Rates of Proton Transfer from Protonated 1,8-Bis(dimethylamino)- and 1,8-Bis(diethylamino)-naphthalene to Hydroxide Ion in 20% and 30% (v/v) Dimethyl Sulphoxide–Water

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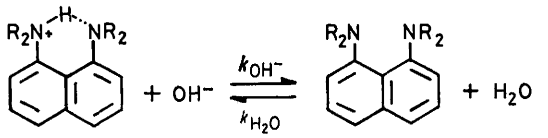
The conjugate acids of 1,8-bis(dimethylamino)naphthalene and 1,8-bis(diethylamino)naphthalene are intramolecularly hydrogen-bonded, and proton transfers to hydroxide ion in 30% (v/v) dimethyl sulphoxide–water occur slowly, with rate coefficients (k_{OH^-}) 6.1×10^5 and 1.6×10^4 l mol^{-1} s^{-1}, respectively. Substitution of ethyl groups for methyl groups in 1,8-bis(dimethylamino)naphthalene has a larger effect on the rate of proton transfer than on the equilibrium constant, and this unusual observation is considered in terms of a two-step mechanism for proton removal from the protonated amines.

We have previously measured[1] the rate of proton transfer from protonated 1,8-bis(dimethylamino)naphthalene to hydroxide ion in aqueous solution [reaction (1) with R = Me]. It was found that thermodynamically favourable proton removal from the protonated amine is an unusually slow reaction, with a rate coefficient below the diffusion limit expected for ionisation of a substituted ammonium ion by a factor of *ca.* 10^5. The low rate is due to the presence of a strong intramolecular hydrogen bond in the protonated amine, and this factor may also partly account for the exceptionally high basicity of the amine.[2]



(1)

In our earlier experiments, chemical relaxation times for the equilibrium (1) were measured in aqueous alkaline buffers containing 1,8-bis(dimethylamino)naphthalene using the temperature-jump method.[1] Although the results indicated that the observed chemical relaxation referred to the equilibrium (1), it seemed desirable to extend our measurements to conditions where the equilibrium (1) could be studied in the absence of buffers. Proton transfer involving 1,8-bis(diethylamino)naphthalene was also studied previously in order to elucidate the effect of a change in substituent, but only tentative conclusions were reached. We now present a complete kinetic study of proton transfer for both amines in 30% (v/v) dimethyl sulphoxide–water containing sodium

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[1] F. Hibbert, *J.C.S. Perkin II*, 1974, 1862.

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

hydroxide and also for 1,8-bis(dimethylamino)naphthalene in 20% (v/v) dimethyl sulphoxide–water.

EXPERIMENTAL

Equilibrium Measurements.—Equilibrium constants (K) for reaction (1) involving 1,8-bis(dimethylamino)- and 1,8-bis(diethylamino)-naphthalene were determined spectrophotometrically (Unicam SP 8000 instrument) by making observations at the absorbance maxima of the free bases (330 nm) in thermostatted dimethyl sulphoxide–water containing low concentrations of sodium hydroxide (5×10^{-4}—10^{-2}M). Dimethyl sulphoxide (AnalaR grade) was distilled under vacuum from calcium hydride and the 30% (v/v) mixed solvent was made up by adding 30 parts of dimethyl sulphoxide to 70 parts of doubly distilled water containing sodium hydroxide and the necessary amount of potassium chloride to maintain an ionic strength of 0.1M. For both amines, optical cells with 4 cm path lengths were used; for 1,8-bis(diethylamino)naphthalene the solubility of the amine is so low that a five-fold absorbance scale expansion was also necessary. Values of $K\{= [B]/[BH^+][OH^-]$, where B represents the 1,8-bis(dialkylamino)-naphthalene$\}$ are shown in the final column of the Table.

Kinetic Measurements.—For 1,8-bis(dimethylamino)- and 1,8-bis(diethylamino)-naphthalene chemical relaxation times for the equilibrium (1) were measured by using the temperature-jump instrument manufactured by Messanlagen Studiengesellschaft. The equilibrium position in 30% dimethyl sulphoxide–water was disturbed by a temperature rise of 9.7 °C brought about by a 25 kV discharge from a 0.05 μF capacitor. The initial temperature was measured with a thermocouple and adjusted so that the final temperature after temperature-jump was 35 °C. Observations of the chemical relaxation occurring after the temperature rise were made at the absorbance maxima of the amines.

