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Bimolecular Decay Routes in the Singlet Quenching of Naphthalenes by Chloroacetonitrile

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Abstract: The fluorescence of naphthalene, 2-methoxynaphthalene, 2,6-dimethoxynaphthalene, and 1,4-dimethoxynaphthalene is quenched by chloroacetonitrile in acetonitrile solution. Quenching rate constants span almost three orders of magnitude. Excited triplet states result from quenching three of the naphthalenes and photochemical reaction is also observed. Radical cations of 2,6- and 1,4-dimethoxynaphthalene were observed by flash spectroscopy. The quantum yields for quenching induced triplet formation and limiting yields of photoproducts (as measured by HCl formation) permit elucidation of the consequences of the quenching process.

A topic of current interest in organic photochemistry is the quenching of electronically excited states by compounds not able to accept energy by classical energy transfer. One aspect of this problem with which we and others have been concerned is the quenching of electron rich aromatics by compounds containing an activated C–Cl or similar bond.[3,4] In particular, we were interested in gaining more specific information as to the precise pathways and consequences of singlet quenching in these systems.

We recently reported a method for the determination of intersystem crossing quantum yields of benzene derivatives which is also useful for other systems in which aromatic triplet-triplet absorption cannot be conveniently measured.[5] The method is based on the enhancement of intersystem crossing in the aromatic by a heavy atom additive such as xenon and determination of increased triplet formation by a chemical "triplet counter". For xenon the only effect of quenching aromatic singlets is assumed to be formation of the aromatic triplet. We pointed out, however, that for other quenchers triplet formation might be only one of the consequences of singlet quenching and that the method could be extended to the determination of the fraction of quenching events which produce triplets if the intersystem crossing quantum yield of the aromatic were independently known. We now report the measurement of triplet formation associated with the singlet quenching of naphthalenes by chloroacetonitrile which, with other results, clarifies the effects of methoxy substitution on the bimolecular decay modes of the naphthalene-chloroacetonitrile system.

Results

Rate constants for chloroacetonitrile quenching of the fluorescence of naphthalene and three methoxy-substituted naphthalenes in acetonitrile solution were determined according to usual Stern–Volmer kinetics and are given in Table I. The agreement of quenching rate constants determined from fluorescence intensities and from fluorescence lifetimes indicates that the quenching we are observing is indeed a dynamic process. Although they increase with increasing methoxy substitution and span almost three orders of magnitude, these values by themselves tell us little about the ultimate consequences of the quenching act.

Preliminary experiments indicated that triplets, photoproducts (including HCl), and ions were produced upon irradiation of these systems. Our initial interest, therefore, was in determining whether quenching-induced triplet formation occurred and, if so, the quantum yield for this process. On the basis of the mechanism outlined in eq 1–11 and under the condition of constant light dose, this fraction can be obtained from relative fluorescence intensities of the aromatic (A) and relative conversions of a triplet counter as a function of quencher (Q) concentration. The triplet counter used in these experiments was *cis*-piperylene (*cis*-P) and the appearance of *trans*-piperylene (*trans*-P) was monitored by GLC. The relationship between these quantities is expressed in eq 12, the derivation of which has been outlined previously.[5] The symbol β is used for the ratio $k_7/(k_7 + k_8)$. Since the fluorescence quenching rate constant (k_q) equals $[k_6(k_7 + k_8)]/(k_{-6} + k_7$

Table I. Fluorescence Quenching Data

Compd	τ, ns	k_q,[a] $M^{-1} s^{-1} \times 10^{-7}$	k_q,[b] $M^{-1} s^{-1} \times 10^{-7}$
Naphthalene	95 ± 5	0.84	0.97
2-Methoxynaphthalene	16 ± 1	8.9	12
2,6-Dimethoxynaphthalene	12 ± 1	20	22
1,4-Dimethoxynaphthalene	5.7 ± 0.5	700	600

[a] From fluorescence intensities, ±20%. [b] From fluorescence lifetimes, ±20%.

