Kinetics of the Alkaline Hydrolysis of 1,8-Bis(trifluoroacetylamino)naphthalene to 1-Amino-8-trifluoroacetylaminonaphthalene in 70%, 80% and 90% (v/v) Me_2SO–H_2O

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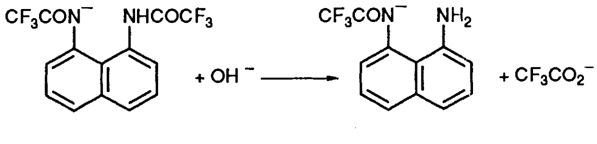
The kinetics of the hydrolysis of 1,8-bis(trifluoroacetylamino)naphthalene to 1-amino-8-trifluoroacetylaminonaphthalene have been studied in 70%, 80% and 90% (v/v) Me_2SO–H_2O in the presence of hydroxide ion. Under these conditions the product of the reaction is present as the amide anion and does not undergo further reaction. Approximate values of pK_1 5.7 and pK_2 15.9 have been measured in 70% (v/v) Me_2SO–H_2O for dissociation of the amide protons of 1,8-bis(trifluoroacetylamino)naphthalene. The hydrolysis involves reaction of the amide monoanion because negligible concentrations of the undissociated amide are present and the dianion is unreactive. The dependence of the first-order rate coefficient (k_{obs}) on $[OH^-]$ in 70% and 80% (v/v) Me_2SO–H_2O is fitted by the expression $k_{obs} = (k_0 + k_1[OH^-] + k_2[OH^-]^2)/(1 + K''[OH^-])$ where K'' is the equilibrium constant for proton removal by hydroxide ion from the monoanion of 1,8-bis(trifluoroacetylamino)naphthalene to give the dianion. The magnitude of k_0 in 70% (v/v) Me_2SO–H_2O suggests that the attack of water on the amide carbonyl at the 1-position is assisted by intramolecular catalysis involving the amide anion at the 8-position. The data in 90% (v/v) Me_2SO–H_2O are fitted by the expression $k_{obs} = (k_2/K'')[OH^-]$. Under these conditions the amide is practically fully dissociated into the dianion and the k_0 and $k_1[OH^-]$ terms are negligibly small in comparison with the $k_2[OH^-]^2$ term.

We have recently reported examples of intramolecular participation involving amide groups in the reactions of 1,8-substituted naphthalenes. For example, the hydrolysis of 1-acyloxy-8-acylaminonaphthalene to 1-hydroxy-8-acylaminonaphthalene in aqueous alkaline solution occurs by an intramolecular acyl transfer[1] from the ester to the amide anion giving an imide which then reacts with hydroxide ion.[2,3] In the hydrolysis of 1-benzoylamino-8-dibenzoylaminonaphthalene to 1,8-bis(benzoylamino)naphthalene in 70% (v/v) Me_2SO–H_2O, evidence has been found that the ionised 1-benzoylamino group catalyses the attack of water at the adjacent imide.[4]

In the present work we have studied the kinetics of hydrolysis of 1,8-bis(trifluoroacetylamino)naphthalene with hydroxide ion in 70%, 80% and 90% (v/v) Me_2SO–H_2O, eqn. (1). Under these conditions the monoanion of the amide is the reactive species. The product of hydrolysis, 1-amino-8-trifluoroacetylaminonaphthalene, is present as the amide anion and does not undergo further reaction. However, if acid is added to the reaction solution following hydrolysis, the undissociated form of 1-amino-8-trifluoroacetylaminonaphthalene is formed and rapid cyclisation to 2-trifluoromethylperimidine then occurs, eqn. (2). In this paper, the kinetics of the hydrolysis reaction (1) are described and studies of the cyclisation will be reported in a future publication.[5]



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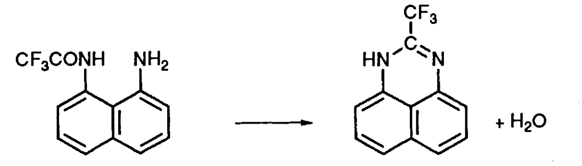