RESULTS AND DISCUSSION

Amplitude of Relaxation.—In the earlier studies we were unable to detect a chemical relaxation for solutions of 1,8-bis(dimethylamino)naphthalene in aqueous sodium hydroxide.[1] In the present work a measurable relaxation was observable for solutions of the amine in dimethyl sulphoxide–water containing sodium hydroxide. In the mixed solvent the change in optical density (amplitude of relaxation) occurring after the temperature perturbation is much larger than in fully aqueous solution; one reason for this is that higher concentrations of the amine can be used in the mixed solvent because of the higher solubility. The amplitude of relaxation for solutions of 1,8-bis(dimethylamino)naphthalene in 20% dimethyl sulphoxide–water containing sodium hydroxide (1.5×10^{-3}M) was shown to be linearly dependent on the total concentration of amine. Extrapolation of these results to the maximum concentration of amine which could be used in fully aqueous sodium hydroxide solutions predicted that the relaxation at this concentration would be undetectable. The amplitude of the relaxation for 1,8-bis(dimethylamino)naphthalene in 20% dimethyl sulphoxide–water was also measured at various hydroxide ion concentrations. For an equilibrium of the type shown in equation (1), under conditions where hydroxide ion is in excess, the amplitude[3] should show a maximum at $[OH^-] = 1/K$. This maximum was observed at $[OH^-] = 1.5 \times 10^{-3}$M and the derived value of K ($7 \pm 2 \times 10^2$) is in good agreement with the separately measured equilibrium constant (Table).

In the earlier work a relaxation was observed for 1,8-bis(dimethylamino)naphthalene (B) in trifluoroethanol–trifluoroethoxide buffers.[1] In buffers, the equilibrium (2) is disturbed by a temperature rise and this rapid change in hydroxide ion concentration brings about a slower shift of the equilibrium (3). In the absence of buffers the shift in the equilibrium (3) occurring as a result of the temperature rise is undetectable in fully aqueous solutions.

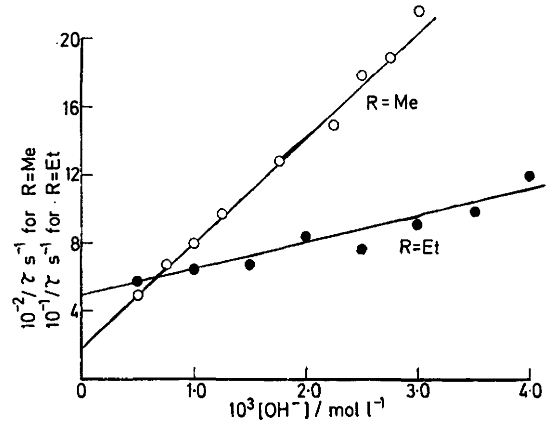
$$CF_3CH_2OH + OH^- \rightleftharpoons CF_3CH_2O^- + H_2O \quad \text{fast} \quad (2)$$

$$BH^+ + OH^- \rightleftharpoons B + H_2O \quad \text{slow} \quad (3)$$

Relaxation Times and Rates of Proton Transfer.—For the equilibrium (1) the concentration dependence of the reciprocal relaxation time under conditions where hydroxide ion and water are in excess over the alkylaminonaphthalenes is given by equation (4). The

$$1/\tau = k_{OH^-}[OH^-] + k_{H_2O}[H_2O] \quad (4)$$

measured reciprocal relaxation times for proton transfer involving 1,8-bis(dimethylamino)- and 1,8-bis(diethylamino)-naphthalene in 30% dimethyl sulphoxide–water at 35.0 °C vary with hydroxide ion concentration as shown in the Figure. The derived values of k_{OH^-} and $k_{H_2O}[H_2O]$ are given in the Table and the values of $k_{OH^-}/k_{H_2O}[H_2O]$ are in good agreement with the separately measured equilibrium constants.



Variation of reciprocal relaxation time with hydroxide ion concentration for 1,8-bis(dialkylamino)naphthalenes in 30% (v/v) dimethyl sulphoxide–water

The rate coefficients for proton transfer involving 1,8-bis(dimethylamino)naphthalene and hydroxide ion in 20% dimethyl sulphoxide–water at 25 °C are compared in the Table with the values determined in buffered aqueous solutions.[1] The change in solvent has a small

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[3] E. F. Caldin, *Chem. in Britain*, 1975, **11**, 4.

effect on the rate of proton transfer and no complications are caused by the use of buffers in the previous work.