Table II. Triplet Formation Data

Compd	β/Φ_{isc}[a]	Φ_{isc}	β
Naphthalene	0.72 ± 0.05	0.80	0.58 ± 0.05
2-Methoxynaphthalene	0.31 ± 0.05	0.55[b]	0.17 ± 0.03
2,6-Dimethoxynaphthalene	0.13 ± 0.05	0.51[b]	0.07 ± 0.04
1,4-Dimethoxynaphthalene	0 ± 0.02	0.50[b]	0 ± 0.02

[a] From plots of eq 12. [b] Calculated as $1 - \Phi_f$, ±10%.

Table III. Calculation of Quenching Parameters

Compd	$(k_6/k_{-6})k_7 \times 10^{-7}$, $M^{-1} s^{-1}$[a]	$(k_6/k_{-6})k_8 \times 10^{-7}$, $M^{-1} s^{-1}$[b]
Naphthalene	0.5	0.3
2-Methoxynaphthalene	1.5	7.4
2,6-Dimethoxynaphthalene	1.5	18
1,4-Dimethoxynaphthalene	≤20[c]	1100

[a] Calculated from eq 13. [b] Calculated from eq 14. [c] Calculated from maximum experimental uncertainty in β.

$+ k_8$), the individual components of k_q can be calculated from eq 13 and 14,[6] taking $k_6 = 2 \times 10^{10}\ M^{-1} s^{-1}$.[7]

$$\mathrm{N} \xrightarrow{h\nu} \mathrm{N}^{*1} \tag{1}$$

$$\mathrm{N}^{*1} \xrightarrow{k_2} \mathrm{N} + h\nu' \tag{2}$$

$$\mathrm{N}^{*1} \xrightarrow{k_3} \mathrm{N}^{*3} \tag{3}$$

$$\mathrm{N}^{*1} \xrightarrow{k_4} \mathrm{N} \tag{4}$$

$$cis\text{-P} + \mathrm{N}^{*1} \xrightarrow{k_5} \mathrm{N} + cis\text{-P} \tag{5}$$

$$\mathrm{Q} + \mathrm{N}^{*1} \underset{k_{-6}}{\overset{k_6}{\rightleftarrows}} (\mathrm{NQ})^{*1} \tag{6}$$

$$(\mathrm{NQ})^{*1} \xrightarrow{k_7} \mathrm{N}^{*3} + \mathrm{Q} \tag{7}$$

$$(\mathrm{NQ})^{*1} \xrightarrow{k_8} \text{all other quenching processes} \tag{8}$$

$$\mathrm{N}^{*3} \xrightarrow{k_9} \mathrm{N} \tag{9}$$

$$cis\text{-P} + \mathrm{N}^{*3} \xrightarrow{k_{10}} \mathrm{N} + \mathrm{P}^{*3} \tag{10}$$

$$\mathrm{P}^{*3} \xrightarrow{k_{11}} \alpha\ trans\text{-P} + (1 - \alpha)\ cis\text{-P} \tag{11}$$

$$(Y_T F'/Y_T' F) - 1 = (\beta/\Phi_{isc})(F^0/F')[(F'/F) - 1] \tag{12}$$

$$(k_6/k_{-6})k_7 = k_q\beta/[1 - (k_q/k_6)] \tag{13}$$

$$(k_6/k_{-6})k_8 = k_q(1 - \beta)/[1 - (k_q/k_6)] \tag{14}$$

Experimentally, we measured relative fluorescence intensities for the aromatic in the absence of any quenchers, in the presence of a constant concentration of a triplet counter only, and in a series of solutions containing the same constant concentration of triplet counter, but with varying concentrations of the quencher chloroacetonitrile (F^0, F', and F, respectively).

