tion that the differences in activation entropies seen in aqueous solution are due to different extents of hydration of the transition state.

It is interesting to note that whereas the enthalpies of activation favor reaction at the α position, the entropies favor reaction at the β position. This opposing tendency results in a leveling effect on the reactivities of the two positions. These results indicate that caution must be exercised in the comparison of calculated reactivities with activation free energies for reactions involving highly solvated reactants. The validity of making such correlations must depend in this case upon the existence of a linear relationship between heats and entropies of activation.

Experimental Section

The α- and β-deuterionaphthalenes were synthesized from commercially available 1- and 2-bromonaphthalene, by hydrolyzing the corresponding Grignard reagents with D_2O. The two isotopically substituted naphthalenes were purified by vacuum sublimation three times, and the melting point was determined to be 80–81°. The isotopic purity was determined by mass spectral analysis. This analysis showed the β-deuterionaphthalene sample to contain approximately 90% monodeuterated compound and 10% naphthalene-h_8, while analysis of the α-deuterionaphthalene sample showed 91% monodeuterated compound and 9% naphthalene-h_8. No further isotopically substituted species were detected. Infrared analysis of the two samples showed less than 1% of the α isomer to be present in the β-deuterionaphthalene sample and placed an upper limit of 4% on the amount of β isomer present in the α-deuterionaphthalene sample. Examination of the 1-bromonaphthalene starting material by means of vapor phase chromatography showed that there was less than 1% of the 2-bromo isomer present. Assuming that no appreciable rearrangement occurred during the isotopic synthesis, this places an upper limit of 1% on the amount of β isomer present in the α sample.

The solutions of naphthalene in sulfuric acid were prepared in the following manner. A solution of approximately 50% sulfuric acid was prepared by dilution of concentrated acid with distilled water. The appropriate isotopic naphthalenes were then dissolved in the acid by shaking for several minutes at elevated temperatures (*ca.* 60°). The solutions were then filtered through a fritted glass funnel to remove undissolved naphthalene. Appropriate amounts of concentrated sulfuric acid were added to make up the solutions of desired acid strength. The exact acid concentration was determined by measurement of the specific gravity of samples of each solution. The range of acid concentrations employed in this study was approximately 50–67% by weight. The concentration of naphthalene in the solutions was estimated spectrophotometrically using a Cary 14 spectrophotometer and ranged from approximately 2×10^{-5} to 4×10^{-5} *M*.

Immediately after preparation, five aliquot samples of each solution were placed into small test tubes and sealed with paraffin. Each of the samples was then placed into one of five constant-temperature baths and the time recorded. After an appropriate time period the reaction was quenched by rapid cooling. The naphthalene was then removed from solution by bubbling a stream of N_2 gas through the cold solution. The sample tube was stoppered with a cap containing influent and effluent tubes of capillary Teflon. A glass capillary tube, cooled in the middle by liquid nitrogen, was connected to the effluent side where the purged naphthalene was condensed. The glass capillary tube was then sealed and the samples were subjected to mass spectral analysis.

The extent of reaction was determined by analyzing each sample mass spectroscopically using a Varian MAT-CH-5 high resolution single focusing instrument and employing an electron accelerating voltage setting of 16 eV. This voltage setting was determined to be less than that necessary to cause fragmentation of the naphthalene cation. The average ratio of peak heights due to mass 128 and 129 was obtained by repeated scanning in this range and the uncertainty in the average values was ascertained to be less than 1% in most cases.

Acknowledgments. The support of this work by the National Science Foundation is gratefully acknowledged. One of us (C. G. S.) also acknowledges the support of a NDEA Fellowship and a NASA Training Grant during the course of this work.

Excited State Hydrogen–Deuterium Exchange and Fluorescence Quenching of Naphthalene in Sulfuric Acid Solutions

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Abstract: The quantum yields of photoinduced hydrogen–deuterium exchange of α- and β-naphthalene-d_1 have been measured in moderately concentrated H_2SO_4. In the range of 54–67% acid the reactivity of the β position exceeds that at the α position by about 15% in marked contrast to the ground-state results. Fluorescence quenching has been measured as a function of acid concentration and temperature; it is found to vary linearly with Hammett acidity and to have an activation energy of about 3–5 kcal/mol. A kinetic scheme is proposed in which both quenching and exchange proceed *via* the formation of a symmetrical intermediate by protonation of the first excited singlet state.

The study of photoinduced aromatic substitution reactions, in particular hydrogen isotopic exchange, has only recently been the subject of experimental investigation.[1–4] These studies have demonstrated a pronounced enhancement of reaction rates, and in one case[1c] interesting changes in the relative positional reactivities have been observed upon molecular ex-

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[1] (a) E. Havinga, R. O. de Jongh, and W. Dorst, *Recl. Trav. Chim. Pays-Bas*, **75**, 378 (1956); (b) E. Havinga and M. E. Kronenberg, *Pure Appl. Chem.*, **16**, 137 (1968); (c) D. A. de Bie and E. Havinga, *Tetrahedron*, **21**, 2395 (1965).

