Exceptional Basic Strength of 1,8-Bis(dimethylamino)- and 1,8-Bis(diethylamino)-2,7-dimethoxynaphthalenes: Kinetic and Equilibrium Studies of the Ionisation of the Protonated Amines in Me_2SO–H_2O Mixtures with Hydroxide Ion

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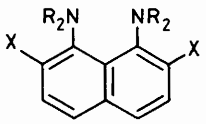
Exceptionally high pK_a values of 16.1 and 16.3 have been obtained for 1,8-bis(dimethylamino)- and 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene respectively from measurements of the equilibrium between the protonated amines and hydroxide ion in Me_2SO–H_2O mixtures. These values make the amines more basic by four pK_a units than 1,8-bis(dimethylamino)naphthalene. This may be a result of an increase in strain in the free amines and of a strengthening of the intramolecular hydrogen bond in the protonated amines. Proton transfer from protonated 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene to hydroxide ion in 35% (v/v) Me_2SO–H_2O occurs in the millisecond range (k_{OH^-} 110 $dm^3\ mol^{-1}\ s^{-1}$) but for 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene the reaction is extremely slow with half-lives in the range of minutes in 50% (v/v) Me_2SO–H_2O (k_{OH^-} 0.18 $dm^3\ mol^{-1}\ s^{-1}$). The steady increase in the rate coefficient for proton transfer from protonated 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene to hydroxide ion over the solvent range 50—90% (v/v) Me_2SO–H_2O is due to a weakening of the intramolecular hydrogen bond in the protonated amine.

In this paper the unusual acid–base properties of 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene (3) and 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene (4) are described. Our initial studies with these amines have been published [1] and we now present a full report of kinetic and equilibrium measurements of the acid–base reactions between the protonated amines and hydroxide ion in a wide range of Me_2SO–H_2O mixtures.

In previous work with diaminonaphthalenes, 1,8-bis(dimethylamino)naphthalene (1) was found [2,3] to be an extremely strong base (pK_a 12.1) and unusually low rates of proton transfer from the protonated amine to hydroxide ion in aqueous solution,[3] in dioxane–water,[3] and in Me_2SO–H_2O[4] were observed. It was further shown [3,4] that for 1,8-bis(diethylamino)naphthalene (2), basicity is increased and the rate of ionisation of the protonated amine is reduced. The C_2 structure of 1,8-bis(dimethylamino)naphthalene minimises the strain resulting from the lone pair and steric interactions of the dimethylamino-groups.[5] In the protonated amine, strain is much reduced because the proton is located in an intramolecular hydrogen bond between the amino-groups which are in a C_{2v} conformation.[6] The high pK_a of the amine may be explained by the presence of the intramolecular hydrogen bond in the protonated amine and by the relief of strain which occurs on protonation. The low rate of ionisation of the protonated amine is partly due to the strong intramolecular hydrogen bond which must be broken if proton transfer occurs and partly due to steric hindrance in the transition state for proton removal. In 1,8-bis(dimethylamino)naphthalene there is a strong interaction between the methyl groups and the hydrogen atoms at positions 2 and 7 in the naphthalene ring. It would therefore be expected that introduction of substituents at these positions would increase this interaction and force the molecule into a structure closer to C_{2v} with the lone pairs almost facing. In this case the amine would be more strained and protonation would be even more favourable than for 1,8-bis(dimethylamino)naphthalene. With this in mind, studies of (3) and (4) were carried out.[7]

