) according to $k_f = 1/\tau_0 = \phi_{t(\text{high } H_0)}/\tau_{(\text{high } H_0)}$. k_f' is the corresponding radiative rate constant for the ionic adduct obtained in the saturation region at low H_0: $k_f' = 1/\tau_0' = \phi_{t(\text{low } H_0)}/\tau'_{(\text{low } H_0)}$. The best computer fit produced values for k_r, k_d, and k_{nf} for quinolinium, *N*-ethylquinolinium, and pseudoisocyanine cations (Table II). Inspection of the calculated rate constants shows that the rate constants k_r for adduct formation in the excited state are lower than diffusion controlled in all systems. They range between 3.3 × 10^7 and 3.2 × 10^8 L/mol·s, quinolinium having the highest value. These relatively low rate constants may indicate that the entering ligand (ClO_4^- or HSO_4^-) displaces solvent molecules in the inner solvation sphere around the excited cation. This (stepwise) solvent displacement is the rate-limiting step in the recombination between the excited cation and the specific anion. If the rate for excited adduct formation would be diffusion controlled, then one would expect to observe a decrease of the adduct quantum yield in the concentrated sulfuric acid solutions whose viscosities reach a value of 25.4 cP at 20 °C. However, our experiments showed the attainment of a plateau region at low H_0 values rather than a decrease of

Table II. Calculated Rate Constants for a Mechanism of Excited-State Adduct Formation (eq 1)

	quinolinium cations		*N*-ethylquinolinium cations			1,1′-diethyl-2,2′ cyanine dications	
	$HClO_4$	$NaClO_4$	$HClO_4$	$NaClO_4$	H_2SO_4	$HClO_4$	H_2SO_4
k_r, L/mol·s	3.2×10^8	5.4×10^7	5.1×10^7	3.3×10^7	3.5×10^7	8.5×10^7	3.5×10^7
k_d, s^{-1}	1.1×10^7	3.5×10^7	1.5×10^6	5.3×10^6	2.6×10^6	4.6×10^6	7.7×10^6
k_f,[c] s^{-1}	4.5×10^7	4.5×10^7	2.3×10^7	2.3×10^7	2.3×10^7	1.0×10^7	1.0×10^7
k_f',[b] s^{-1}	2.2×10^7	1.8×10^7	3.2×10^7	2.7×10^7	2.9×10^7	1.5×10^7	1.5×10^7
τ_s',[a]	3.5×10^{-8}	3.9×10^{-8}	2.5×10^{-8}	2.9×10^{-8}	2.6×10^{-8}	4.2×10^{-8}	4.1×10^{-8}
k_{nf}, s^{-1}	1.1×10^9	4.0×10^8	3.2×10^7	3.0×10^7	3.6×10^7	1.2×10^8	1.7×10^8
$k_{SO_4^{2-}}$, L/mol·s					2.1×10^9		7.4×10^9
k_r/k_d	29.1	1.5	34.0	6.2	13.5	18.4	4.7

[a] Experimental value (see Table I). [b] Calculated from τ_s' and ϕ_1: $k_f' = 1/\tau_0' = \phi_1/\tau_s'$. [c] Calculated from τ_s and ϕ_f: $k_f = 1/\tau_0 = \phi_1/\tau_s$.

ϕ_1. Furthermore, the fluorescence enhancement is equally substantial for the $HClO_4$ as well as the $NaClO_4$ solutions whose viscosity increments are substantially lower. Therefore viscosity effects play only a minor role in the present systems.

The relatively low stability of the ionic adduct in the excited state is reflected by the individual k_r/k_d ratios. They are highest in the $HClO_4$ system where their corresponding ΔF_0 values range between −1.7 and −2.0 kcal/mol and lower in the $NaClO_4$ and H_2SO_4 systems whose ΔF_0 are between −0.2 and −1.5 kcal/mol. The lower stability of the adducts in $NaClO_4$ than in $HClO_4$ may indicate some stabilization by protons in the $HClO_4$ solutions. The rate constant k_{nf} for quenching by nonradiative processes comprises quenching by solvent molecules, internal conversion, and intersystem crossing, where solvent quenching represents the most important contribution at room temperature. Thus the rate constant for solvent quenching is remarkably high for quinolinium cations which may be partially due to hydrogen bond formation between a water molecule and the protonated nitrogen atom which is not possible when the nitrogen is quaternized. The quantum yields at high electrolyte concentrations are similar ($\simeq$0.8) for quinolinium and *N*-ethylquinolinium and somewhat lower for pseudoisocyanine dications, indicating that ClO_4^- (or HSO_4^-) exerts a certain leveling effect by preventing the quenching process of the water molecules. The quenching rate constant for SO_4^{2-} is practically diffusion controlled (2.1×10^9 and 7.4×10^9 L/mol·s for *N*-ethylquinolinium and pseudoisocyanine, respectively), as expected for a doubly negatively charged quenching ion interacting with positively and doubly positively charged singlets.

