Ground State Hydrogen–Deuterium Exchange of Naphthalene in Sulfuric Acid Solutions

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Abstract: Hydrogen–deuterium exchange reactions of α- and β-naphthalene-d_1 have been studied in 50–67% H_2SO_4 solutions as a function of acid concentration and temperature. Exchange at the α position is faster than that at the β position by roughly a factor of 10. The logarithm of the pseudo-first-order rate constant is found to increase linearly with Hammett acidity; the slope for exchange at the β position exceeds that for exchange at the α position at all temperatures studied. Activation enthalpies and entropies are reported as a function of acid concentration. The activation enthalpy for reaction at the β position is 3–4 kcal/mol greater than for reaction at the α position, but the activation entropy is 4–5 cal/(deg mol) less negative. A modified hydration treatment is presented, and the results of this work are used to examine the extent to which hydration contributes to "excess reaction rates" in this system. The difference in activation entropy is interpreted as being due largely to differences in hydration of the respective transition states. The observation of entropy differences for two such closely related reactions indicates that caution must be used in correlating calculated reactivities with free energies of activation in such systems.

Hydrogen exchange in aromatic hydrocarbons represents an important type of electrophilic substitution reaction, and the mechanism of this reaction has been the subject of a considerable amount of research. It is now generally agreed that the reaction involves a two-step process forming a relatively stable intermediate en route. Several quantum mechanical theories have been developed which attempt to describe the nature of this intermediate and the energy of the transition state for the reaction.[1] The prime examples have been the Wheland model[2] (localization energies) in which a pair of π electrons are localized at the reacting carbon atom and the Fukui model[3] (super delocalizability) in which the delocalization of the π-electron system over the reacting center occurs. The calculated reactivities using these and other models have been compared with relative rate constants of reactions in solution and reasonably good correlations have been obtained with all indices. Daudel and coworkers[4] found that the best statistical correlation is obtained using localization energies. This type of observation has led most workers to favor the localization energy index.

The basis of the reactivity indices is an estimate of relative energies of transition states, and this should be related to activation enthalpies. The rather good agreement obtained with reaction rates suggests that calculated reactivities correlate well with activation free energies, and Dewar[5] has presented plausible arguments as to why this might be so. However, it would be very interesting to have enough information to be able to compare calculated reactivities with activation enthalpies, and it is not certain that the localization energy index would be the best in such a correlation.

The dominant role of solvation in determining the overall magnitude of the thermodynamic activation parameters is dramatically illustrated by the results of Field and coworkers[6] who studied the gas-phase protonation of benzene by CH_5^+. Their results show that the gas phase reaction $H^+ + C_6H_6 \rightarrow C_6H_7^+$ should proceed with an energy *release* of approximately 100 kcal/mol contrasting sharply with the rather large activation barrier observed in solution. Furthermore, SCF–MO calculations of the localization energy of benzene gives the π-system energy of the protonated intermediate almost 60 kcal/mol higher in energy than benzene itself.[7] It is seen that a rather large energy release occurs within the σ core during the protonation process and this, coupled with the large solvent effect, makes the observed correlations quite remarkable.

The importance of solvation of the electrophile is obvious in this case, and proper analysis of solution reactivity awaits a more complete understanding of this effect. It is now well established that the proton in aqueous solution is strongly hydrated, having on the average roughly four water molecules associated with it.[8] The importance of hydration as a major factor in determining the protonating ability of acids in aqueous solutions was first pointed out by Bascombe and Bell[9] and by Wyatt.[10] Bascombe and Bell suggested that the difference between pH and the Hammett acidity function, H_0,[11] could be understood in terms of a standard hydration change occurring upon protonation. Bunnett[12] and later Perrin[13] generalized this approach to allow for changes in the average hydration as a function of medium composition. Their work has established that hydration changes, at least

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[1] L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966, Chapter 6.

[2] G. W. Wheland, *J. Amer. Chem. Soc.*, 64, 900 (1942).

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[5] M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 281.