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Experimental

Preparations.—1,8-*Bis*(*trifluoroacetylamino*)*naphthalene*. Trifluoroacetic anhydride (3.0 g, 14 mmol) was added slowly with stirring to a solution of anhydrous pyridine (4.9 g) and 1,8-diaminonaphthalene (0.8 g, 5 mmol) in methylene dichloride (15 cm^3) at 0 °C under reflux. The mixture was kept, with stirring, at 0 °C for 2 h and at room temperature overnight. The product which separated was filtered off and washed with chloroform to give 1,8-bis(trifluoroacetylamino)naphthalene as an off-white solid in 60% yield with m.p. 268 °C (lit.,[6] 258 °C), δ_H(360 MHz, $[^2H_6]Me_2SO$) 11.31 (s, 2 H, NH) and 8.05–7.51 (m, 6 H, arom.), and mass spectrum *m*/*z* (intensity, %); M^+, 350.05 (100); $M^+ - CF_3COO$, 237.04 (49.9); $M^+ - CF_3CO - CF_3$, 184.07 (89.0), $M^+ - CF_3CO - CF_3 - H_2O$, 166.04 (32.3).

2-*Trifluoromethylperimidine*. The reaction of 1,8-diaminonaphthalene (3.2 g, 20 mmol) and trifluoroacetic anhydride (21 g, 100 mmol) with stirring at room temperature for 2 h in the absence of solvent gave a red solid which was collected by filtration and refluxed with water for 30 min. The undissolved material was collected and extracted with chloroform. The chloroform was evaporated to give a yellow product with m.p. 165 °C (lit.,[6] 157 °C) and identified as 2-trifluoromethylperimidine from the NMR spectrum, δ_H(360 MHz, $[^2H_6]Me_2SO$) 11.40 (s, 1 H, NH), 7.18–6.52 (m, 6 H, arom.) and mass spectrum *m*/*z* (intensity %): M^+, 236.06 (100%); $M^+ - HF$, 215.96 (77.5); $M^+ - CF_3 - H$, 166.05 (38.6); $M^+ - H - CF_3CN$, 140.05 (16.7).

Products of Reaction.—The reaction which occurs when 1,8-bis(trifluoroacetylamino)naphthalene is introduced into a solution of tetramethylammonium hydroxide in 70%, 80% and 90% (v/v) Me_2SO–H_2O is accompanied by changes in the UV spectrum with time which give clear isosbestic points, and it will be shown that the hydrolysis in eqn. (1) is occurring. The final product spectrum differs from that of 2-trifluoromethylperimidine under the reaction conditions but when the solution after hydrolysis was acidified with excess hydrochloric acid the spectrum of the resulting solution was found to be identical with that of 2-trifluoromethylperimidine in acidic Me_2SO–H_2O. When the solution after hydrolysis was partially acidified to pH *ca.* 7 a solid separated which was identified (m.p., UV and NMR spectrum) as 2-trifluoromethylperimidine and was isolated in 99% yield. These observations are consistent with the formation of the monoanion of 1-amino-8-trifluoroacetylaminonaphthalene under the hydrolysis conditions, which on acidification is protonated and rapidly forms 2-trifluoromethylperimidine. The latter process was followed kinetically using the stopped-flow method and these studies will be the subject of a subsequent publication.[5]