As predicted by eq 12, plots of $(Y_T/Y_T')(F'/F) - 1$ vs. $(F^0/F')[(F'/F) - 1]$ were linear and values of β/Φ_{isc} were obtained from the slopes. These values, which are listed in Table II and which represent the average of two or more independent determinations, indicate that aromatic triplet states are formed via singlet quenching with three of the naphthalenes. Since it was apparent from these data that the exact value of β would be relatively insensitive to the precise value of Φ_{isc}, and since internal conversion processes such as eq 4 are known to be insignificant for most aromatic hydrocarbons,[8] Φ_{isc} was approximated as $1 - \Phi_f$. Values of β calculated in this manner are also listed in Table II. Table III lists the values of the components of k_q calculated from eq 13 and 14.

Although there are a number of possible complications to this method, they were not included in the kinetic scheme because they are probably not important in the present case. For example, singlet quenching of naphthalenes by conjugated dienes is known not to yield triplets.[12] Moreover, values of β/Φ_{isc} were unaffected by changes in the triplet counter concentration. Furthermore, there was no measurable disappearance of the diene and no detectable isomerization of the diene in the dark either before or after irradiation. Although radical ions were formed in the quenching process (vide infra), we could account for all of the diene after irradiation and were unable to detect isomerization resulting from the quenching act in the case of 1,4-dimethoxynaphthalene. These observations would appear to rule out photochemically induced radical isomerization of the diene as a significant complication in the present application of the method.

Since values of β (quenching-induced intersystem crossing) were smaller than values of Φ_{isc} (unimolecular intersystem crossing), we carried out flash spectroscopic studies on the methoxynaphthalenes. In agreement with the steady state

Table IV. HCl Yield Data

Compd	Intercept/slope, M^{-1} [a]	$k_q\tau_f^0$, M^{-1} [b]	Φ_{HCl}^{∞} [a,c]	$\Phi_{HCl}^{\infty}/(1-\beta)$
Naphthalene	0.81	0.80	0.03	0.07 ± 0.02
2-Methoxynaphthalene	1.4	1.42	0.05	0.06 ± 0.01
2,6-Dimethoxynaphthalene	2.0	2.4	0.07	0.07_5 ± 0.01
1,4-Dimethoxynaphthalene	37	40	0.10	0.10 ± 0.01

[a] From plots of $1/\Phi_{HCl}$ vs. $1/[ClCH_2CN]$, ±25%. [b] From fluorescence intensities, ±20%. [c] Calculated as 1/intercept.

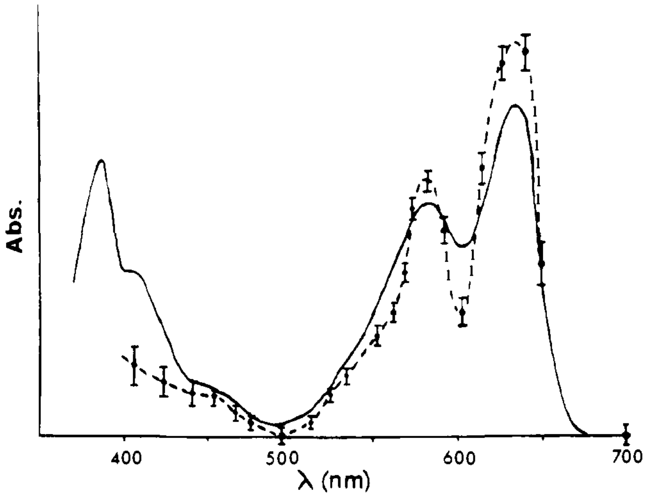

Figure 1. Spectrum of the transient observed in the chloroacetonitrile quenching of 2,6-dimethoxynaphthalene fluorescence in acetonitrile solution (- - -) and that of the radical cation of 2,6-dimethoxynaphthalene in a boric acid glass (—).