[6] (a) F. H. Field, *J. Amer. Chem. Soc.*, 91, 2828 (1969); (b) M. S. B. Munson and F. H. Field, *ibid.*, 89, 1047 (1967).

[7] Value determined from Figure 8.5 of ref 5.

[8] E. Glueckauf, *Trans. Faraday Soc.*, 51, 1235 (1955).

[9] R. P. Bell and K. N. Bascombe, *Discuss. Faraday Soc.*, 24, 158 (1957).

[10] P. A. H. Wyatt, *Discuss. Faraday Soc.*, 24, 162 (1957).

[11] L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, 54, 2721 (1932).

[12] J. F. Bunnett, *J. Amer. Chem. Soc.*, 83, 4973 (1961).

[13] C. Perrin, *J. Amer. Chem. Soc.*, 86, 256 (1964).

in dilute to moderately concentrated acid solutions, make an important contribution to excess acidity. However, it is certainly not clear that *all* of the excess acidity can be ascribed to hydration or, in the case of more concentrated acids, whether the changes in activity coefficients provide the major influencing factor.

In previous formulations of the influence of hydration on reaction rates,[12] the point of view was adopted that a formal net change in the "average" number of hydrating water molecules takes place upon formation of the transition state. This treatment leads to the explicit involvement of the activity of water in the rate expression. However, in the following section we will show that the same kinetic expression can be obtained using an alternative approach which offers a clearly defined and possibly more realistic description of the protonation process.

Hydration Treatment of Reaction Rates

In the present approach it will be assumed that multiple equilibria of the type $H(H_2O)_n^+ + H_2O \rightleftharpoons H(H_2O)_{n+1}^+$ exist with associated equilibrium constants $K_{n+1} = a_{n+1}/a_n a_w$, where we have introduced the symbols a_n and a_w to denote the activities of the species $H(H_2O)_n^+$ and H_2O, respectively. Using this expression repeatedly the activities of all proton hydrates can be conveniently expressed in terms of a_0, the activity of the unhydrated proton. This gives

$$a_n = a_0 a_w^n \prod_{i=1}^{n} K_i = a_0 a_w^n \mathbf{K}_n \tag{1}$$

where $\mathbf{K}_n$ symbolizes the product of successive equilibrium constants from 1 to n. The protonation reaction is now considered to take place between the substrate and each of the several hydrated forms of the proton, each having its own rate constant. For example, the protonation by the nth hydrate is represented by the scheme

$$S + H(H_2O)_n^+ \xrightarrow{k_n} [S\text{—}H(H_2O)_n^+]^\ddagger \longrightarrow \text{(intermediate)} \tag{2}$$

The transition state in the first (rate determining) step is visualized as having the same number of water molecules as the reactants but more or less loosely bound. The substrate will not be considered as hydrated to any extent in this treatment. The rate equation for this step is given by

$$(\text{rate})_n = k_n[S]a_n f_s/f_n^\ddagger \tag{3}$$

where $f_n^\ddagger$ is the activity coefficient for the transition state. The total rate is given by the sum of the individual rates. Thus

$$\text{rate} = k_\psi[S] = [S]\sum_n k_n a_n f_s/f_n^\ddagger \tag{4}$$

where k_ψ is the pseudo-first-order rate constant. Using eq 1, k_ψ can be expressed as

$$k_\psi = a_0\sum_n k_n \mathbf{K}_n a_w^n f_s/f_n^\ddagger = a_0\sum k_\psi(n) \tag{5}$$

The second-order rate constant is given by $k_\psi/[H^+]$ where $[H^+] = \Sigma_n[H(H_2O)_n^+] = \Sigma_n[H_n^+]$ and represents the total hydrogen ion concentration. Again using eq 1 the following expression is obtained

$$\frac{k_\psi}{[H^+]} = \frac{\sum_n k_n \mathbf{K}_n a_w^n f_s/f_n^\ddagger}{\sum_n \mathbf{K}_n a_w^n/f_{H_n^+}} = \frac{\sum_n k_\psi(n)}{\sum_n [H_n^+]} \tag{6}$$