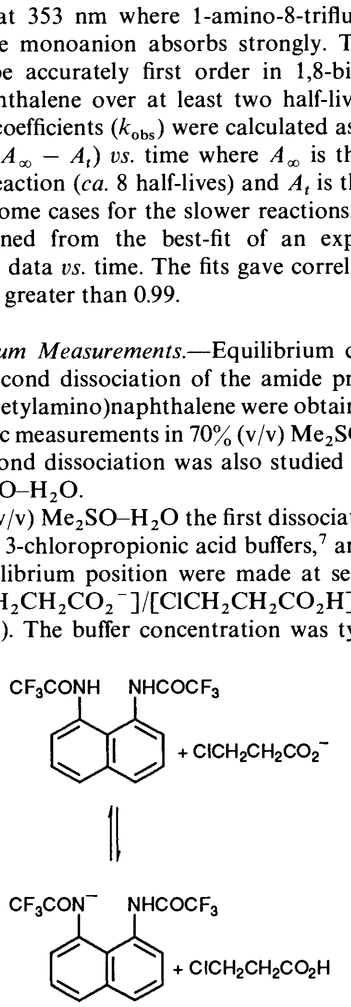
To provide support for the proposal that 1,8-bis(trifluoroacetylamino)naphthalene reacts according to eqn. (1) in Me_2SO–H_2O mixtures containing hydroxide ion, the reaction was monitored by ^{19}F NMR spectroscopy. Measurements were made at *ca.* 298 K in a solvent of 3.5 cm^3 Me_2SO, 0.5 cm^3 H_2O with 1.0 cm^3 D_2O as an internal lock. The solution initially contained 1,8-bis(trifluoroacetylamino)naphthalene at a concentration of 9×10^{-5} mol dm^{-3}, 0.0098 mol dm^{-3} potassium hydroxide, and trifluorotoluene as a chemical shift reference. The first spectrum (235 MHz) run *ca.* 10 min after mixing showed peaks $(-\delta)$ at 60.71 ($C_6H_5CF_3$), 72.34 (1-amino-8-trifluoroacetylaminonaphthalene), 72.74 [1,8-bis(trifluoroacetylamino)naphthalene] and 73.66 (trifluoroacetic acid). The peaks at 72.34 and 73.66 were of equal integral and each *ca.* 7.5% of the integral of the reactant peak at 72.74. Spectra were recorded at intervals of time and it was observed that the integrals of the peak at 72.74 decreased and the integrals of the peaks at 72.34 and 73.66 increased with time. After 2 h the integral of the product peaks were each *ca.* 3 fold greater than the reactant peak and after 4 h the product peak was *ca.* 5-fold greater. Reaction was complete after *ca.* 8 h. After 64 h a further peak of very low integral appeared at 70.74 and the peak due to 1-amino-8-trifluoroacetylaminonaphthalene had decreased slightly relative to that for trifluoroacetic acid. The peak at 70.74 corresponds to 2-trifluoromethylperimidine as confirmed from the ^{19}F NMR spectrum of a separately prepared sample. As noted above this is formed from 1-amino-8-trifluoroacetylaminonaphthalene by a cyclisation, eqn. (2), which occurs negligibly slowly unless the solution is acidified. Under basic conditions the cyclisation does not interfere with the hydrolysis of 1,8-bis(trifluoroacetylamino)naphthalene. Approximate values for the first-order rate coefficient (k_{obs}) for the hydrolysis were calculated from the decrease with time of the ^{19}F peak of 1,8-bis(trifluoroacetylamino)naphthalene (k_{obs} *ca.* $1.7 \pm 0.5 \times 10^{-4}$ s^{-1}) and from the increase of the peak due to trifluoroacetic acid (k_{obs} *ca.* $2.0 \pm 0.5 \times 10^{-4}$ s^{-1}). These results are compatible with the more precise value k_{obs} 1.0×10^{-4} s^{-1} obtained from UV spectrophotometric measurements at 298.15 K in 70% (v/v) Me_2SO–H_2O containing 0.01 mol dm^{-3} tetramethylammonium hydroxide with 0.19 mol dm^{-3} tetramethylammonium chloride (see below).