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

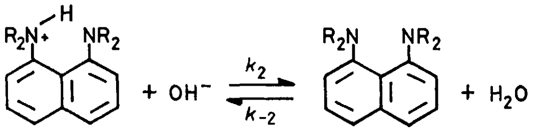
$K = [B]/[BH^+][OH^-]$, ionic strength 0.1M

R in B	Solvent	t/°C	$10^{-5}k_{OH^-}$/l mol^{-1} s^{-1}	$k_{H_2O}[H_2O]/s^{-1}$	$k_{OH^-}/k_{H_2O}[H_2O]$	K/l mol^{-1}
Me	H_2O *	25	1.9 ± 0.4	$3\,900 \pm 500$	49 ± 15	52 ± 14
Me	20% Me_2SO-H_2O	25	2.9 ± 0.2	350 ± 50	830 ± 150	660 ± 60
Me	30% Me_2SO-H_2O	35	6.1 ± 0.5	200 ± 30	$3\,100 \pm 700$	$2\,800 \pm 200$
Et	30% Me_2SO-H_2O	35	0.16 ± 0.02	47 ± 4	340 ± 70	380 ± 80

* Results in water taken from ref. 1.

The rate coefficients for proton transfer from the protonated amines are several orders of magnitude below the diffusion limit (*ca.* 3×10^{10} l mol^{-1} s^{-1}) expected for the thermodynamically favourable ionisation of a protonated amine.[4] The reactions are slow because of strong intramolecular hydrogen bonds in the protonated amines. The rate coefficient for proton transfer from protonated 1,8-bis(diethylamino)naphthalene to hydroxide ion is 38-fold lower than the rate coefficient observed for 1,8-bis(dimethylamino)naphthalene. A difference in rate of 10^2-fold was estimated from the earlier studies,[1] but this was approximate since a complete analysis was not possible. The data in the Table lead to the unusual observation that replacing methyl by ethyl groups causes a larger effect on the rate of proton transfer (38-fold decrease) than on the overall equilibrium constant for the reaction (7-fold decrease). A Brønsted exponent (α) of 1.8 ± 0.3 for proton transfer from the protonated amines to hydroxide ion is calculated from the results. Although anomalous Brønsted exponents outside the usual range $0 \leqslant \alpha \leqslant 1$ have been observed for proton transfer from carbon,[5] to our knowledge no examples involving proton transfer from nitrogen have been reported previously.

(5)



(6)

The low rates of proton transfer and the effect of replacing methyl groups by ethyl groups will be discussed in terms of a two-step mechanism for proton transfer shown in equations (5) and (6). This mechanism was shown to operate for proton transfer from a substituted salicylate ion,[6] and we will assume the same mechanism applies in the present case. An alternative mechanism involves a one-step direct attack by base on the intramolecularly hydrogen-bonded proton [6] and the present results cannot distinguish between these possibilities. For the mechanism shown in equations (5) and (6), the measured rate coefficients k_{OH^-} and k_{H_2O} and the overall equilibrium constant K are related by equations (7)—(9), in which K_1 is the equilibrium constant between hydrogen-bonded and non-hydrogen-bonded forms of the

$$k_{OH^-} = K_1k_2 \qquad (7)$$

$$k_{H_2O} = k_{-2} \qquad (8)$$

$$K = K_1k_2 \qquad (9)$$

protonated amines and K_2 is the equilibrium constant for reaction (6). Reaction (6) will be strongly thermodynamically favourable for both amines and, if normal proton transfer behaviour is assumed, the forward rate coefficient will be diffusion-limited ($k_2 = 3 \times 10^{10}$ l mol^{-1} s^{-1}). Hence values of K_1 for the intramolecular hydrogen bonds in protonated 1,8-bis(dimethylamino)- and 1,8-bis(diethylamino)-naphthalene of 2×10^{-5} and 5×10^{-7}, respectively, can be calculated from equation (7), using the values of k_{OH^-} in 30% dimethyl sulphoxide–water.