The dependence of $k_\psi/[H^+]$ on the activity of water finds its simplest expression in terms of the logarithms of these quantities. The slope of a plot of $\log k_\psi/[H^+]$ *vs.* $\log a_w$ will be given by the derivative of the logarithm of eq 6 with respect to $\log a_w$. Thus after some manipulation one obtains eq 7. It can be shown that these

$$\frac{d \log k_\psi/[H^+]}{d \log a_w} = \frac{\sum_n k_\psi(n)\left[n + \frac{d \ln (f_s/f_n)}{d \ln a_w}\right]}{\sum_n k_\psi(n)} - \frac{\sum_n [H_n^+]\left[n + \frac{d \ln (1/f_{H_n^+})}{d \ln a_w}\right]}{\sum_n [H_n^+]} \tag{7}$$

terms represent weighted averages of the quantities in brackets; $k_\psi(n)/\Sigma_n k_\psi(n)$ represents the fraction which proceeds by way of the nth hydrate, and $[H_n^+]/\Sigma_n[H_n^+]$ gives the fraction of protons existing as the nth hydrate. Expression 7 simplifies to eq 8, where

$$\frac{d \log k_\psi/[H^+]}{d \log a_w} = \bar{t} - \bar{n} + \overline{\frac{d \ln (f_s/f_n^\ddagger)}{d \ln a_w}} - \overline{\frac{d \ln (1/f_{H_n^+})}{d \ln a_w}} \tag{8}$$

t and n represent the hydration numbers of the transition state and proton, respectively, and the bars indicate weighted averages.

This approach emphasizes the role played by preequilibrium amongst the various hydrates and assumes that the passage through the transition state by way of a particular hydrate occurs with no net change in the extent of hydration. It is felt that, while this describes the basic changes occurring upon protonation, the possibility of some net hydration loss cannot be ruled out.

To the extent that hydration effects are important, or can be isolated in the description of the activation process, one would expect this to be reflected in the entropy of activation as noted by Bunnett.[12] In this paper a study of dedeuteration of α- and β-naphthalene-d_1 in aqueous H_2SO_4 is presented and used to examine further the limitations of the hydration model in the description of "excess reaction rates." The comparison of the reaction of two positions in the same molecule provides certain simplifications which enable one to focus more clearly on the influence of hydration as well as to examine the assumption that activation entropies are essentially the same for structurally related molecules.

Results and Discussion

The rates of exchange of α- and β-naphthalene-d_1 have been examined at five different temperatures in aqueous sulfuric acid ranging in composition from 50 to 67% by weight. The pseudo-first-order rate constants for exchange, k_ψ, were calculated using the expression

$$k_\psi t = \ln\frac{1 + R}{1 + R_0} \tag{9}$$

where R_0 and R are the ratios of naphthalene to naphthalene-d_1 before and after exchange, respectively, and t is the time of reaction. These ratios were determined

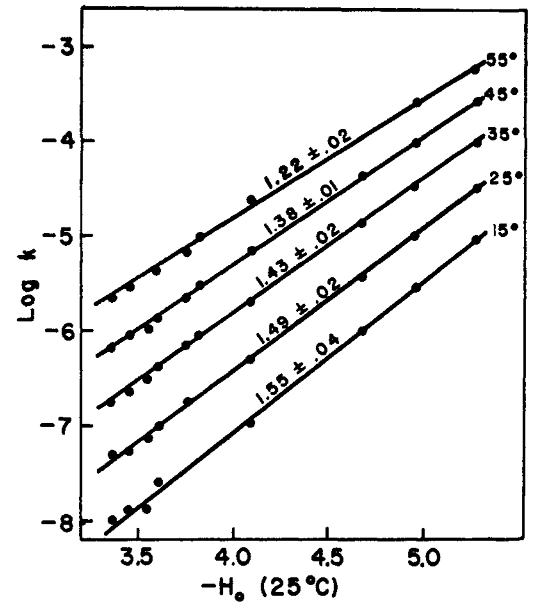

Figure 1. A plot of the logarithm of the pseudo-first-order rate constant *vs.* the Hammett acidity function for α-deuterionaphthalene at several temperatures. The slopes and their expected standard deviations are shown.

by measurement of the appropriate mass spectral peak heights as described in the Experimental Section. Expression 9 was derived under the assumption that the reverse exchange reaction was negligible, a reasonable assumption since the concentration of deuterated species in solution was approximately 3 × 10^{-5} *M*. The rate constants determined in this way are given in Tables I and II for α- and β-naphthalene-d_1, respectively.