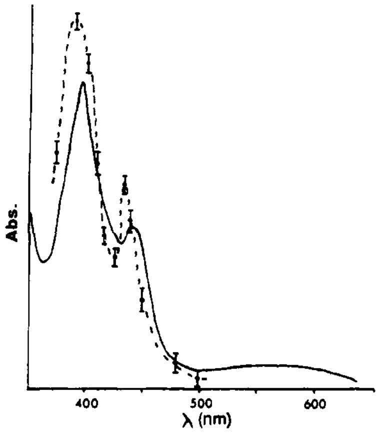

Figure 2. Spectrum of the transient observed in the chloroacetonitrile quenching of 1,4-dimethoxynaphthalene fluorescence in acetonitrile solution (- - -) and that of the radical cation of 1,4-dimethoxynaphthalene in a boric acid glass (—).

results, the intensity of 2-methoxy- and 2,6-dimethoxynaphthalene triplet-triplet absorption decreased with increasing chloroacetonitrile concentration, confirming that quenching-induced intersystem crossing was less efficient than intersystem crossing from the unperturbed excited singlet state. In both cases the triplet lifetimes (ca. 100 μs) appeared to be unaffected by the presence of chloroacetonitrile (up to ca. 0.6 M), indicating that triplet quenching by chloroacetonitrile is relatively inefficient.

Quantitative analysis of the flash experiments was precluded by the appearance of new, long-lived (greater than 1 ms) transients when the methoxynaphthalenes were flashed in the presence of chloroacetonitrile. These transients decayed by a combination of second- and pseudo-first-order kinetics and their intensities increased with increasing chloroacetonitrile concentration. Flashing in the presence of oxygen (air) resulted in complete quenching of the triplet-triplet absorption, but only partial (ca. 50%) quenching of the long-lived transient absorption. These observations suggest that the long-lived transients derive from the singlet quenching act. Absorption spectra of the long-lived transients were obtained with 2,6- and 1,4-dimethoxynaphthalene and are shown in Figures 1 and 2.[13] These transients were identified as radical cations by the similarity of their spectra to those obtained upon irradiation of the aromatic in a boric acid glass,[17] a method known to produce the radical cations via biphotonic ionization.[18]

The observation of radical cations is consistent with mechanisms proposed for the formation of photoproducts in similar systems.[19-21] In the present study gas chromatographic analysis of preparative irradiations of 2,6- or 1,4-dimethoxynaphthalene-chloroacetonitrile systems indicated rather complex product mixtures. Attempts to isolate characterizable products by column and preparative gas chromatography were unsuccessful and indicated that at least part of the complexity of the mixtures was due to the instability of the products. Since hydrogen chloride formation accompanied the other products and was known to parallel photochemical reaction in similar systems,[3,19,20] we used the quantum yield for HCl formation (Φ_{HCl}) to monitor the extent of photochemical reaction resulting from quenching. Plots of $1/(\Phi_{HCl})$ vs. $1/[Q]$ were linear and had intercept/slope ratios in reasonable agreement with values of $k_q\tau^0$ determined from fluorescence data, as expected for products resulting from singlet quenching.[22] Limiting quantum yields for HCl formation at infinite quencher concentration (Φ_{HCl}^{∞}) were obtained from the reciprocal of the intercept. These data are collected in Table IV.

Discussion

The observation that radical cations result from the quenching act clearly suggests that electron transfer is associated with the quenching process at some point. If a simple outer sphere electron transfer were involved, the rate constant should be relatable to the singlet excitation energy of the aromatic and the appropriate redox potentials as demonstrated by Weller.[23] Strictly valid application of the Weller treatment requires, however, that the redox potentials be reversible (i.e., true $E_{1/2}$ values). The electrochemiluminescence data of Zweig[11] indicate reversibility of the electrochemical oxidation of the methoxynaphthalenes employed here. Gough and Peover[24] have concluded from cyclic voltammetry data that the oxidation of naphthalene and other unsubstituted aromatics involves reversible one-electron transfer followed by rapid chemical destruction of the radical cation. Despite the irreversibility of the measured oxidation potential of naphthalene on an electrochemical time scale, the measured potential should not differ from the true thermodynamic potential by more than about 0.1 V.[25] Based on data for the reduction of methyl chloroacetate[26,27] and for electron capture by chloroacetonitrile,[28] one can conclude that the electrochemical reduction of chloroacetonitrile is undoubtedly irreversible, with the electron addition being followed by rapid loss of chloride ion to give $\cdot CH_2CN$. Insufficient electrochemical data exist,