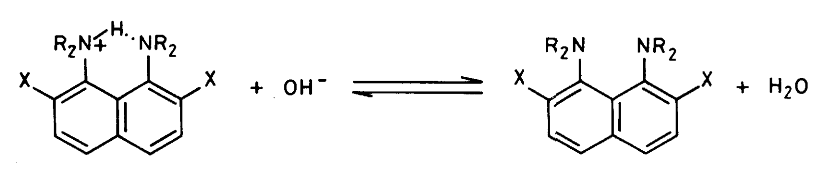


(1) X = H, R = Me
(2) X = H, R = Et
(3) X = OMe, R = Me
(4) X = OMe, R = Et

Experimental and Results

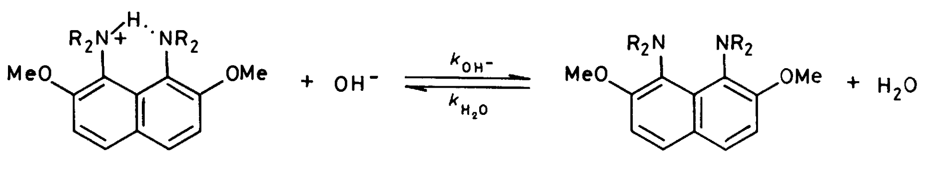
Basicity in Me_2SO–H_2O *Mixtures.*—The protonation of 1,8-bis(dimethylamino)naphthalene (1) (pK_a 12.1) was studied in aqueous solution.[2,3] However, for 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene (3) and 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene (4) this was not possible because these amines are stronger bases and only slight dissociation of the protonated forms occurs in concentrated sodium hydroxide solutions. To overcome this problem the acid–base equilibrium in equation (1) involving (3) and (4) was studied in Me_2SO–H_2O mixtures containing sodium hydroxide. These mixtures are much more basic than an aqueous solution containing the same concentration of sodium hydroxide.[8] An additional advantage is that the amines are more soluble in the mixed solvent.

Observations of equilibrium (1) for (3) and (4) were made spectrophotometrically at 350 nm where the free amines absorb strongly. The amines were present at concentrations of *ca.* 1.0×10^{-4} mol dm^{-3} and cells with 4 cm optical path length were used. In a typical experiment in 60% (v/v) Me_2SO–H_2O at 20.1 °C with 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene, the absorbance at 350 nm was measured in the presence of various concentrations of sodium hydroxide in the range 0.002—0.04 mol dm^{-3}. The ionic strength was kept constant at 0.10 mol dm^{-3} by the addition of potassium chloride. An equilibrium constant for reaction (1), $K = [\text{amine}]/[\text{amine H}^+][\text{OH}^-]$, was calculated from the measured absorbance at each hydroxide ion concentration and the average $K = 116 \pm 13$ mol dm^{-3} was taken. The results for experiments with 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene in 60% (v/v) Me_2SO–H_2O and for 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene in 45, 50, 60, and 70% (v/v) Me_2SO–H_2O are given in the second column of Table 1.



(1)

Table 1. Acid–base properties of 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene (3) and 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene (4) in Me_2SO-H_2O mixtures



$K = k_{OH^-}/k_{H_2O}[H_2O]$; ionic strength 0.1 mol dm^{-3}, temperature 20.1 °C

	K/dm^3 mol^{-1}	k_{OH^-}/dm^3 mol^{-1} s^{-1}	$k_{H_2O}[H_2O]$/s^{-1}	$k_{OH^-}/k_{H_2O}[H_2O]$
R = Me (3)				
60% (v/v) Me_2SO-H_2O	252 ± 40	440 ± 50	1.6 ± 0.3	273 ± 100
R = Et (4)				
45% (v/v) Me_2SO-H_2O	1.8 ± 0.1			
50% (v/v) Me_2SO-H_2O	8 ± 3	0.18 ± 0.04	0.014 ± 0.002	13 ± 4
60% (v/v) Me_2SO-H_2O	116 ± 13	3.3 ± 0.4	0.030 ± 0.003	110 ± 30
70% (v/v) Me_2SO-H_2O	3 000 ± 1 000	10.4 ± 0.8	0.003 ± 0.001 [a]	
80% (v/v) Me_2SO-H_2O	>20 000	45 ± 5		
90% (v/v) Me_2SO-H_2O	>20 000	*ca.* 250		

[a] Calculated as $k_{H_2O}[H_2O] = k_{OH^-}/K$.