Table I. Pseudo-First-Order Rate Constants for Hydrogen–Deuterium Exchange of α-Deuterionaphthalene in Aqueous H_2SO_4

% H_2SO_4	Temp, °C 15.05	24.90	34.95	45.13	55.65
	10^7k, sec^{-1}				
49.84	0.100	0.474	1.78	6.57	22.7
50.67	0.131	0.538	2.28	8.41	29.4
51.54	0.120	0.703	2.89	10.4	
52.12	0.272	1.03	4.45	13.5	45.6
53.52	0.463	1.82	7.02	23.0	70.3
54.09			9.06	30.1	103
56.69	1.03	4.90	19.3	70.6	249
61.95	10.4	38.1	139	439	
64.31	29.0	97.8	344	1030	2980
66.97	90.2	328	1010	2730	5290

Previous investigations of reactions of this type have shown that in most cases a linear relationship exists between log k_ψ and H_0. A good linear relationship of this type is obtained for both α- and β-naphthalene-d_1 at every temperature. This is shown in Figures 1 and 2 which include the slope values as determined by a least-squares analysis along with their standard deviations. Only those runs in which the exchange exceeded 1% are included in this plot. The values for H_0 (determined at 25°) were obtained by interpolation of the values given by Jorgenson and Hartter[14] and where necessary by Long and Paul.[15]

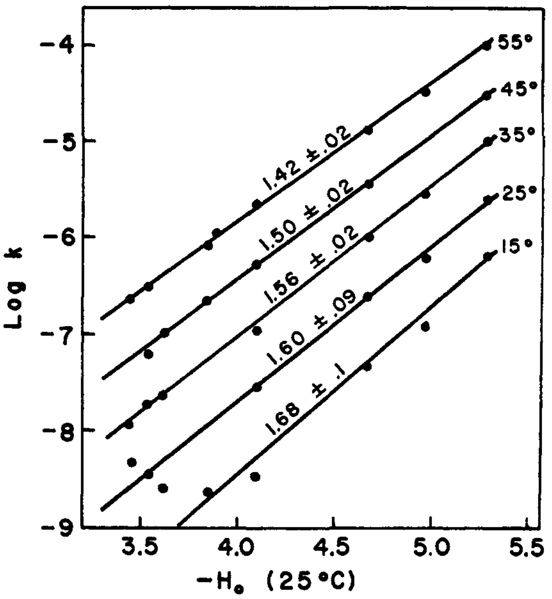

Figure 2. A plot of the logarithm of the pseudo-first-order rate constant *vs.* the Hammett acidity function for β-deuterionaphthalene at several temperatures. The slopes and their expected standard deviations are shown.

Table II. Pseudo-First-Order Rate Constants for Hydrogen–Deuterium Exchange of β-Deuterionaphthalene in Aqueous H_2SO_4

% H_2SO_4	Temp, °C 15.05	24.90	34.95	45.13	55.65
	10^8k, sec^{-1}				
50.64		0.493	1.22		23.3
51.50		0.367	1.87	6.37	30.8
52.21		0.242	2.34	10.5	54.3
54.27	0.243	1.12	6.85	14.5	80.7
54.74	0.199	2.80		24.7	112
55.51	0.543	3.27	14.5	38.7	83.8
56.69	0.311	2.87	11.2	53.9	227
61.93	4.70	25.0	99.7	345	1340
64.41	12.5	63.0	294		3320
66.96	68.9	270	985	3160	9920

The apparent temperature dependence of the slopes is most likely due to the temperature dependence of both H_0 and log k_ψ. The slopes for α-naphthalene-d_1 are significantly different from those for β-naphthalene-d_1 at each temperature studied. This result coupled with previous studies of aromatic exchange indicates that different slopes can be expected not only for each reactant but also for each position in the same reactant. Since the slope of these plots describes the rate of change of the acidity as measured by a given substrate relative to that measured by the standard H_0 bases, it is clear that the "acidity" of a medium is a quite sensitive function of the nature of the base used to measure this quantity.