[2] J. P. Colpa, C. Maclean, and E. L. Mackor, *Tetrahedron Suppl. 2*, 65 (1963).

[3] M. G. Kuz'min, B. M. Uehinov, G. Szent György, and I. V. Berezin, *Russ. J. Phys. Chem.*, **41**, 400 (1967).

[4] G. F. Vesley, *J. Phys. Chem.*, **75**, 1775 (1971).

citation. Examination of photoinduced reactions under conditions such that the corresponding ground-state reactions can also be measured allows a direct comparison of the chemical properties of the ground and excited states. This in turn provides an additional criterion for testing various quantum mechanical reactivity theories which have been used to describe these reactions.[5]

In the following we report a study of the positional reactivity of photoinduced dedeuteration of α- and β-naphthalene-d_1 in aqueous H_2SO_4 solutions as well as acid-induced quenching of the lowest singlet and triplet states of naphthalene. The results are interpreted in terms of a mechanism involving formation of a σ-type intermediate in the excited state followed by a radiationless return to the ground state.

Investigations and Results

H–D Exchange Quantum Yields. The most commonly used technique for the determination of quantum yields of photochemical reactions involves the total absorption of light by the reacting species. This method offers the advantages of efficient use of the light and direct methods of determining the amount of light absorbed. In the case of naphthalene in aqueous H_2SO_4, however, the low solubility coupled with the low molar absorptivity of the first electronic transition renders this method impractical. Furthermore, under conditions of high absorbance the reaction cannot be allowed to proceed too far lest the inner filtering effect of the products obscure the determination of the amount of light actually absorbed by the reactant. We examined the exchange reaction using an alternative approach which involved low absorbances (<0.02 optical density), where the absorbing species act independently and the total absorbance is the simple sum of the individual absorbances. Under these conditions the rate of light absorption by the deuterated naphthalenes is given to a good approximation by $I_a = 2.303 I_0 \bar{\epsilon}[\mathrm{ND}]$ for unit path length, where I_0 is the photon flux through the solution, $\bar{\epsilon}$ is an effective molar extinction coefficient, and [ND] is the concentration of deuterated naphthalene. The use of an effective extinction coefficient is necessitated by the finite band width of the excitation used. The extent of exchange was monitored mass spectrometrically, and under the conditions of the experiments (low absorbances) the quantum yield for exchange is given by the expression

$$\Phi_{\mathrm{ex}} = \frac{\log[(1 + R)/(1 + R_{\mathrm{G}})]}{I_0 t \bar{\epsilon}} \qquad (1)$$

for unit path length. In this expression t is the time of irradiation, R is the ratio of naphthalene to naphthalene-d_1, and R_G is the same ratio for the corresponding dark reaction run under otherwise identical conditions.

Two apparatuses were used in the quantum yield determinations and are described in the Experimental Section. Apparatus I was used to measure quantum yields of several solutions directly against a potassium ferrioxalate standard actinometer.[6] The majority of the determinations, particularly at low acid concentrations, were made with apparatus II because of a considerable increase in light intensity. A concentration matched solution of α-naphthalene-d_1, whose quantum yield was carefully measured with apparatus I, was used as a secondary actinometric standard in this apparatus.

To the extent that the conditions necessary for the validity of expression 1 are met, $\log[(1 + R)/(1 + R_G)]$ should be directly proportional to the total light exposure ($I_0 t$) and should be independent of naphthalene concentration. This was verified for up to 16% exchange and for concentrations of naphthalene up to $7 \times 10^{-5}\ M$. All runs were made within these limits.

The photoinduced exchange reactions of both α- and β-naphthalene-d_1 were studied in aqueous H_2SO_4 ranging in composition from 30 to 67% by weight at a constant temperature of 25.6 ± 0.2°. The quantum yields were calculated by means of expression 1 using a value of 135 l. mol^{-1} cm^{-1} for $\bar{\epsilon}$, and the results are shown in Table I. The quantum yields show a marked dependence upon the acid composition, particularly in the less acidic region. In the range 54–64% the quantum yields for exchange at the β position are larger than those at the α position by approximately 15%, a result which contrasts dramatically with ground-state exchange at these positions.[7] Near 50% acid composition, the relative quantum yields appear to reverse in value with the yield at the α position becoming increasingly larger than at the β position as the acidity decreases.

Table I. Absolute Quantum Yields for Hydrogen–Deuterium Exchange of Deuterionaphthalenes

α-Naphthalene-d_1		β-Naphthalene-d_1	
% H_2SO_4	$10^2\Phi_{ex}$	% H_2SO_4	$10^2\Phi_{ex}$
		66.3	3.7 ± 0.3
63.8	3.26	63.9	3.46
61.4	2.75 ± 0.03	61.4	3.16 ± 0.02
58.8	1.86 ± 0.09	58.8	2.11 ± 0.02
58.7	1.76 ± 0.07	58.7	2.06 ± 0.07
		56.7	1.68
56.4	1.39 ± 0.02	56.3	1.58 ± 0.02
54.1	1.02	54.1	1.13
51.5	0.71	51.4	0.72
49.8	0.69	50.1	0.62
36.5	0.092	36.5	0.058
30.1	0.019	30.1	0.010

The effect of oxygen on the exchange quantum yield was investigated in 30.1% H_2SO_4. After extensive degassing the quantum yields for α- and β-naphthalene-d_1 were found to be $1 \pm 1 \times 10^{-4}$ and $2 \pm 1 \times 10^{-4}$, respectively. The rather large limits of error were the result of uncertainty in the amount of exchange taking place in the ground state coupled with the rather small amount of exchange that took place by irradiation. The results, however, do show that within the limits of error the quantum yields are the same as in the presence of oxygen at its ambient concentration.