Table V. Calculation of Energy Parameters

Compd	ΔG_{et}, eV[a]	E_{et}, kcal/mol[b]	E_{T}, kcal/mol[c]	$E_{\mathrm{et}} - E_{\mathrm{T}}$, kcal/mol
Naphthalene	−0.74	74.7	60.6	14.1
2-Methoxynaphthalene	−0.55	74.3	62	12.3
2,6-Dimethoxynaphthalene	−0.59	69.9	61.4	8.5
1,4-Dimethoxynaphthalene	−0.65	64.6	60.3	4.3

[a] Calculated from eq 15. [b] Calculated from eq 16. [c] Maximum of highest energy phosphorescence band in EPA at 77 K.

however, to allow an estimate of the extent to which the measured reduction potential might differ from the true $E_{1/2}$.

Since the methoxynaphthalene oxidation potentials are reversible and the quencher is invariant, values of ΔG_{et} (Table V, calculated from eq 15 in the usual manner,[29] but with the nonreversible reduction potential of $\mathrm{ClCH_2CN}$), while lacking quantitative significance, should predict trends correctly.

$$\Delta G_{\mathrm{et}} = -\Delta E_{0,0} + E_{\mathrm{D/D^+}} - E_{\mathrm{A^-/A}} - 0.06 \text{ eV} \quad (15)$$

Although a trend in the appropriate direction is evident for the methoxynaphthalenes, quantitative correlation of k_q (or $k_q(1 - \beta)$, vide infra) within the framework of the Weller theory would require that the true $E_{1/2}$ for the reduction of chloroacetonitrile differ by −0.5 to −0.7 V (depending on the methoxynaphthalene) from the measured potential (−1.79 V vs. SCE)[4] and that for oxidation of naphthalene by at least 0.3 V. Thus, we are reluctant to accept outer sphere electron transfer in a simple encounter complex as the model for the quenching process.

The fact that we see such a large range in quenching rate constants severely limits our choice of alternative models. Our observation that excited triplet states, radical ions, and HCl formation are consequences of the singlet quenching act indicates that bimolecular association in the excited naphthalene–chloroacetonitrile system results in intermolecular interactions which are of sufficient magnitude to give rise to photophysics and photochemistry unique to the association. Furthermore, the fact that the observed values of k_q are significantly smaller than calculated or experimental values of the diffusion-controlled rate would imply that the association lifetime is *at least as long* as that for a noninteracting encounter complex (ca. 10^{-11} s).[34] Unique photobehavior and finite lifetime seem to us to be sufficient grounds for postulation (eq 6–8) of such an exciplex intermediate, regardless of the magnitude of the intermolecular interaction relative to kT.

The relative insensitivity of $(k_6/k_{-6})k_7$ to methoxy substitution implies that either such substitution has only a small effect on both the bimolecular association equilibrium (k_6/k_{-6}) and the intermolecular mixing which gives rise to triplets via k_7 or that changes in binding are largely offset by changes in k_7. Since we would anticipate that increased binding would lead in turn to stronger intermolecular mixing, we find the former alternative more appealing. This would imply that it is not perturbation of the binding equilibrium but, rather, enhancement of the other rates for exciplex reactivity (k_8) which is responsible for the large increase in $(k_6/k_{-6})k_8$ with increasing methoxy substitution. On the basis of these considerations, therefore, we propose that the binding in the intermediate exciplex state is at best weakly influenced by charge-transfer interactions, with the excitation remaining largely localized on the aromatic. We envision the formation of ion pair states as a subsequent process, the rate of which is governed by a substitution-dependent coupling of the exciplex and ion pair states.