Some insight into the origin of these differences in measured acidity can be gained by the use of eq 8. If the assumption is made that the activity coefficient terms remain constant as the medium changes, the tangent to the curve obtained by plotting log $k_\psi/[H^+]$ against log a_w should give $\bar{l} - \bar{n}$ for the medium cor-

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[14] M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, **85**, 878 (1963).

[15] M. A. Paul and F. A. Long, *Chem. Rev.*, 57, 1 (1957).

responding to the chosen tangent point. This function has been plotted and is shown in Figure 3. The values for the activity of water were obtained by interpolating those listed by Bunnett.[16] The total hydrogen ion concentration [H^+] was calculated from the data on (HSO_4^-) and (SO_4^{2-}) determined by Young[17] from Raman studies. The plots have a slight apparent curvature and the values of the tangents to the curves at the midpoint of the acid range (60% H_2SO_4) are approximately −4.3 and −4.6 for α- and β-naphthalene-d_1, respectively. A reasonable value of $\bar{n}$ can be estimated from the data provided by Young. In the range of acid employed in this study (50–67%), the ratio of water to proton concentration ranges from approximately 4.4 (50%) to 2.4 (67%). Given that the most stable hydrated form of the proton involves four or more water molecules, these ratios should provide a reasonable approximation to $\bar{n}$. In 60% H_2SO_4, this ratio is roughly 3.3. In view of the scarcity of water and the nonpolar nature of the aromatic substrate, we believe the neglect of the hydration of the substrate to be justified.

Under the assumption that the activity coefficient part of expression 8 remains constant over this acid range, one obtains the result that $\bar{l}_\alpha = -1$ and $\bar{l}_\beta = -1.3$. These results are clearly unreasonable, implying that more waters of hydration are released than were originally bound to the reactants. This same result is found to be the case for exchange involving other aromatic substrates in moderately concentrated H_2SO_4. For example, the exchange rate data found in the literature for *o*- and *p*-anisole-d_1,[18] *p*-toluene-d_1,[19] *m*-toluene-t_1 and benzene-t_1[20] show that the corresponding $\bar{l}$ values are all negative over the entire range of concentrations studied. These results clearly show that the activity coefficient term is not constant and in fact must make a substantial contribution to the slope of these plots. In the case of naphthalene, the contribution of the activity coefficient term to the apparent $\bar{l}$ exceeds 1.0. These results do not necessarily imply that hydration does not play an important role in these reactions, but rather show that there are other substantial contributions to "excess reaction rates" in the moderately concentrated H_2SO_4 region.

The effect of changes in the activity coefficient term can certainly be minimized and possibly even removed by comparing the slopes of log $k_\psi/[H^+]$ *vs.* log a_w for different positions in the same molecule. In the case of α- and β-naphthalene-d_1 we have, from expression 8

$$\frac{d \log (k_\psi^\alpha/k_\psi^\beta)}{d \log a_w} = \bar{l}_\alpha - \bar{l}_\beta + \left[\frac{d \ln \overline{(f_n^{\ddagger})_\beta}}{d \ln a_w} - \frac{d \ln \overline{(f_n^{\ddagger})_\alpha}}{d \ln a_w}\right] \qquad (10)$$

In view of the structural similarity of the two transition states, it seems a reasonable assumption to neglect the activity coefficient term in this equation. Expression 10 then gives a measure of the differences in the hydration of the two positions. The quantity $\bar{l}_\alpha - \bar{l}_\beta$ varies from 0.35 to 0.25 from 50 to 67% H_2SO_4. Using the approach of this paper, this is interpreted as meaning that protonation at the α position proceeds through a transition state containing more waters of hydration on the average than does protonation at the β position. This should be reflected in differences in the entropy of activation for reaction of the two positions.