The unusual substituent effect may be accounted for in terms of the mechanism shown in equations (5) and (6) in two ways. If the assumption is made that reaction (6) is a normal proton transfer with a diffusion-limited rate coefficient ($k_2 = 3 \times 10^{10}$ l mol^{-1} s^{-1}) for both amines, then from equation (7) the rate difference results from a 38-fold difference in the values of K_1 for the methyl and the ethyl derivative. The unusual substituent effect on the rate and equilibrium constant may arise because of opposite substituent effects on K_1 and K_2. The observed 7-fold difference in overall equilibrium constants and the 38-fold difference in the values of K_1 are only compatible with equation (9) if the value of K_2 is *ca.* 5-fold larger for 1,8-bis(diethylamino)- than for 1,8-bis(dimethylamino)-naphthalene. The equilibrium constant K_2 refers to dissociation of the non-hydrogen bonded ammonium ions. For aliphatic and aromatic amines, the usual effect of replacing methyl by ethyl groups is to reduce the acid dissociation constant,[7] in contrast to the effect on K_2 required to explain our data. We have only been able to find one example where replacement of methyl by ethyl groups increases the dissociation constant.[8] This explanation of the sub-

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[4] M. Eigen, *Angew. Chem. Internat. Edn.*, 1964, **3**, 1.

[5] F. G. Bordwell and W. J. Boyle, *J. Amer. Chem. Soc.*, 1972, **94**, 3907.

[6] F. Hibbert and A. Awwal, *J.C.S. Chem. Comm.*, 1976, 995.

[7] D. D. Perrin, ' Dissociation Constants of Organic Bases in Aqueous Solution,' Butterworths, London, 1965; Supplement, 1972.

[8] J. Fakstorp and G. Speggers, *Acta Chem. Scand.*, 1958, **12**, 350.

stituent effect therefore seems unlikely, but since we cannot be sure that the effect of substituting ethyl for methyl groups on the value of K_2 will be the same as the effect on the acidity of simple ammonium ions, the values of K_2 for 1,8-bis(dimethylamino)- and 1,8-bis(diethylamino)-naphthalene required by this analysis cannot be ruled out.

The anomalous substituent effect can also be explained in terms of a change in the value of k_2 in going from 1,8-bis(dimethylamino)- to 1,8-bis(diethylamino)-naphthalene. If the values of K_2 for the two amines are roughly similar, the substituent effect on the overall equilibrium constant ($K = K_1K_2$) arises from an effect on K_1, and the substituent effect on the rate of proton transfer ($k_{OH^-} = K_1k_2$) is a result of substituent effects on K_1 and k_2. Our experimental results would then require that the value of k_2 for 1,8-bis(dimethylamino)-naphthalene is *ca.* 5-fold larger than the value for 1,8-bis(diethylamino)naphthalene. This rate difference is not incompatible with diffusion-limited values for k_2, since different diffusion limits have been observed previously for proton transfers from substituted ammonium ions.[4,9] For example the rate coefficients for proton transfer from methylammonium and trimethylammonium ion to hydroxide ion are 3.7×10^{10} and 2.1×10^{10} l mol^{-1} s^{-1}, respectively. This difference may result from a disruption of the hydrogen-bonded solvent network in the vicinity of the ammonium ions by the methyl substituents,[5] and a similar effect may operate here. Alternatively, a difference in the values of k_2 for the amines may be attributed to steric hindrance to the attack of hydroxide ion on the non-hydrogen-bonded ammonium ions, which would mean that the transition state for proton removal is strained. By the Principle of Microscopic Reversibility, the same transition state will be involved in the reverse reaction in which a proton is transferred from water to the amines. Models based on the *X*-ray crystal structure of 1,8-bis-(dimethylamino)naphthalene [10] indicate that attack by water on the amines will be hindered and cannot occur without a change in conformation of the dimethylamino-groups. The result of this may be a lowering in the value of k_2 for 1,8-bis(dimethylamino)naphthalene below the diffusion limit, and the rate coefficient for 1,8-bis-(diethylamino)naphthalene may be lower still.

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[9] M. Eigen and L. de Maeyer, ' Technique of Organic Chemistry,' eds. S. L. Friess, E. S. Lewis, and A. Weissberger, Interscience, New York, 1963, vol. VIII, part 2, p. 895.

[10] H. Einspahr, J-B. Robert, R. E. Marsh, and J. D. Roberts, *Acta Cryst.*, 1973, 1611.