In the above discussion, we have implicitly assumed that the triplets produced as a result of the quenching process are formed directly from the exciplex state. This assumption merits further consideration in view of the possibility that triplet states may result from radical anion–radical cation annihilation within the ion pair state.[35] The energies of the ion pair states calculated using the equation

$$E_{\mathrm{et}} = 23.06(E_{\mathrm{D/D^+}} - E_{\mathrm{A^-/A}} - 0.06) \text{ kcal/mol} \quad (16)$$

(and which therefore represent minimum values, vide supra) are listed in Table V. Since the naphthalene triplet energies are in the range of 60–62 kcal/mol (Table V), formation of triplet states via the ion pair annihilation route should be energetically feasible in all the systems. Although our data do not allow us to distinguish unambiguously between these two mechanisms, the lack of observable triplet formation in the quenching of 1,4-dimethoxynaphthalene[36] and the large yield in the case of naphthalene itself suggest to us that triplets are formed from the exciplex state in competition with formation of ion pair states.[37]

The flash results and the HCl yield data clearly imply that product formation is a consequence of the singlet quenching process. The limiting HCl yield per quench ($\Phi_{\mathrm{HCl}}{}^{\infty}$) tends to increase with increasing methoxy substitution of the aromatic, but this in itself is not very informative. However, if we utilize our conclusion that triplet formation and ion formation are competitive processes and calculate the limiting HCl yield per nontriplet-producing quench—a quantity given by the ratio $\Phi_{\mathrm{HCl}}{}^{\infty}/(1 - \beta)$, Table IV—we obtain values which are quite similar. Since these values are independent of bimolecular association equilibria, this similarity suggests a common mechanism of HCl formation for all of the naphthalenes. Furthermore, the observed values are comparable to estimates of cage escape probabilities for radical ions in acetonitrile (5–10% for a +1,−1 ion pair).[39] The most attractive mechanism is, therefore, one in which the nontriplet-producing quenching process (eq 8) is dominated by formation of ion pair states with relatively little contribution from other decay routes. Decomposition of the free chloroacetonitrile radical anion (by fast, irreversible expulsion of $\mathrm{Cl^-}$) following cage escape would lead ultimately to formation of HCl and a complex mixture of naphthalene-derived products resulting from reaction of the acetonitrile radical ($\cdot\mathrm{CH_2CN}$) with the aromatic and its radical cation.

Conclusion

Quenching rate constants are complex functions of association and reactivity. Substituent effects on k_q for a series of related compounds can result from changes in either or both. What is significant, therefore, is not k_q but, rather, the rates of the individual quenching processes. Our data suggest that in the systems studied here it is the rate of exciplex decay to ion-pair states and not bimolecular association which is strongly affected by methoxy substitution and which is the principal contributor to the substituent effects on k_q.

Although substituent effects on k_q are often interpreted in terms of binding alone, this study indicates that substituent effects on reactivities can in fact dominate. Our work emphasizes the inadequacies of using k_q values alone to develop models of bimolecular excited-state reactivity.

Experimental Section

Materials. Commercial samples of naphthalene, 2-methoxynaphthalene, and 2,6-dimethoxynaphthalene were purified by recrystallization from ethanol and by sublimation. 1,4-Dimethoxynaphthalene was prepared as described by Baker and Carlson[41] and purified by column chromatography (alumina) followed by three sublimations. The material used had mp 87–88 °C. Chloroacetonitrile (MCB) was distilled from P_2O_5 and from anhydrous K_2CO_3 and stored at less than 0 °C until use. Acetonitrile (MCB spectroquality) was used as received. *cis*-Piperylene (ChemSampCo) was distilled from $LiAlH_4$ and stored at less than 0 °C until use. *n*-Heptane (Phillips Research Grade) was purified by the method of Murray and Keller.[42]