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(5) See L. Salem, "Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966, Chapter 6, and references therein.

(6) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

(7) Preceding paper: C. G. Stevens and S. J. Strickler, *J. Amer. Chem. Soc.*, **95**, 3918 (1973).

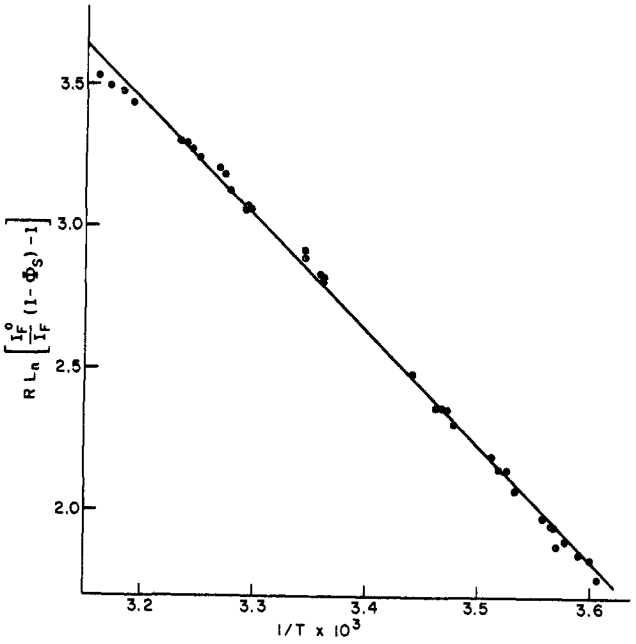

Figure 1. Arrhenius-type plot of fluorescence quenching of naphthalene as a function of temperature in 64.5% H_2SO_4.

An investigation of possible isotope effects was made by studying the exchange of naphthalene-h_8 in D_2SO_4 at the molar equivalent of 57.1% H_2SO_4. Högfeldt and Bigeleisen[8] have shown that the protonating abilities of D_2SO_4 and H_2SO_4 are identical at equimolar concentrations. The results show the ratio of quantum efficiencies for exchange of the naphthalene–D_2SO_4 to the deuterionaphthalene–H_2SO_4 system to be 1.1 ± 0.35. Unfortunately, some impurity was present in the D_2SO_4 which absorbed light in the region of excitation, and the limits of error represent the uncertainty with which the inner filtering effect could be estimated.

Fluorescence Quenching. Quenching of naphthalene fluorescence in aqueous H_2SO_4 was examined quantitatively both as a function of acid concentration and temperature. Using the apparatus described in the Experimental Section, the intensity of fluorescence, I_F, is given by the expression $I_F = K\phi_F I_a$, where ϕ_F is the quantum yield of fluorescence, I_a is the rate of light absorption, and K is a geometrical factor. The fluorescence intensity of naphthalene in acid solution was measured relative to that in water at nearly the same concentration. Corrections were made for small differences in absorbance between the acid solutions and the water standard and for quenching by oxygen. The ambient oxygen concentration in water (~3 × 10^{-4} M)[9] was found to quench approximately 4% of the fluorescence. Because of the decreased solubility of oxygen in aqueous H_2SO_4 coupled with a large increase in viscosity, the rate constant in these solutions should be less than that in water by at least a factor of 10 and hence was assumed to be negligible. The corrected expression used for the determination of the quantum efficiency of fluorescence quenching, Φ_Q, is

$$\Phi_Q = 1 - 0.96(A^0/A)(I_F/I_F^0) \qquad (2)$$

where A stands for absorbance and the superscript zeros indicate the water standard.

The fluorescence quenching quantum efficiencies were measured on a series of solutions of differing acid concentration ranging from approximately 54 to 70% H_2SO_4 with a naphthalene concentration of approximately 2 × 10^{-5} M. Naphthalene was excited at both 275 and 313 mμ with no apparent difference. The temperature was maintained at 25 ± 1°. The results of this study are given in Table II. The quantum yields listed represent the average of a large number of determinations on a given solution and the error limits where shown represent the average deviation from the mean of measurements made on different solutions of the same acid concentration. The results show a dramatic quenching dependence on acid concentration.

Table II. Relative Efficiencies of Quenching of Fluorescence by Sulfuric Acid[a]

% H_2SO_4	Φ_Q	% H_2SO_4	Φ_Q
70.3	0.944	58.6	0.529
69.7	0.932 ± 0.002	58.1	0.464 ± 0.001
68.6	0.906 ± 0.01	56.1	0.354 ± 0.01
65.0	0.814 ± 0.003	55.6	0.333
64.5	0.806	54.1	0.268
63.9	0.767 ± 0.003	53.9	0.293 ± 0.01
60.0	0.602 ± 0.006	53.8	0.222 ± 0.06
59.4	0.533		
59.2	0.525 ± 0.002		

[a] Errors quoted are average deviations of measurements on two or more solutions of the same acid concentration.