The "protective" effect of ClO_4^- against solvent quenching is clearly exemplified by the presence of 1 M $NaClO_4$ in an aqueous *N*-ethylquinolinium solution, to which strongly quenching CH_3OH or C_2H_5OH molecules are added (Figure 9). The Stern–Volmer quenching constants of CH_3OH and C_2H_5OH are approximately halved by "protective" excited adduct formation in the presence of 1 M $NaClO_4$, which converts about half of the excited cations to adducts. The use of iodide as the counterion in the case of *N*-ethylquinolinium will not lead to charge transfer formation in solvents of high dielectric constant[11] at room temperature. Furthermore, the iodide concentration is very low ($\sim 10^{-5}$ M) whereas the added electrolyte concentrations are several orders of magnitude larger. Excited adduct formation does not occur with anions capable of forming charge transfer complexes in solvents of low dielectric constants. These anions (e.g., halides) strongly quench cation fluorescence in water. Importantly, the ionization energies of perchlorate[11] and bisulfate ions are too high to undergo any charge transfer with these cations in solvents of high or low polarity.

Adduct formation of ClO_4^- (or HSO_4^-) with the present excited cations cannot be solely due to the structure-breaking properties of ClO_4^- or to simple electrostatic interactions, since other ions such as SO_4^{2-} are strong quenchers. Specific interaction with the solvent may be important possibly through formation of solvent subspecies.[13,14] It may be worth mentioning that ClO_4^- may undergo specific interactions with other cations such as Na^+ and Li^+ as shown by its strongly increasing effect on the nuclear quadrupole relaxation rate[15,16] of $^{23}Na^+$ and $^7Li^+$.

At present we can only speculate why perchlorate or bisulfate interact specifically with the above cations whereas most other ions are quenchers. It might be conceivable that excited adduct formation occurs with the ^1L_b state which is degenerate with the ^1L_a state in quinolinium. Schulman and Capomacchia[2] have used this argument to explain fluorescence enhancement by *proton* transfer to the ^1L_b state. In fact they observed a fluorescence increase in the Hammett acidity region only for those substituted quinolinium cations which showed degeneracy of the ^1L_a and ^1L_b bands. If the ^1L_a and ^1L_b states of quinolinium, *N*-ethylquinolinium, and pseudoisocyanine cations are nearly degenerate as might be surmised from their spectra, then Schulman and Capomacchia's explanation may apply to excited ion adduct formation rather than excited-state protonation in the Hammett acidity region. Precise excitation polarization measurements[2] as carried out for indole[12] might settle this point.

Thus it appears that quinolinium shows only one excited state pK_a^* ($\simeq$ 7) which is more basic than the ground-state pK_a (= 6.1) as expected from the bathochromic shift of the ^1L_a absorption band (277 to 313 nm) of quinoline upon protonation in aqueous solution.

Transient experiments should show a double exponential decay for cation emission if the excited-state equilibrium is reversible and rapid. However, we observed only a single exponential decay at the common emission wavelength of the cation and the adduct. The signal due to any second decay is either too small to be observed or its decay time is too close to the other decay process to be resolvable. We conclude that the dissociation rate constant which was obtained from steady-state experiments is not sufficiently large to establish equilibrium during the lifetime of the excited species in a pulse experiment. Fluorescence enhancement is accompanied by an increase of the fluorescence lifetime at increasing ClO_4^- or HSO_4^- concentrations as expected. Since the nature of the emitting species changes from $(A_s^+)^*$ to $(A^+S^-)_s^*$ any simple model would be inadequate that considers only water quenching to be responsible for the observed fluorescence changes. Furthermore, the assumption of adduct formation in the ground state alone that might be monitored by fluorescence is not consistent with the observed kinetics of the $(S^-)_s$ dependence. Experiments with frozen solutions in glasses at low temperatures below about −120 °C show the disappearance of the excited adduct process and the appearance of a slow phosphorescence emission as expected. Work in other solvents and phosphorescence lifetime studies in low-temperature glasses are in progress.