Apparatus. Relative fluorescence intensities were measured with a Hitachi-Perkin Elmer MPF-3 fluorescence spectrophotometer. GLC analyses were performed with a Hewlett-Packard Model 700 gas chromatograph (flame ionization detection), and peak integrals were measured by means of a Hewlett-Packard Model 3307B electronic integrator. Flash photolysis experiments were performed with two different instruments, both of which have been described.[43,44] The pH determinations were made with a Corning Model 610 pH meter. Absorption spectra were determined with a Cary Model 14 spectrophotometer. Singlet lifetimes were determined with a TRW Model 31A Nanosecond Spectral Source (D_2 lamp) with decay time computer coupled to either a Tektronix Type 556 dual beam oscilloscope or a Tektronix 7704 oscilloscope operated in the dual-trace dual-sweep-rate mode.

Triplet Yield Experiments. Solutions were prepared containing (1) only the aromatic, (2) the same concentration of aromatic as in (1) plus *cis*-piperylene (0.05–1.0 M) and *n*-heptane as internal standard, and (3) the same concentrations of aromatic, *cis*-piperylene, and *n*-heptane as in (2) plus varying concentrations of chloroacetonitrile. Aliquots (4.0 mL) of these solutions were transferred via syringe to clean, dry preconstricted test tubes and degassed by three freeze–pump–thaw cycles (pressure less than 5×10^{-4} Torr) on a mercury-free vacuum line and the tubes then sealed. After equilibration to room temperature in the dark, relative fluorescence intensities were recorded. The tubes were then irradiated simultaneously (constant dose) at 313 nm in a merry-go-round apparatus.[45] Conversions of *cis*- to *trans*-piperylene were low (less than 3%) in all cases. *trans*-Piperylene analyses were performed by GLC on a column consisting of 7 × ⅛ in. of 10% UCW-98 and 22 ft × ⅛ in. of 25% β,β'-oxydipropionitrile plus 5% $AgNO_3$ on Chromosorb P, operated at room temperature. The internal standard was *n*-heptane. The data were treated according to eq 11 as described in the Results section.

Flash Photolysis Experiments. Kinetic flash experiments were performed with the apparatus at California State University Fullerton.[43] For the observation of transient decay kinetics, acetonitrile solutions of the aromatic were degassed in conventional 20-cm path length "T" cells by four freeze–pump–thaw cycles (pressure < 10^{-5} Torr) on a mercury-free vacuum line. Absorption spectra of the long-lived transients were determined point-by-point on the flash apparatus at UNC.[44] Solutions were contained in 5-cm path length cells and were not degassed (in order to avoid interference from triplet–triplet absorption).

Generation of Radical Cations in a Boric Acid Matrix. 2,6-Dimethoxynaphthalene (ca. 1 mg) was mixed with boric acid (ca. 500 mg) on a microscope slide which had been coated with silicone oil (General Electric). The slide was heated at 240 °C in a muffle furnace for 7 min, then removed. The hot syrupy boric acid matrix was covered with another hot microscope slide which was applied with only light pressure. After the slides had cooled to room temperature and the boric acid matrix had hardened, an absorption spectrum of the slide assembly vs. air was recorded. The slide assembly was then suspended immediately in front of a quartz immersion lamp well and irradiated with a 450-W medium pressure mercury lamp filtered through a Kimax sleeve. After ca. 1.5 h a blue color developed in the boric acid matrix. An absorption spectrum of the slide assembly was again recorded and the baseline from the first spectrum was subtracted to give the absorption due to the radical cation. The absorption spectrum for the radical cation of 1,4-dimethoxynaphthalene was recorded in a similar manner.