The temperature dependence of acid quenching was examined over the range of approximately 5–40° for acid compositions of 55.6, 59.4, 64.5, and 70.3% H_2SO_4. A representative Arrhenius plot showing the results obtained in 64.5% H_2SO_4 is given in Figure 1, where the quantity $R \ln [I_F^0/I_F(1 - \Phi_s) - 1]$ is plotted against $1/T$ using the absorbance corrected I_F values. The reason for this functional choice will become clear later. The analysis of the data using a least-squares fit leads to the activation energies and intercepts given in Table III along with their expected standard deviations. The values obtained in 59.4% H_2SO_4 appear to be somewhat large in comparison with the other values; this may be due to a smaller number of data points taken in this run.

Table III. Activation Energies and Intercepts from the Arrhenius-Type Plots for Fluorescence Quenching by Acid

% H_2SO_4	E_a, kcal/mol	Intercept
55.6	5.2 ± 0.1	16.2 ± 0.4
59.4	5.4 ± 0.2	18.5 ± 0.6
64.5	4.04 ± 0.04	16.4 ± 0.1
70.3	3.22 ± 0.07	16.5 ± 0.2

Triplet Quenching. The essentially complete removal of oxygen from a solution of naphthalene in water resulted in the observation of delayed fluorescence and excimer emission. This delayed emission arises from a triplet–triplet annihilation process[10] and offers a

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[8] E. Högfeldt and J. Bigeleisen, *J. Amer. Chem. Soc.*, 82, 15 (1960).

[9] C. D. Hodgman, Ed., "Handbook of Chemistry and Physics," 41st ed, Chemical Rubber Publishing Co., Cleveland, Ohio, p 1708.

[10] C. A. Parker and C. G. Hatchard, *Proc. Roy. Soc., Ser. A*, **269**, 574 (1962).

means whereby the quenching of the triplet state can be monitored. A 30% H_2SO_4 solution containing naphthalene was carefully degassed, and then the naphthalene and *ca.* two-thirds of the water from the H_2SO_4 solution were distilled into a cuvette side arm and delayed fluorescence was monitored at 333 mμ with the aid of a phosphoroscope. The remainder of the H_2SO_4 solution was then mixed to make up the 30% solution. The delayed emission was considerably reduced and could only clearly be seen at slightly elevated temperatures. Since the delayed emission depends upon the diffusion together of two triplets, some reduction in emission is to be expected due to the decreased concentration of naphthalene upon addition of the H_2SO_4 and also due to the increased viscosity in 30% H_2SO_4.[11] It is estimated that these factors alone should account for a reduction of approximately 80% so that it appears that the triplet state is in fact quenched by some species in 30% sulfuric acid.

Side Product Quantum Yields. An unidentified photoinduced side reaction is observed to occur upon irradiation of naphthalene in sulfuric acid. This may contribute to the observed reduction of fluorescence intensity as well as influence the analysis of the exchange quantum yields. The quantum yields of this side-product formation were determined by measuring the absorbance of naphthalene before and after known light exposures for various acid concentrations, and the results are presented in Table IV. The quantum yields have a smaller acid dependence than the total fluorescence quenching quantum yields and are considerably smaller in magnitude.

Table IV. Absolute Quantum Yields of Photoinduced Side-Product Formation

% H_2SO_4	Φ_s	% H_2SO_4	Φ_s
77.9	0.098	53.9	0.035
67.8	0.074 ± 0.002	49.1	0.025
64.5	0.069	44.2	0.018
59.2	0.053 ± 0.001		

Discussion

The establishment of the nature of the excited state involved in the exchange reaction is of utmost importance in the analysis of the results. Excitation at 313 mμ populates both the lowest singlet and triplet states of naphthalene. Kuz'min and coworkers[12] have made spectroscopic measurements of the basicities of these two states and find that the singlet state is almost 17 orders of magnitude more basic than the triplet. Due to the presence of O_2 in solution, the lifetime of the triplet should be shortened to a value close to that of the singlet and, considering its much lower basicity, this state is not expected to compete with the singlet as an exchanging state. If, in fact, the triplet were significantly involved in the exchange, removal of oxygen should have a pronounced effect upon the quantum yields provided that quenching by other species in aqueous H_2SO_4 is not so fast as to make oxygen unimportant. This latter possibility has been ruled out by the observation of only partial quenching of delayed fluorescence by H_2SO_4 and essentially complete quenching by O_2. Thus the observation that O_2 has no noticeable effect on the exchange effectively eliminates this state from consideration.

