Quenching of Fluorescence by Substituted Ethylenes. Substituent and Salt Effects as Criteria of Quenching Mechanism

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Linear free energy relationships and salt effects can be used to distinguish between the fluorescence quenching mechanisms of exciplex or ion-pair formation.

Formation of exciplexes[1] or of ion-pairs[2] results in fluorescence quenching of aromatic compounds. The exciplexes are often, but not always, fluorescent while the ion-pairs are non-fluorescent. Complex formation takes place in non-polar solvents such as hexane, and electron-transfer leading to ion-pairs occurs in very polar solvents. Both processes can occur simultaneously in moderately polar solvents.[3] The quenching mechanism has been discussed using various kinetic schemes.[4,5]

From the photochemical viewpoint, the quenching mechanism is of considerable interest, since both exciplexes[6] and ion-pairs[7] can be reaction intermediates and the products obtained from each are usually different.[6-8] We have described reactions of naphthalene and its derivatives with substituted ethylenes in which the product distribution depends on the solvent.[7,9] We now report results on the quenching mechanism. (i) Fluorescence of a series of methylnaphthalenes is quenched by acrylonitrile; the quenching rate is related to the Hammett σ-constant for the naphthalene substitution, and the relationship indicates quenching *via* a polar complex, rather than by an ion-pair. (ii) Exciplex fluorescence from 1-naphthonitrile and tetramethylethylene,[4a,b,10] in moderately polar solvents, is quenched by added salts, and the exciplex lifetime is shortened. This strongly suggests that ion-pairs are formed from the exciplex in this particular system.

From the plot in Figure 1, a linear free energy relationship exists between fluorescence quenching rate for the series of naphthalenes (measured by Stern–Volmer slope divided by lifetime = K_{SV}/τ), and the sum of the substituent σ-constants.‡ Although we do not know the precise interpretation

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‡ σ-values (σ-*para*) were taken from L. P. Hammett 'Physical Organic Chemistry,' 2nd Edn., McGraw-Hill, 1970, p. 356. The additivity principle for substituent constants was used (C. D. Johnson, 'The Hammett Equation,' Cambridge University Press, 1973, pp. 164, 166). Since α- and β-methylnaphthalenes are different (points 2 and 3 on plot), different substituent constants were used for α- and β-methyl groups. σ_β was taken as -0.17, and a value of -0.42 calculated for σ_α using the difference in k_{SV}/τ between α- and β-methylnaphthalenes.

Table 1. Salt effects on exciplex fluorescence from 1-naphthonitrile–tetramethylethylene.[a]

Solvent	Salt (M)	Fluorescence quantum yield[b]	Exciplex lifetime/ns[c]	Radiative decay constant (k_f)/s^{-1}[e]
Dimethoxyethane	0	0.051	9.70	5.25×10^6
Dimethoxyethane	NBu_4BF_4(0.1)	0.012	2.10	5.60×10^6
Bu^{t}OH[d]	0	0.055	14.66	3.75×10^6
Bu^{t}OH[d]	$LiClO_4$(0.05)	0.029	7.38	3.98×10^6
Bu^{t}OH[d]	$LiClO_4$(0.1)	0.019	5.10	3.76×10^6

[a] Measurements carried out at limiting olefin concentration (1.0 M) and 10^{-4} M naphthonitrile. [b] Excitation was at 310 nm, emission maximum at 435 nm. [c] Lifetime measured by single photon counting technique (ref. 6d). All samples were deoxygenated by argon purging (fluorescence) or freeze–pump–thaw (lifetime). [d] Solution contained 10% dimethoxyethane. [e] Calculated using (quantum yield) = k_f × (lifetime).