Table 2. Comparison of acid–base properties in 35% (v/v) Me_2SO-H_2O at 25.0 °C

$$BH^+ + OH^- \underset{k_{H_2O}[H_2O]}{\overset{k_{OH^-}}{\rightleftharpoons}} B + H_2O$$

$K = [B]/[BH^+][OH^-]$

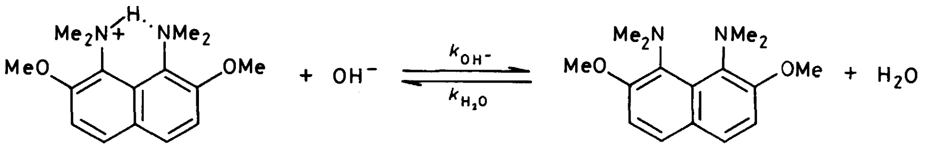
B	Solvent	K/dm^3 mol^{-1}	pK_a [a]	k_{OH^-}/dm^3 mol^{-1} s^{-1}	$k_{H_2O}[H_2O]$/s^{-1}
(1)	H_2O [b]	52 ± 14	12.1	1.9 ± 0.4 × 10^5	3 900 ± 500
(1)	35% (v/v) Me_2SO-H_2O [c]	4 100 ± 500	12.1	4 ± 1 × 10^5	90 ± 10
(3)	35% (v/v) Me_2SO-H_2O [c]	0.4 ± 0.1	16.1 [a]	110 ± 30	270 ± 30
(4)	35% (v/v) Me_2SO-H_2O [c]	0.26 ± 0.1	16.3 [d]		

[a] The pK_a value for 1,8-bis(dimethylamino)naphthalene (1) was determined [3] in aqueous solution at ionic strength 0.1 mol dm^{-3}. The pK_a values for 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene (3) and 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene (4) refer to aqueous solution at ionic strength 0.1 mol dm^{-3}. [b] Results for (1) in aqueous solution are taken from ref. 3 and refer to ionic strength 0.1 mol dm^{-3}. [c] Values of K, k_{OH^-}, and $k_{H_2O}[H_2O]$ determined in the present work at ionic strength 0.4 mol dm^{-3}. [d] These values differ by 0.2 pK units from previously quoted results, see footnote *.

For 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene in 80% and 90% (v/v) Me_2SO-H_2O the hydroxide ion concentrations necessary to bring about dissociation of the protonated amine were very low so that accurate measurements were not possible and the values for K given in these mixtures are estimated lower limits.

A comparison of the basicities of (1), (3), and (4) was obtained from equilibrium measurements with each amine in 35% (v/v) Me_2SO-H_2O at 25.0 °C and ionic strength 0.40 mol dm^{-3}. In solvent mixtures containing less than 35% (v/v) Me_2SO, the concentrations of sodium hydroxide necessary to generate (3) and (4) from their protonated forms were too high to permit measurements. For 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene in 35% (v/v) Me_2SO-H_2O the amine is half-protonated even in the presence of 4 mol dm^{-3} NaOH and this together with the low solubility of the amine meant that it was necessary to measure low absorbances (<0.2) in optical cells with 10 cm path length in order to study the acid–base equilibrium in this solvent. For 1,8-bis(dimethylamino)naphthalene, very low concentrations of sodium hydroxide are needed to bring about ionisation of the protonated amine in 35% (v/v) Me_2SO-H_2O. The values of the equilibrium constants for reaction (1) involving (1), (3), and (4) in 35% (v/v) Me_2SO-H_2O are given in Table 2. From these results and the value pK_a = 12.1 determined [3] for (1) in aqueous solution it is possible to estimate pK_a values referring to aqueous solution for (3) and (4) by assuming that the change in solvent from aqueous solution to 35% (v/v) Me_2SO-H_2O has the same effect on K for (1), (3), and (4). The calculated pK_a values at 25.0 °C and ionic strength 0.10 mol dm^{-3} are given in Table 2.