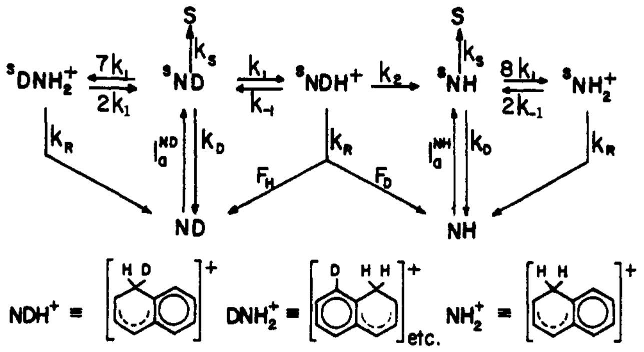

Figure 2. Kinetic scheme for fluorescence quenching and excited singlet state exchange of naphthalene-d_1.

The nature of the detailed reaction mechanism for excited-state substitutions has been previously considered,[4,13] and the suggestion put forth that the reaction takes place *via* highly excited vibrational levels of the ground state σ complex, bypassing the formation of a true intermediate in the excited state. However, if one proceeds on the reasonable assumption that quenching and exchange proceed *via* the same mechanism, the observed activation energies of up to 5 kcal indicate that considerable solvent rearrangement has taken place *prior* to deactivation to the ground state and suggest the formation of an excited-state intermediate. A kinetic scheme which allows for this possibility is illustrated in Figure 2. The singlet state is protonated with a rate constant k_1 at each position leading to a symmetrical σ-type intermediate This intermediate then can undergo a radiationless transition to the ground state with rate constant k_R,[14] exchange within the excited state manifold *via* k_2, or return *via* k_{-1}. The symbols F_H and F_D represent the fraction of molecules which lose a proton or deuteron during the radiationless return to the ground state. Because of the symmetrical nature of the intermediate assumed in this scheme, these fractions should equal 0.5 in the absence of isotope effects. The formation of side product, S, is assumed to be formed in the excited singlet state with a rate constant k_s. The symbols I_a^{ND} and I_a^{NH} represent the rate of light absorption by naphthalene-d_1 and naphthalene and k_D is the rate constant for decay of the singlet state by normal radiative and radiationless processes.

The rate expression for the step involving the protonation of the deuterated naphthalene in this scheme will be given by

$$\text{rate} = k_1[^sND](a_{H^+}f_{^sND}/f^{\ddagger}) \qquad (3)$$

where a_{H^+} represents the proton activity, $f_{^sND}$ the ac-

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[11] E. W. Washburn, Ed., "International Critical Tables," Vol. V, McGraw-Hill, New York, N. Y., 1928, p 12.

[12] M. G. Kuz'min, B. M. Uzhinov, and I. V. Berezin, *Russ. J. Phys. Chem.*, 41, 222 (1967).

[13] E. Havinga, *Reactiv. Photoexcited Org. Mol., Proc. Conf. Chem. 13th, 1965*, 201 (1967).

[14] A search for fluorescence originating from the protonated intermediate was made in 60% sulfuric acid and found to be less than 1/50 of normal fluorescence. Thus nonradiative processes appear to be the dominant mode of decay.

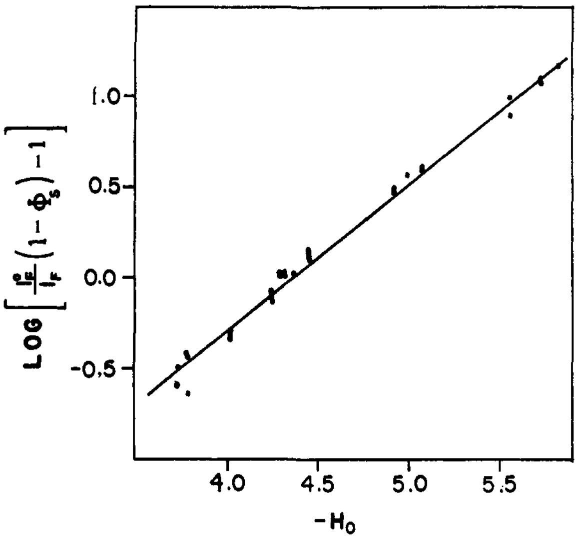

Figure 3. Fluorescence quenching as a function of the Hammett acidity (H_0) of H_2SO_4 at 25 ± 1°.

tivity coefficient of the excited singlet naphthalene-d_1, and $f^{\ddagger}$ the activity coefficient of the transition state. The highly nonideal behavior of the proton in moderately concentrated H_2SO_4 solutions has been amply demonstrated and necessitates the use of a rate expression of this form. By analogy with ground-state reactions, the term $a_{H^+}f_{^sND}/f^{\ddagger}$ is expected to be related to the Hammett acidity (h_0) of the solution.