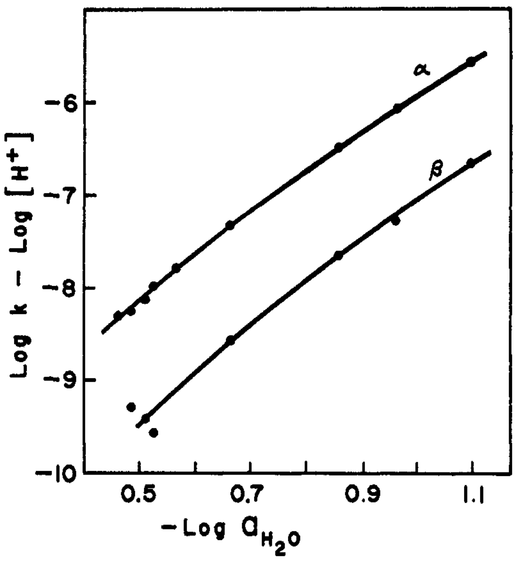

Figure 3. A plot of the logarithm of the second-order exchange rate constant for α- and β-deuterionaphthalene *vs.* the logarithm of the activity of water in aqueous H_2SO_4 at 25°.

The entropies and enthalpies of activation have been determined from the appropriate Arrhenius plots, and the results for certain selected concentrations are given in Table III. The results clearly show that there is a significant difference in the activation entropy for exchange at the two positions. In all cases, $\Delta S^{\ddagger}(\beta)$ is less negative than $\Delta S^{\ddagger}(\alpha)$. This is in qualitative agreement with expectations based on the assumption that changes in hydration provide the largest contribution to entropy changes. It is also interesting to compare these results with those of Eaborn and coworkers[21] who studied the detritiation of α- and β-naphthalene-t_1 in anhydrous trifluoroacetic acid. The entropies of activation have been calculated from their data and are essentially the same for exchange at the two positions, having a value of approximately −31 cal/(deg mol). This result supports the conten-

Table III. Enthalpies and Entropies of Activation for Hydrogen–Deuterium Exchange of α- and β-Deuterionaphthalene in Aqueous H_2SO_4 at 300°K

% H_2SO_4	$\Delta H^{\ddagger}$, kcal/mol α	$\Delta H^{\ddagger}$, kcal/mol β	$\Delta S^{\ddagger}$, cal/(deg mol) α	$\Delta S^{\ddagger}$, cal/(deg mol) β
50.6	24.7 ± 0.2	28.1 ± 0.2	−8.7 ± 0.6	−3.7 ± 0.6
52.1	24.4 ± 0.2	27.6 ± 0.2	−8.8 ± 0.6	−3.9 ± 0.5
54.2	23.9 ± 0.2	27.0 ± 0.1	−9.0 ± 0.6	−4.3 ± 0.4
56.7	23.2 ± 0.2	26.4 ± 0.1	−9.3 ± 0.5	−4.6 ± 0.3
61.9	21.9 ± 0.1	24.9 ± 0.2	−9.9 ± 0.5	−5.4 ± 0.6
64.3	21.2 ± 0.1	24.1 ± 0.2	−10.2 ± 0.4	−5.8 ± 0.7
67.0	20.5 ± 0.1	23.3 ± 0.3	−10.5 ± 0.4	−6.3 ± 0.9

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(16) J. F. Bunnett, *J. Amer. Chem. Soc.*, **83**, 4956 (1961).
(17) T. F. Young, *Rec. Chem. Progr.*, **12**, 81 (1951).
(18) D. P. N. Satchell, *J. Chem. Soc.*, 3911 (1956).
(19) V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 3609 (1955).
(20) C. Eaborn and R. Taylor, *J. Chem. Soc.*, 3301 (1960).
(21) C. Eaborn, P. Goldborn, R. E. Spillett, and R. Taylor, *J. Chem. Soc. B*, 1112 (1968).

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.

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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).

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