Rates of Proton Transfer for 1,8-*Bis*(*dimethylamino*)-2,7-*dimethoxynaphthalene*.—The kinetics of equilibrium (2) were studied by the temperature-jump method in 60% (v/v) Me_2SO-H_2O at 15.0 and 20.1 °C. The equilibrium was



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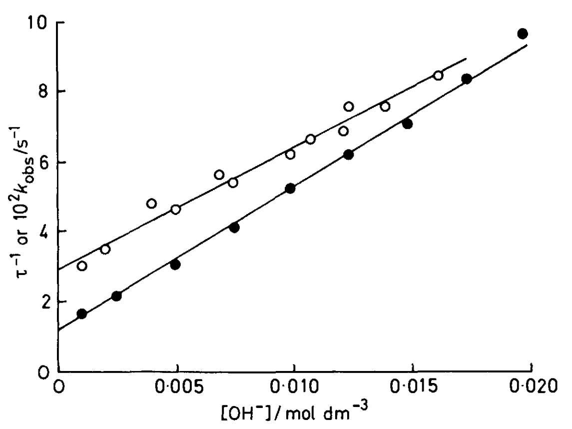


Rate coefficients for proton transfer in 60% (v/v) Me_2SO-H_2O containing hydroxide ion: ●, 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene at 15.0 °C, ordinate τ^{-1}/s^{-1}; ○, 1,8-bis-(diethylamino)-2,7-dimethoxynaphthalene at 20.1 °C, ordinate $10^2\ k_{obs.}/s^{-1}$

disturbed in favour of products by a rapid temperature jump of 3.5 °C which was brought about using a 30 kV discharge from a 0.01 μF capacitor. The reaction solution was thermostatted 3.5 °C below the required reaction temperature and contained sodium hydroxide (0.001—0.02 mol dm^{-3}) and 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene (*ca.* 2×10^{-4} mol dm^{-3}) at a total ionic strength of 0.1 mol dm^{-3}. The increase in concentration of the free amine as a result of the temperature jump was followed spectrophotometrically at 350 nm. The relaxation times were measured at different concentrations of sodium hydroxide and the results at 15.0 °C are shown in the Figure. For equilibrium (2) with hydroxide ion present in excess, the dependence of reciprocal relaxation time on hydroxide ion concentration is given by equation (3)

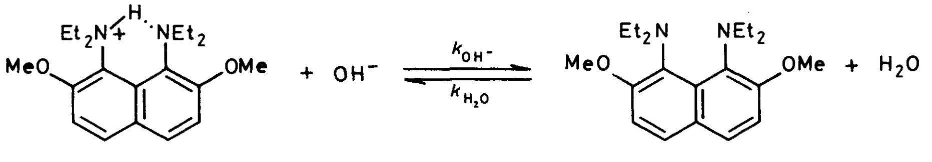
$$\tau^{-1} = k_{OH^-}[OH^-] + k_{H_2O}[H_2O] \qquad (3)$$

At 15 °C the values k_{OH^-} 380 ± 50 $dm^3\ mol^{-1}\ s^{-1}$ and $k_{H_2O}[H_2O]$ 1.4 ± 0.2 s^{-1} were obtained from the linear plot of τ^{-1} against $[OH^-]$ and at 20.1 °C the results were k_{OH^-} 440 ± 50 $dm^3\ mol^{-1}\ s^{-1}$ and $k_{H_2O}[H_2O]$ 1.6 ± 0.3 s^{-1}. At each temperature the value of the ratio $k_{OH^-}/k_{H_2O}[H_2O]$ obtained from the kinetic experiments was in good agreement with the value of the equilibrium constant for reaction (2) determined from spectrophotometric equilibrium measurements.