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Proton Exchange in the Lowest Excited Singlet State of 2-Naphthol-6,8-disulfonate. Demonstration of the Establishment of Prototropic Equilibrium in the Excited State

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Abstract: The pH dependences of the fluorescence spectra of 2-naphthol-6,8-disulfonate were evaluated in terms of the kinetics of excited-state proton transfer. Deviations from ideal fluorometric titration behavior were compensated by a simple Brønsted kinetic activity factor which accounted for the primary kinetic salt effect. Criteria for the establishment of prototropic equilibrium in the lowest excited singlet state are stated and when applied to 2-naphthol-6,8-disulfonate, it is found that equilibrium prevails over most of the inflection region in the fluorometric titration.

The variations of the relative fluorescence efficiencies of hydroxy aromatics and their conjugate bases with pH are known to depend upon the kinetics of proton-transfer in the lowest excited singlet state.[1] Under the assumption of steady-state proton transfer in the lowest excited singlet state, the relative fluorescence efficiencies of the excited phenolic species have been shown to vary, approximately according to

$$\phi/\phi_0 = \frac{1 + \overleftarrow{k}\tau_0'[\mathrm{H_3O^+}]}{1 + \vec{k}\tau_0 + \overleftarrow{k}\tau_0'[\mathrm{H_3O^+}]} \qquad (1)$$

while those of the excited conjugate base, phenolate species vary according to

$$\phi'/\phi_0' = \frac{\vec{k}\tau_0}{1 + \vec{k}\tau_0 + \overleftarrow{k}\tau_0'[\mathrm{H_3O^+}]} \qquad (2)$$

where $[H_3O^+]$ is the molar concentration of hydrogen ions, τ_0 and τ_0' are the actual lifetimes of excited acid and conjugate base in the absence of proton transfer (i.e., in the low and high pH limits, respectively), and $\vec{k}$ and $\overleftarrow{k}$ are the rate constants for dissociation of the excited phenolic species and protonation of the excited phenolate species, respectively. More refined treatments have corrected eq 1 and 2 for transient reprotonation of the phenolate species prior to the establishment of the steady state and for the effect of ionic strength on the "equilibrium" between the reactants and the activated complex in the transition state.[2,3] At higher pH the probability of protonation of the excited phenolate is negligibly small causing eq 1 and 2 to reduce to the pH-independent forms

$$(\phi/\phi_0)_{\mathrm{const}} = \frac{1}{1 + \vec{k}\tau_0} \qquad (3)$$

$$(\phi'/\phi_0')_{\mathrm{const}} = \frac{\vec{k}\tau_0}{1 + \vec{k}\tau_0} \qquad (4)$$

Because of the short duration of the lowest excited singlet state it is in order to question whether or not prototropic equilibrium can be fully established during the lifetime of the lowest excited singlet state and if so, under what conditions can equilibrium be realized and recognized? In order to answer these questions the pH dependences of the fluorescence spectra of 2-naphthol-6,8-disulfonate and its conjugate base were examined. This molecule was chosen for investigation because at near neutral pH it is extensively dissociated in the lowest excited singlet state (i.e., $(\phi/\phi_0)_{\mathrm{const}} \approx 0$, $(\phi'/\phi_0')_{\mathrm{const}} \approx 1$), a fact that suggested intuitively that at low pH, proton exchange in both directions might be considerably faster than fluorescence and nonradiative deactivation and might lead to the establishment of prototropic equilibrium in the lowest excited singlet state.

Experimental Section

The dipotassium salt of 2-naphthol-6,8-disulfonate was purchased from Pfaltz and Bauer, Inc. Stamford, Conn., and triply recrystallized from 50 vol % aqueous ethanol.

Fluorescence spectra were taken, at ambient temperature (25 °C), on a Perkin-Elmer MPF-2A fluorescence spectrophotometer whose output was corrected for wavelength variable response by means of a rhodamine B quantum counter and whose monochromators were calibrated against the xenon line emission spectrum. Fluorescence decay times were measured on a TRW instrument employing an 18-W deuterium lamp as its source. Absorption spectra were taken on a Beckman DB-GT spectrophotometer. Data analysis was performed on a digital computer.

Solutions of which spectra were taken were prepared by diluting

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