Preparation of Solutions.—Kinetic and equilibrium measurements were made in solutions of 70%, 80% and 90% (v/v) Me_2SO–H_2O containing tetramethylammonium hydroxide and with the necessary quantity of tetramethylammonium chloride to maintain a constant ionic strength of 0.2 mol dm^{-3}. Solutions of tetramethylammonium hydroxide were prepared from the solid pentahydrate and standardised by titration with hydrochloric acid. Tetramethylammonium chloride was dried under reduced pressure at room temperature for 24 h before use. The solvent mixtures were made up by volume, for example 70% (v/v) Me_2SO–H_2O was prepared from 7 parts by volume of dimethyl sulfoxide (Analar) and 3 parts by volume of double distilled water.

Kinetic Procedures.—The kinetics of the reaction of 1,8-bis(trifluoroacetylamino)naphthalene to 1-amino-8-trifluoroacetylaminonaphthalene, eqn. (1), were studied spectrophotometrically. The initial concentration of 1,8-bis(trifluoroacetylamino)naphthalene was *ca.* 5×10^{-5} mol dm^{-3} and the reaction was begun by injecting 0.01 cm^3 of a concentrated solution of the amide in Me_2SO into 3 cm^3 of the reaction solution thermostatted at 298.15 K. The change with time in the spectrum over the range 200–400 nm showed clean isosbestic points at *ca.* 290 and 340 nm. The changes in the spectrum which occurred as a result of the hydrolysis varied slightly with the hydroxide ion concentration and the solvent composition. Kinetic results were obtained from the change in absorbance with time at 353 nm where 1-amino-8-trifluoroacetylaminonaphthalene monoanion absorbs strongly. The reaction was found to be accurately first order in 1,8-bis(trifluoroacetylamino)naphthalene over at least two half-lives and the first-order rate coefficients (k_{obs}) were calculated as the gradients of plots of $\ln(A_\infty - A_t)$ *vs.* time where A_∞ is the absorbance at complete reaction (*ca.* 8 half-lives) and A_t is the absorbance at time t. In some cases for the slower reactions, rate coefficients were obtained from the best-fit of an exponential to the absorbance data *vs.* time. The fits gave correlation coefficients which were greater than 0.99.

Equilibrium Measurements.—Equilibrium constants for the first and second dissociation of the amide protons in 1,8-bis(trifluoroacetylamino)naphthalene were obtained from spectrophotometric measurements in 70% (v/v) Me_2SO–H_2O at 298.15 K. The second dissociation was also studied in 80% and 90% (v/v) Me_2SO–H_2O.

In 70% (v/v) Me_2SO–H_2O the first dissociation occurs in the presence of 3-chloropropionic acid buffers,[7] and measurements of the equilibrium position were made at seven buffer ratios ($r = [ClCH_2CH_2CO_2^-]/[ClCH_2CH_2CO_2H]$) between 0.1 and 1.0, eqn. (3). The buffer concentration was typically 0.01 mol dm^{-3}. The amide was introduced into the buffer as a concentrated solution in Me_2SO to give a total concentration of 7×10^{-5} mol dm^{-3} and the spectrum (200–400 nm) was recorded at different buffer ratios. The spectrum of undissociated 1,8-bis(trifluoroacetylamino)naphthalene was obtained in the absence of buffer and the spectrum of the monoanion was obtained in the presence of a 1:1 benzimidazole buffer.[8] The largest difference in spectrum between the monoanion and undissociated forms of 1,8-bis(trifluoroacetylamino)naphthalene occurs at 356 nm. The equilibrium constant (K') for the reaction in eqn. (3) was calculated from eqn. (4) in which A is the

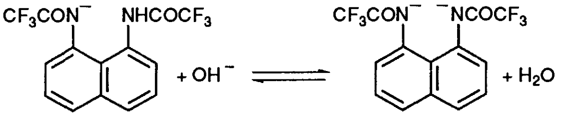


(3)

$$K' = (A - A_u)/(A_m - A)r \qquad (4)$$

absorbance at 356 nm of a solution of the amide in the presence of 3-chloropropionate buffer at a buffer ratio r, and A_m and A_u are the absorbances of solutions in which the amide is entirely in the monoanion and undissociated forms respectively. The values of the equilibrium constant calculated from readings at seven buffer ratios gave an average K' 3.6 ± 0.2. This result was used to estimate pK_1 *ca.* 5.7 for the first dissociation of 1,8-bis(trifluoroacetylamino)naphthalene in 70% (v/v) Me_2SO-H_2O (see later).