To confirm that the observed chemical relaxations referred to equilibrium (2), the variation of relaxation amplitude with hydroxide ion concentration was measured. For equilibrium (2) the displacement from equilibrium following a temperature jump will be largest when equal concentrations of the amine and the protonated form are present. At 20.1 °C, half-dissociation of the protonated amine occurs at $[OH^-]$ 0.0040 ± 0.0006 mol dm^{-3} and this result is in agreement with the observation of a maximum in the relaxation amplitude at $[OH^-]$ 0.004 ± 0.001 mol dm^{-3}.

A comparison between the rates of proton transfer for 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene and 1,8-bis-(dimethylamino)naphthalene was obtained from temperature-jump studies of both amines in 35% (v/v) Me_2SO-H_2O at 25.0 °C and ionic strength 0.40 mol dm^{-3}. To observe a chemical relaxation for 1,8-bis(dimethylamino)naphthalene in this solvent it was necessary to use very low concentrations of sodium hydroxide (0.0005—0.001 mol dm^{-3}). From the observed linear dependence of τ^{-1} on hydroxide ion concentration over this range an approximate value k_{OH^-} $4 \pm 1 \times 10^5$ $dm^3\ mol^{-1}\ s^{-1}$ was obtained. To observe a chemical relaxation for 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene in this solvent extremely high hydroxide ion concentrations were needed, in the range 0.2—0.4 mol dm^{-3}. Even in this range the first term in equation (3) makes a small contribution and the reciprocal relaxation time was found to have a constant value of 270 ± 30 s^{-1} which corresponds to $k_{H_2O}[H_2O]$. The result k_{OH^-} 110 ± 30 $dm^3\ mol^{-1}\ s^{-1}$ was calculated for 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene in 35% (v/v) Me_2SO-H_2O by combining the measured value of $k_{H_2O}[H_2O]$ with the value of the equilibrium constant. The kinetic and equilibrium results for amines (1), (3), and (4) in 35% (v/v) Me_2SO-H_2O are collected in Table 2.

Rates of Proton Transfer for 1,8-*Bis*(*diethylamino*)-2,7-*dimethoxynaphthalene.*—Reaction (4) involving 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene was sufficiently slow that kinetic measurements were made with a conventional u.v. spectrophotometer. The reaction was studied at 20.1 °C in 50, 60, 70, 80, and 90% (v/v) Me_2SO-H_2O with a concentration of 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene of 8×10^{-5} mol dm^{-3} in the presence of various concentrations of sodium hydroxide. The ionic strength was kept constant at 0.10 mol dm^{-3} by addition of potassium chloride except in 90% (v/v) Me_2SO-H_2O for which the ionic strength was maintained at 0.08 mol dm^{-3} because of the lower solubility of potassium chloride in this solvent mixture. The kinetics were studied by observing the slow increase in absorbance at 350 nm which accompanied formation of the free amine when 0.01 ml of a concentrated solution of sodium hydroxide was introduced into an optical cell with 4 cm path length containing 10 ml of a solution of protonated 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene in Me_2SO-H_2O. Proton transfer took minutes to reach equilibrium. Experiments were also carried out in which the equilibrium was disturbed in the opposite direction by diluting an equilibrium mixture of the amine and protonated form containing sodium hydroxide. A slow decrease in absorbance at 350 nm was then observed. However this procedure was less convenient experimentally and few measurements were made in this way.



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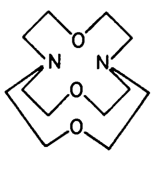

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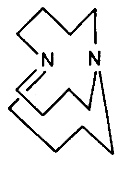

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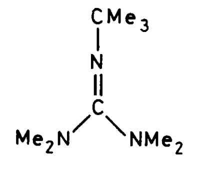

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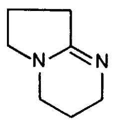