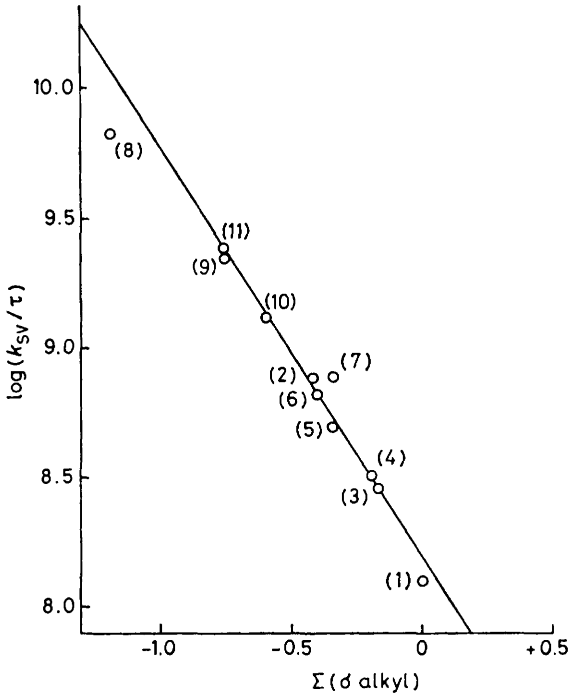

Figure 1. Hammett plot of quenching rate for a series of alkylnaphthalenes (fluorescers) by acrylonitrile in 95% ethanol. Fluorescers were (1), naphthalene; (2), 1-methyl-; (3), 2-methyl-; (4), 2-t-butyl-; (5), 2,6-dimethyl-; (6), 2,6-di-t-butyl-; (7), 2,3-dimethyl-; (8), 1,2,3,4-tetramethyl-; (9), 1,2,3-trimethyl-; (10), 2,3,6-trimethyl-; (11), 2,3,5-trimethyl-naphthalene. Least-squares treatment gave log(k_{SV}/τ) = 8.196—1.613Σ(σ)‡ with correlation coefficient of −0.982. Point (8) was not included (diffusion controlled rate).

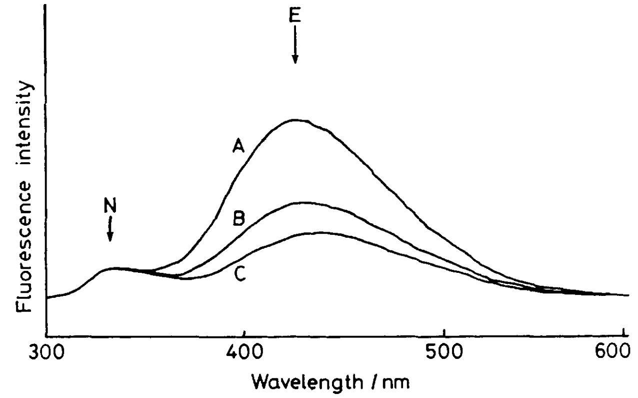

Figure 2. Fluorescence spectra of 1-naphthonitrile–tetramethylethylene at limiting (1.0 M) alkene concentration. Exciplex (E) (435 nm) and 1-naphthonitrile (N) (340 nm) are visible. A, no salt, B, 0.05 M $LiClO_4$; C, 0.1 M $LiClO_4$. Solvent was 10% dimethoxyethane in t-butyl alcohol.

of K_{SV}/τ,§ the plot allows us to deduce the mechanism of the quenching process. The plot has slope $\rho = -1.613$, indicating formation of moderately polar complexes with partial positive charge on the naphthalene ring.¶ Apparently ion-pair formation is not involved, since ρ should be more negative if the naphthalene radical-cation or an exciplex with a full positive charge in the naphthalene ring was formed.¶ Also interesting is the faster quenching of t-butylnaphthalenes *vs.* the corresponding methyl compounds, showing that electronic and not steric factors are important in exciplex formation. This is consistent with our results on the formation of fluorescent exciplexes.[6d]

The effect of added salt on the exciplex fluorescence of 1-cyanonaphthalene–tetramethylethylene is shown in Figure 2 and Table 1. In the medium-polarity solvents dimethoxyethane (dielectric constant $\epsilon = 3.49$) and t-butyl alcohol ($\epsilon = 10.9$) both tetra-n-butylammonium fluoroborate and lithium perchlorate quench the exciplex fluorescence and shorten the exciplex lifetime. The naphthonitrile fluorescence is not affected, and indeed, exciplex formation should be irreversible in these solvents.[4a,b] Although we have not observed the ions directly, we suggest that the above quenching is due to a primary salt effect which increases the rate of ionic dissociation from the exciplex. Salt effects are widely used in ground state chemistry, but *until* recently[11] have not been employed to study photodissociation processes. These salts are stable to oxidation and reduction,[12] and have no low-lying excited states, precluding quenching *via* electron- or energy-transfer. In the solvents used, some ions should be formed in the absence of salt.[3] Interestingly, the exciplex radiative decay constant k_f (Table 1) is unaffected by salt, whose major effect should be on the ion pair and not on the exciplex structure. This contrasts with the solvent effect on k_f.[13]

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§ For discussion, we assume that k_{SV}/τ is a bimolecular rate constant (k_q); although if quenching is reversible, k_{SV}/τ is a more complex function of rate constants and the exciplex lifetime (ref. 4a). Since no exciplex emission is observed, a full kinetic analysis is difficult.

¶ For comparison, reaction of phenols with acetyl bromide has $\rho = -1.45$; reactions in which a full positive charge is developed have $\rho = -3.00$ to -5.00 (K. B. Wiberg, 'Physical Organic Chemistry,' Wiley, New York, 1964, p. 404).

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