Dissociation of the second proton, eqn. (5), was studied in the



(5)

presence of varying concentrations of tetramethylammonium hydroxide in 70%, 80% and 90% (v/v) Me_2SO-H_2O. A concentrated solution of 1,8-bis(trifluoroacetylamino)naphthalene in Me_2SO was introduced into the basic solutions to give a total amide concentration of 7×10^{-5} mol dm^{-3} and the UV spectrum was recorded immediately. As before, the spectrum of the monoanion was obtained in the presence of a 1:1 benzimidazole buffer and the spectrum of the dianion was obtained in the presence of tetramethylammonium hydroxide at a concentration of 0.2 mol dm^{-3}. For the results in 70% (v/v) Me_2SO-H_2O the value of the equilibrium constant (K'') for the reaction in eqn. (5) was calculated using eqn. (6) in which A_m, A_d

$$K'' = (A_m - A)/(A - A_d)[OH^-] \qquad (6)$$

and A are absorbance readings taken at 354 nm for solutions in which the amide is present, respectively, as the monoanion, dianion or as an equilibrium mixture of both species. The result K'' 73 ± 8 dm^3 mol^{-1} was obtained as the average from measurements at five hydroxide ion concentrations in the range 0.002–0.03 mol dm^{-3}. This value was used to calculate pK_2 *ca.* 15.9 for the second acid dissociation of 1,8-bis(trifluoroacetylamino)naphthalene in 70% (v/v) Me_2SO-H_2O (see below). In 80% (v/v) Me_2SO-H_2O the spectrum of the dianion obtained at high hydroxide ion concentrations was unreliable because of the more rapid hydrolysis that occurred under these conditions. To overcome this problem the data at hydroxide ion concentrations in the range 0.001–0.01 mol dm^{-3} were plotted in the form of eqn. (7). The resulting linear plot of $(A_m - A)/[OH^-]$

$$(A_m - A)/[OH^-] = K''A - K''A_d \qquad (7)$$

vs. A (correlation coefficient 0.995) gave K'' 258 ± 20 dm^3 mol^{-1} as gradient. In 90% (v/v) Me_2SO-H_2O spectral measurements at low hydroxide ion concentrations showed that within experimental error the amide was fully dissociated into the dianion and the value $K'' > 2000$ dm^3 mol^{-1} was deduced for this solvent mixture.

Results and Discussion

Values of the equilibrium constants K' and K'' for the reactions in eqns. (3) and (5) were converted into approximate pK_1 and pK_2 values respectively for the first and second acid dissociation of 1,8-bis(trifluoroacetylamino)naphthalene. The first dissociation was observed in the presence of 3-chloropropionic acid buffers for which pK_a 6.22 has been measured[7] at 293.15 K and ionic strength 0.25 mol dm^{-3} in 70% (v/v) Me_2SO-H_2O. Assuming the same value applies under the present conditions [298.15 K and ionic strength 0.20 mol dm^{-3} in 70% (v/v) Me_2SO-H_2O] the value of the equilibrium constant K' 3.6 ± 0.2 for reaction (3) leads to pK_1 *ca.* 5.7 for dissociation of 1,8-bis(trifluoroacetylamino)naphthalene. For dissociation of the second proton the equilibrium constant K'' 73 ± 8 dm^3 mol^{-1} for the reaction in eqn. (5) was combined with the value[7] K_s 1.62×10^{-18} mol^2 dm^{-6} for the ionic product of water in 70% (v/v) Me_2SO-H_2O at 298.15 K and ionic strength 0.25 mol dm^{-3} to give a pK_2 *ca.* 15.9.