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The first-order approach to equilibrium for both experimental procedures is given by equation (5) in which [B] represents the concentration of the basic form of 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene present at time t during reaction and $[B]_e$ is the concentration when equilibrium is reached. The first-order rate coefficient ($k_{obs.}$) for the approach to equilibrium was calculated as the gradient of the linear plot of $\ln(A_e - A)$ against time where A_e is the absorbance reading at 350 nm after equilibrium is reached and A is the absorbance at time intervals during the reaction. The dependence of $k_{obs.}$ on hydroxide ion concentration in 60% (v/v) Me_2SO–H_2O is shown in the Figure and in this solvent the half-lives of the proton transfer are in the range 8—23 s. In 70% (v/v) Me_2SO–H_2O the reactions occurred with half-lives between 0.5 and 2 min. In each solvent mixture, plots of $k_{obs.}$ against hydroxide ion concentration were used to determine values for k_{OH^-} and $k_{H_2O}[H_2O]$ and the results are given in Table 1. The values of the ratios $k_{OH^-}/k_{H_2O}[H_2O]$ were compatible within experimental error with the value of the equilibrium constant determined separately from equilibrium measurements.

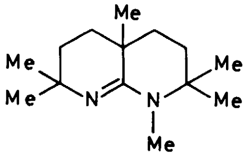
$$\ln[B]_e - \ln([B]_e - [B]) = k_{obs.}t \qquad (5)$$

$$k_{obs.} = k_{H_2O}[H_2O] + k_{OH^-}[OH^-] \qquad (6)$$

Discussion

The results in Table 2 show that the amines studied in this work are very strong bases. 1,8-Bis(diethylamino)-2,7-dimethoxynaphthalene with a pK_a value of *ca.* 16.3 * is 10—11 units more basic than expected for an aromatic amine. Indeed this amine is the strongest uncharged base whose acid–base equilibrium has been directly observed. Studies [9] have shown that the cryptand (5) has a much higher pK_a, >17.8, but the acid–base equilibrium could not be observed directly. It is thought [9,10] that 1,6-diazabicyclo[4.4.4]-tetradecane (6) is even more basic although, again, direct studies of protonation–deprotonation could not be made. There is considerable interest in the development of strong bases for use in organic synthesis. Besides (5) and (6) the strongest uncharged bases which are known include 2-t-butyl-1,1,3,3-tetramethylguanidine [11] (7) (pK_a *ca.* 14), 1,5-diazabicyclo[4.3.0]non-5-ene (8) (pK_a *ca.* 13.5 [11,12]) and the hexamethyl-2,10-diazabicyclo[4.4.0]dec-1-ene [13] (9) which is more basic than the pentamethylpiperidine (10) (pK_a 11.25 [14]). It remains to be seen whether the slow proton transfer behaviour observed for the alkylaminonaphthalenes will limit their usefulness in organic synthesis.

The exceptionally high basicity of the alkylaminonaphthalenes results from stabilisation of the protonated amines by an intramolecular hydrogen bond and from destabilisation of the free amine by strain. Comparison of the data in Table 2 for 1,8-bis(dimethylamino)naphthalene and 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene in 35% (v/v) Me_2SO–H_2O shows that methoxy-substituents increase the basicity of the amine by a factor of *ca.* 10^4. The effect of methoxy-substituents on the basicity of aniline is small and brings about a change in pK_a of less than one unit.[15] The two-fold difference in basicity between 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene and 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene in 35% (v/v) Me_2SO–H_2O indicates that replacing methyl by ethyl groups has only a modest effect. A similar difference in basicity of the two amines is found in 60% (v/v) Me_2SO–H_2O, although in this solvent the actual values of the equilibrium constants for equilibrium between the protonated amines and hydroxide ion are 500-fold higher than in 35% (v/v) Me_2SO–H_2O. The change in equilibrium constant with solvent composition arises mostly because of the enhanced basicity of hydroxide ion in Me_2SO–H_2O solvent mixtures containing a greater proportion of Me_2SO. This effect is well known.[8]