The intensity of fluorescence in this scheme is given by the expression $I_F = k_F\{[^sNH] + [^sND]\}$, where k_F is the rate constant for fluorescence. The corrected ratio of fluorescence intensity for naphthalene in water, I_F^0, and in acid, I_F, is given by

$$I_F^0/I_F = 1 + k_s\tau_0 + \frac{k_R}{(k_R + 2k_{-1})}8k_1h_0\tau_0 \qquad (4)$$

where $\tau_0 = 1/k_D$ and the assumption has been made that $k_{-1} = k_2$. Kinetic analysis of the quantum yield of side-product formation enables expression 4 to be recast in the following form.

$$\log\,[(I_F^0/I_F)(1 - \Phi_s) - 1] = \log\frac{8k_Rk_1\tau_0}{(k_R + 2k_{-1})} - H_0 \qquad (5)$$

A plot of log $[(I_F^0/I_F)(1 - \Phi_s) - 1]$ *vs.* H_0 is shown in Figure 3. The plot shows rather good linearity and has a slope of 0.85. This illustrates quite convincingly that the protonating ability of the medium is the determining factor in fluorescence quenching in much the same manner as occurs in ground state acid catalysis reactions. The slope value of 0.85 contrasts with the value of 1.55 for exchange at the two positions of ground-state naphthalene in the same acid range and shows the importance of the basicity or reactivity of the substrate in determining the protonating ability of the solvent. The comparison of substrate–solvent interactions for different electronic states of the same molecule minimizes the effects of molecular size and steric hindrance and focuses attention on the electronic properties of the species involved. Taking the view that differences in activity coefficient between the two electronic states are minimal, an examination of the rate dependence on the activity of water can be made in the same manner as was done for the ground state exchange reaction.[7] This analysis shows that, on the average, quenching proceeds with approximately 1.5 more water molecules effectively bound to the transition state than does ground-state exchange. An examination of the entropy of activation for the quenching process is interesting in this regard. Equation 5 can be rewritten in the form

$$I_F^0/I_F(1 - \Phi_s) - 1 = \frac{k_R}{(k_R + 2k_{-1})}8k_1h_0\tau_0 \qquad (6)$$

Following reasoning to be given later, k_{-1} is expected to be much less than k_R which reduces the right-hand side to $8k_1h_0\tau_0$. The pseudo-first-order rate constant for protonation, $k_\psi = k_1h_0$, can be expressed by the use of transition state theory as

$$k_\psi = (kT/h)e^{\Delta S^{\ddagger}/R}e^{-\Delta H^{\ddagger}/RT} \qquad (7)$$

where k is the Boltzmann constant. Substitution into eq 6 results in the following expression for $\Delta S^{\ddagger}$

$$\Delta S^{\ddagger} = I - R\ln\,(8kT/h) - R\ln\tau_0 \qquad (8)$$

where I represents the intercept of the Arrhenius plot of the type shown in Figure 1. The value of τ_0 has not been measured in water but it should not be substantially different from the value of approximately 100 nsec in hydrocarbon solvents.[15] Using this value then, $\Delta S^{\ddagger}$ at 298°K will be given by $I - 29.9$. Using the intercept values listed in Table III results in an estimated $\Delta S^{\ddagger}$ in the range −12 to −14 cal/(deg mol). These values are significantly more negative than those found for the ground state exchange reaction,[7] in agreement with the conclusion that excited-state protonation proceeds with more water molecules bound to the transition state than does ground-state protonation.

The quantum yield for exchange based upon the proposed reaction scheme is given by the following expression[16]

$$\Phi_{ex} = \frac{[k_RF_D + k_2(1 - \Phi_s)]k_1h_0\tau_0}{(1 + k_s\tau_0)(k_R + 2k_{-1}) + (8k_R + k_2)k_1h_0\tau_0} \qquad (9)$$

This expression suggests that log Φ_{ex} should depend linearly upon H_0 at low acid concentration and become independent of this function at high acidity. This dependence is shown in Figure 4. The points represent the average of the quantum yields for exchange at the α and β positions and the expected acidity dependence is seen. The line drawn through the points represents the predicted dependence based upon information obtained from the quenching experiments. It has been assumed that the linear relationship between quenching and Hammett acidity can be extended to lower acidities beyond the range of observation.

In the region of overlapping observation, a more informative plot can be constructed by considering explicitly the dependence of Φ_{ex} on Φ_Q and Φ_s.

The quantum yield for quenching is given by the expression

$$\Phi_Q = \frac{k_s\tau_0 + 8k_Rk_1h_0\tau_0}{(1 + k_s\tau_0)(k_R + 2k_{-1}) + 8k_Rk_1h_0\tau_0} \qquad (10)$$

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(15) G. N. Taylor and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3684 (1972).

(16) For details, see C. G. Stevens, Ph.D. Thesis, University of Colorado, 1970; University Microfilms, Ann Arbor, Mich.

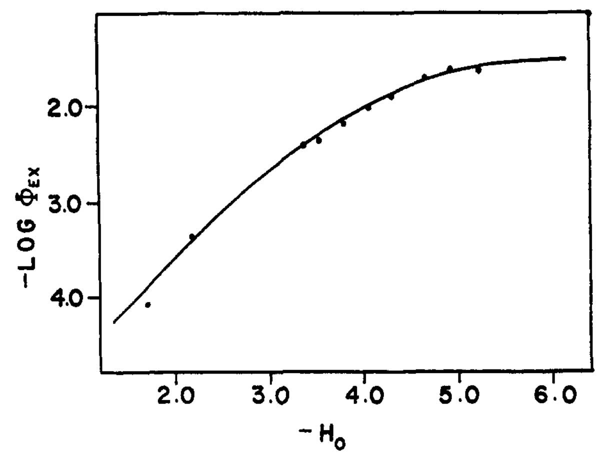

Figure 4. Dependence of the average exchange quantum yields for α- and β-naphthalene-d_1 on the Hammett acidity of H_2SO_4. The line drawn through the points represents the predicted dependence based upon fluorescence quenching experiments.