HCl Yield Experiments. A set of solutions was prepared containing a constant concentration of the naphthalene derivative (0.02–0.025 M) and increasing concentrations of chloroacetonitrile. Aliquots (3.0 mL) were transferred to test tubes and degassed as described for the triplet yield experiments. The tubes were irradiated simultaneously at 313 nm in a merry-go-round apparatus and light intensities were monitored with potassium ferrioxalate actinometry.[46] At the end of the irradiation, the tubes were opened and their contents quantitatively diluted to 10.0 mL with 0.143 M aqueous NaCl (to give a final ionic strength of 0.1 M). Values of the pH of these and of similarly diluted but unirradiated aliquots allowed determination of the concentration of HCl produced as a result of irradiation. These data were used to calculate Φ_{HCl} as a function of chloroacetonitrile concentration.

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Aromatic Protonation. 12. Solvent Isotope Effects in H_2O-D_2O Mixtures on the Detritiation of Trimethoxybenzene[1,2]

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Abstract: The problem of kinetic solvent isotope effects in H_2O-D_2O mixtures on systems for which proton transfer from H_3O^+ and some subsequent reaction step are each partly rate determining is considered, and an expression relating the isotope effect to the atom fraction of deuterium in the solvent is derived for a symmetrical isotope exchange process such as acid-catalyzed aromatic hydrogen exchange. This expression is then applied to data presented here for the detritiation of 1,3,5-trimethoxybenzene-*2-t* as well as to literature values for the same reaction and the detritiation of azulene-*1-t*. The analysis yields isotopic (Bronsted) exponents, $\alpha_i = 0.67$ for trimethoxybenzene and $\alpha_i = 0.57$ for azulene, which are not affected substantially by inclusion of corrections for nonadherence to the rule of the geometric mean and which are in good agreement with conventional Bronsted exponents as well as other measures of transition-state structure for these reactions.

Solvent isotope effects in mixtures of light and heavy water have excited the interest of chemists studying acid-base catalysis almost since the discovery of deuterium in 1932. This long history has produced a simple theory[6] which provides a good first approximation to complete quantitative interpretation of both kinetic and equilibrium phenomena in H_2O-D_2O mixtures. Enough is understood, moreover, about some of the assumptions upon which this theory is based, such as neglect of medium effects or adherence to the rule of the geometric mean, to permit their removal, and thus to provide a second level of understanding, albeit at a considerable reduction in simplicity.[7]

This simple theory uses fractionation factors (D/H ratios at particular exchangeable sites relative to the D/H ratio of the solvent) to relate rate or equilibrium constants measured in H_2O-D_2O mixtures to the deuterium content of the solvent. In favorable situations, these fractionation factors may be evaluated from the experimental data and, through them, information about reaction mechanism and/or transition state structure may be gained.

Application of the simple theory to equilibria is straightforward, as it is also to rates of even complex reactions, provided that a single step is wholly rate determining. When two or more steps are each partly rate determining, however, the analysis becomes considerably more difficult. Consider, for example, the reaction sequence shown in Scheme I. When the proton transfer step (k_1) is wholly rate determining, the dependence of rate upon isotopic content of the medium is given by

Scheme I

$$\mathrm{S} + \mathrm{H_3O^+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{SH^+} + \mathrm{H_2O}$$

$$\mathrm{SH^+} + \mathrm{H_2O} \xrightarrow{k_2} \mathrm{H_2O\text{-}SH^+} \xrightarrow{\text{fast}} \text{products}$$

$$\frac{k_x}{k_H} \frac{(1 - x + x\phi_1{}^{\ddagger})(1 - x + x\phi_2{}^{\ddagger})^2}{(1 - x + xl)^3} \qquad (1)$$

where k_H and k_x are rate constants for reactions in pure H_2O and an H_2O-D_2O mixture of atom fraction x, respectively, and l, $\phi_1{}^{\ddagger}$, are fractionation factors for the hydronium ion and the isotopically equilibrated positions of the proton transfer transition state **1**. The analysis is equally straightforward when