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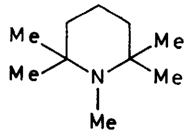

(10)

Perhaps the kinetic behaviour of these amines is even more surprising than their unusual basicity. The deprotonation of protonated 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene by hydroxide ion occurs with half-lives in the range of minutes. For example in 70% (v/v) Me_2SO–H_2O in the presence of sodium hydroxide (0.001 45 mol dm^{-3}) the half-life for ionisation of the protonated amine is 54 s. This is a remarkable observation for thermodynamically favourable proton removal by hydroxide ion from a relatively simple ammonium ion. Apart from proton transfer involving the cryptand (5) the reactions studied here are the slowest proton transfers which have been observed between hydroxide ion and an ammonium ion. Deprotonation of the inside-protonated form of (5) is too slow to be directly measurable but the estimated [9] value for the rate coefficient is much lower than the values obtained for the alkylaminonaphthalenes. The acid–base site in (6) is even more hindered and formation of the inside protonated ammonium ion does not take place by simple proton transfer even under the most severe conditions.[10]

The kinetic effects which have been observed for the alkylaminonaphthalenes can be explained by the presence of a strong intramolecular hydrogen bond in the protonated amines which must open prior to proton transfer, to give a low concentration of a non-hydrogen-bonded form from which the proton is removed.[16] In addition it is necessary to propose that attack by hydroxide ion on the open ammonium ion is sterically hindered. The results in Tables 1 and 2 show that the introduction of 2- and 7-methoxy-substituents into

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* For (3) and (4) pK_a values of 16.3 and 16.5 respectively were previously quoted.[1] These results were based on a pK_a value for (1) of 12.3 [2] instead of the value pK_a 12.1 [3] used here.

1,8-bis(dimethylamino)naphthalene reduces the rate of hydroxide-ion-catalysed ionisation of the protonated amine by a factor of 4 000 and the equilibrium constant for the reaction is reduced by a factor of 10 000. The results for 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene and 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene in 60% (v/v) Me_2SO-H_2O show that replacement of *N*-methyl by *N*-ethyl substituents reduces the rate 100-fold and the equilibrium constant by a factor of 2. This effect is similar to the results obtained in 30% (v/v) Me_2SO-H_2O for 1,8-bis(dimethylamino)naphthalene and 1,8-bis(diethylamino)naphthalene for which the rate coefficients differ 40-fold and the equilibrium constants seven-fold.[4] In all cases, proton transfer from the protonated amines to hydroxide ion is thermodynamically favourable and for most amines under these conditions the rate coefficients would have the diffusion-limited value of *ca.* 1×10^{10} dm^3 mol^{-1} s^{-1}. For 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene the rate coefficient in 50% (v/v) Me_2SO-H_2O is 11 orders of magnitude below this value. The effect of 2- and 7-methoxy-substituents in reducing the rate coefficient for proton removal from the protonated amines and increasing the basicity of the amines is best explained by an increase in crowding in the molecules which stabilises the hydrogen-bonded form of the protonated amine relative to the open form and this has a roughly similar effect on the acidity of the protonated amine (or basicity of the amine) and on the rate coefficient for proton removal. The larger effect of replacing methyl by ethyl groups on the rate coefficient for proton removal than on the equilibrium constant is best explained as being due to steric hindrance to the attack of hydroxide ion on the open form of the protonated amines.