Substituting this expression into (9) yields

$$\frac{1}{8\Phi_{ex}} = \frac{(1/8)k_2}{k_2(1-\Phi_s)+k_RF_D} + \frac{k_R}{k_2(1-\Phi_s)+k_RF_D}\frac{1}{(\Phi_Q-\Phi_s)} \quad (11)$$

This expression predicts a linear relationship between $1/8\Phi_{ex}$ and $1/(\Phi_Q - \Phi_s)$, since Φ_s is considerably less than unity. The appropriate plot is shown in Figure 5, where the values of Φ_{ex} represent the average of the two positions. The slope of this plot has the value 2.5 which represents to a good approximation $k_R/[k_2 + k_RF_D]$ giving the result that $k_2/k_R + F_D = 0.4$. The ratio of intercept to slope of this plot represents $k_2/8k_R$, but the small value of the intercept prevents an accurate determination of this quantity. The quantity F_D represents the fraction of molecules which lose a deuteron during decay to the ground state. In terms of the assumed mechanism, this fraction can be related to an isotope effect for the exchange reaction. The lack of precision in the value of k_2/k_R prevents an accurate determination of F_D but certain observations can be made concerning its magnitude. The value of k_2/k_R must obviously lie within the limits 0 to 0.4. Choosing the value of 0.4 leads to the awkward conclusions that all exchange occurs completely within the excited state, and that all quenching would have to occur prior to the formation of a symmetrical intermediate. The most reasonable choice of k_2/k_R would seem to lie close to zero, in which case F_D is 0.4 and all exchange occurs during the decay of the symmetrical complex. This value of F_D implies that the symmetrical complex is 1.5 times as likely to lose a proton as a deuteron, and this implies an isotope effect of 1.5 in comparing the quantum yield of exchange for the naphthalene–D_2SO_4 system and the deuterionaphthalene–H_2SO_4 system. The observed value of 1.1 ± 0.35 is probably close enough to this in view of uncertainties about other processes. We cannot rule out the possibility that quenching might occur prior to formation of a symmetrical intermediate, but our data do not require this added complication.

The expression for exchange quantum yields at one of the positions in napthalene (using the α position as an example) is given by

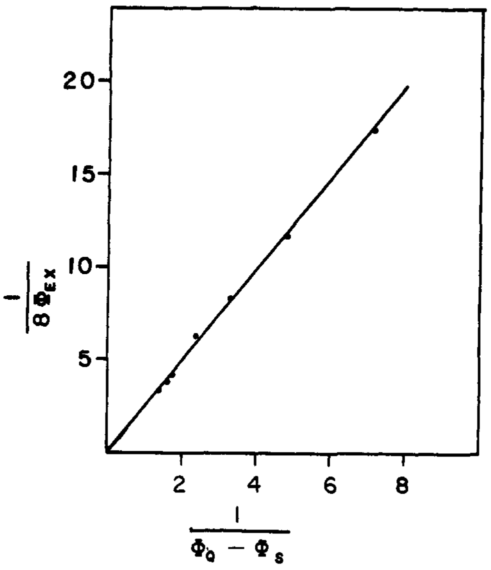

Figure 5. Dependence of average exchange quantum yields on the quantum yield for fluorescence quenching.

$$\Phi_{ex}{}^{\alpha} = \frac{F_D{}^{\alpha}k_{\psi}{}^{\alpha}\tau_0}{1 + 4[k_{\psi}{}^{\alpha} + k_{\psi}{}^{\beta}]\tau_0}$$

where the assumption has been made that $k_R \gg k_2$, k_{-1}. The ratio for quantum yields at the two positions is then given by

$$\frac{\Phi_{ex}{}^{\alpha}}{\Phi_{ex}{}^{\beta}} = \frac{F_D{}^{\alpha}k_{\psi}{}^{\alpha}}{F_D{}^{\beta}k_{\psi}{}^{\beta}}$$

The ratio $F_D{}^{\alpha}/F_D{}^{\beta}$ is expected to be very nearly unity in which case the ratio of quantum yields represents the ratio of rate constants for protonation of the excited state. In the region of 54–66% acid, then the rate constant for β protonation exceeds α protonation by approximately 15%. In the same acid concentration region, the ground-state reactivity of the two positions is reversed with α exceeding β protonation by roughly a factor of 10. Furthermore, with an assumed singlet lifetime of 100 nsec, the rate of protonation has been enhanced by some 13 to 14 orders of magnitude upon excitation. These results offer interesting challenges to present reactivity theories.

Experimental Section

Materials. The α- and β-deuterated naphthalenes were the same as those used in a previous study[7] and the sulfuric acid solutions were prepared and analyzed in the manner described in that study.