The effect of increasing Me_2SO content on the values of the rate coefficients for proton transfer from the protonated amines implies that if 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene could have been studied in aqueous solution, even lower rates of proton transfer would have been observed. The value of k_{OH^-} for 1,8-bis(dimethylamino)naphthalene is *ca.* two-fold higher in 35% (v/v) Me_2SO-H_2O than in aqueous solution and for 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene k_{OH^-} increases about four-fold from 35 to 60% (v/v) Me_2SO-H_2O. For 1,8bis-(diethylamino)-2,7-dimethoxynaphthalene, k_{OH^-} is 1 000-fold higher in 90% (v/v) Me_2SO-H_2O than in 50% (v/v) Me_2SO-H_2O. For most protonated amines for which ionisation is diffusion limited the value of k_{OH^-} would vary slightly with solvent composition as a result of the small variation in viscosity of Me_2SO-H_2O mixtures with solvent composition.[17] The variation in the value of k_{OH^-} observed here is much larger. The effects of solvent composition on the rates of other proton transfers in Me_2SO-H_2O mixtures have been investigated [18] but no consistent picture emerges. In the present work the increase in rate coefficient which accompanies an increase in the fraction of Me_2SO could be due to a solvent effect on the stability of the open form of the protonated amine. It is known [19] that Me_2SO is a better hydrogen-bond acceptor than H_2O. Therefore in solvent mixtures richer in Me_2SO, the non-hydrogen-bonded form will be stabilised relative to the intramolecularly hydrogen-bonded form. Since proton transfer occurs through a low concentration of the open form this will have the effect of increasing the rate of the overall proton transfer.

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References

1 R. W. Alder, N. C. Goode, N. Miller, F. Hibbert, K. P. P. Hunte, and H. J. Robbins, *J. Chem. Soc., Chem. Commun.*, 1978, 89.

2 R. W. Alder, P. Bowman, W. R. S. Steele, and D. R. Winterman, *Chem. Commun.*, 1968, 723.

3 F. Hibbert, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1862.

4 A. Awwal and F. Hibbert, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1589.

5 H. Einspahr, J.-B. Robert, R. E. Marsh, and J. D. Roberts, *Acta Crystallogr.*, 1973, **29B**, 1611.

6 M. R. Truter and B. L. Vickery, *J. Chem. Soc., Dalton Trans.*, 1972, 395.

7 Full details of the preparation of (3) and (4) have been published, see R. W. Alder, M. R. Bryce, N. C. Goode, N. Miller, and J. Owen, *J. Chem. Soc., Perkin Trans. 1*, 1981, 2840.

8 D. Dolman and R. Stewart, *Can. J. Chem.*, 1967, **45**, 911; C. H. Rochester, ' Acidity Functions,' Academic Press, London, 1970.

9 J. Cheney and J.-M. Lehn, *J. Chem. Soc., Chem. Commun.*, 1972, 487; P. B. Smith, J. L. Dye, J. Cheney, and J.-M. Lehn, *J. Am. Chem. Soc.*, 1981, **103**, 6044.

10 R. W. Alder, A. Casson, and R. B. Sessions, *J. Am. Chem. Soc.*, 1979, **101**, 3652.

11 D. H. R. Barton, J. D. Elliott, and S. D. Géro, *J. Chem. Soc., Perkin Trans. 1*, 1982, 2085.

12 H. Oedinger, F. Möller, and K. Eiter, *Synthesis*, 1972, 591.

13 F. Heinzer, M. Soukup, and A. Eschenmoser, *Helv. Chim. Acta*, 1978, **61**, 2851.

14 H. K. Hall, Jr., *J. Am. Chem. Soc.*, 1957, **79**, 5444; H. Z. Sommer, H. I. Lipp, and L. L. Jackson, *J. Org. Chem.*, 1971, **36**, 824.

15 D. D. Perrin, ' Dissociation Constants of Organic Bases in Aqueous Solution,' Butterworths, London, 1965; supplement, 1972.

16 F. Hibbert and H. J. Robbins, *J. Am. Chem. Soc.*, 1978, **100**, 8239.

17 R. G. Le Bel and D. A. J. Goring, *J. Chem. Eng. Data*, 1962, **7**, 100.

18 C. F. Bernasconi, M. C. Muller, and P. Schmid, *J. Org. Chem.*, 1979, **44**, 3189; C. F. Bernasconi and A. Kanavarioti, *ibid.*, p. 4829.

19 M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, 1976, **98**, 377.

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