Exchange Quantum Yields. Apparatus I consisted of a 1000-W A-H6 high-pressure Hg lamp light source which was passed through a Bausch and Lomb high-intensity grating monochromator passing a band of light centered at 313 mμ with a 99% width of 40 mμ. The light then passed through a collimating lens and Corning Cs-7-54 visible filter and onto a 1-cm cylindrical quartz reaction cell equipped with a small Teflon stirring bar. The cell housing was insulated and maintained at a constant temperature. A small fraction of the incident light was reflected 90° prior to entry into the cell by use of a Vycor plate and continuously monitored during each run using a microphotometer and a strip chart recorder. The area under the recording is proportional to the number of photons incident on the solution during sample exposure, and the areas were calibrated using the standard potassium ferrioxalate actinometer.[8] This method is particularly suited to monitoring exposures when the lamp intensity changes with time.

Apparatus II differed from apparatus I in that a Pyrex filter was used instead of a monochromator which allowed considerably greater excitation intensity. The area under the recorded output was calibrated before and after each run using a standard solution of α-naphthalene-d_1 whose quantum yield for exchange had been carefully determined using apparatus 1.

Fluorescence Quenching. The apparatus for measuring fluorescence consisted of a high-pressure Hg light source focused through a Bausch and Lomb high-intensity grating monochromator and a Corning CS-7-54 visible filter. A 1-cm rectangular quartz cell was used, which was maintained at a desired temperature by submersion in a constant-temperature water bath. The fluorescence was monitored at right angles using a Jarrell-Ash 0.75-m, $f/6.3$ grating spectrometer.

Delayed Emission. Delayed fluorescence and excimer emission were observed upon direct excitation with the high-pressure Hg lamp with the aid of a phosphoroscope. The phosphoroscope consisted of two rapidly rotating chopper blades situated on the entrance and exit sides of the sample cell and offset sufficiently to completely suppress normal fluorescence. The emission was recorded using the 0.75-m spectrometer.

Degassing was achieved by repeated freeze-thaw cycles, and the observation of delayed emission was used as the criterion for oxygen removal. As many as 20 cycles were necessary in some cases to effect removal.

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On the Interaction of Electron Pairs at Peri Positions. Base-Catalyzed Hydrogen–Deuterium Exchange of Quinoline and 1,5-Naphthyridine

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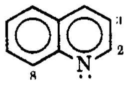
Abstract: Rate constants for hydrogen–deuterium exchange of quinoline and 1,5-naphthyridine in CH_3ONa–CH_3OD at 190.6° were obtained by an nmr method. Values for quinoline are 4.5×10^{-5} (H-2), 3.0×10^{-4} (H-3), 9.4×10^{-4} (H-4), and 4.5×10^{-5} (H-8) M^{-1} sec^{-1}. For 1,5-naphthyridine the values are 2.5×10^{-4} (H-2,6), 2.1×10^{-3} (H-3,7), and 9.2×10^{-3} (H-4,8) M^{-1} sec^{-1}. Isotope exchange is believed to take place by deprotonation of the substrates. H-3 and H-8 of quinoline have similar reactivities, and the H-4 to H-3 rate constant ratios are nearly the same for both compounds. Therefore, it is concluded that the effect of electron pair interactions on the rate of formation of a carbanion at a position peri to an annular nitrogen atom is not significantly different from the effect on a carbanion at a position meta to an annular nitrogen atom.

Recent molecular orbital calculations[1-3] and photoelectron spectra[4] indicate that the "unshared" electron pairs of the annular nitrogen atoms of diazabenzenes and diazanaphthalenes interact. Pair-pair interaction is not found to be limited to adjacent pairs as was once thought; widely separated pairs may also interact strongly. The interaction is transmitted both through space and through σ bonds, the latter mode of transmission being of major importance for pairs separated by large distances.

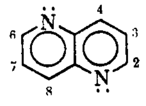
In view of these new results it becomes of interest to examine new systems and even to reconsider old results in order to seek chemical evidence of such interactions, particularly for widely separated electron pairs. At this infant stage in the search for chemical evidence of pair-pair interactions it is not yet clear what kinds of reactions will be sensitive to this effect and how large any effect will be. Many different systems will have to be examined for pair-pair repulsion effects before the chemical significance of this effect can be revealed.

We here consider the interaction of electron pairs at peri positions and employ base-catalyzed hydrogen-deuterium exchange as the chemical probe. Two molecules were examined, quinoline (I) and 1,5-naphthyridine (II). The reactivities of H-8 in I and of H-4 in II which are located in positions peri to an annular nitrogen atom are of special interest. It is expected that both these molecules will undergo H-D exchange by a mechanism involving cleavage of a CH bond to give carbanions such as III and IV where pair-pair interactions are possible at the peri positions.

Note that clear chemical evidence does exist for the interaction of electrons in peri positions in the case of aryne V. The evidence is found in the stereochemistry



I



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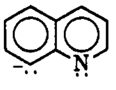
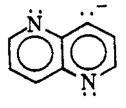
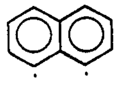


III



IV



V

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