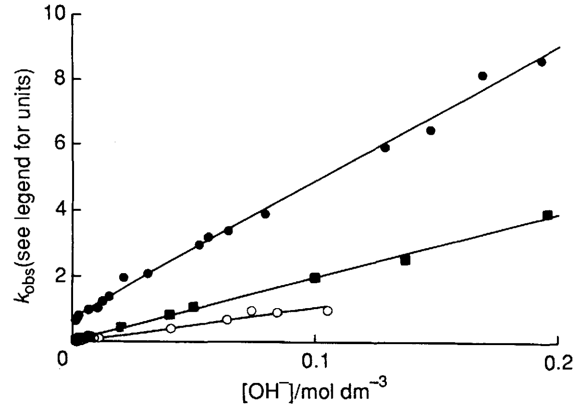
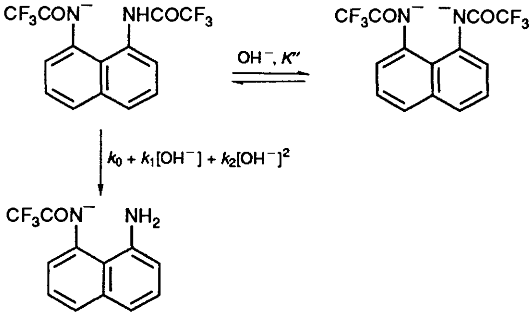


Fig. 1 Observed first-order rate coefficient (k_{obs}) for the hydrolysis of 1,8-bis(trifluoroacetylamino)naphthalene to 1-amino-8-trifluoroacetylaminonaphthalene in Me_2SO-H_2O mixtures in the presence of hydroxide ion; ● $k_{obs}/10^{-4}$ s^{-1} in 70% (v/v) Me_2SO-H_2O; ■ $k_{obs}/5 \times 10^{-4}$ s^{-1} in 80% (v/v) Me_2SO-H_2O: ○ $k_{obs}/2 \times 10^{-3}$ s^{-1} in 90% (v/v) Me_2SO-H_2O

The pK_1 and pK_2 values for acid dissociation of the amide protons from 1,8-bis(trifluoroacetylamino)naphthalene refer to 70% (v/v) Me_2SO-H_2O as solvent but the results may not differ greatly from the values in aqueous solution. The value of pK_1 is lower and the value of pK_2 is higher than the result, pK_a 9.5, determined[9] for the dissociation of trifluoroacetanilide in aqueous solution. The difference $pK_2 - pK_1$ is much larger than expected for a dibasic acid with two identical acidic groups. A possible reason for this is the presence of a strong intramolecular hydrogen bond in the monoanion of 1,8-bis(trifluoroacetylamino)naphthalene which is thereby stabilised relative to the undissociated form and the dianion. A similar explanation was used to account for the lower pK_1 value of 1,8-bis(benzoylamino)naphthalene than for 1-benzoylaminonaphthalene.[10]

The hydroxide-ion dependence of the observed first-order rate coefficient (k_{obs}) for the disappearance of 1,8-bis(trifluoroacetylamino)naphthalene or the appearance of 1-amino-8-trifluoroacetylaminonaphthalene in 70%, 80% and 90% (v/v) Me_2SO-H_2O is shown in Fig. 1. At low hydroxide ion concentrations the reaction occurs most rapidly in 70% (v/v) Me_2SO-H_2O but at high hydroxide ion concentrations the observed value of k_{obs} at a particular hydroxide ion concentration increases in the order 70% < 80% < 90% (v/v) Me_2SO-H_2O. The experimental results can be explained by the steps in Scheme 1. It is necessary to assume that under the



Scheme 1

Table 1 Kinetic results for the hydrolysis of 1,8-bis(trifluoroacetylamino)naphthalene[a,b]

Solvent/% (v/v) Me_2SO-H_2O	$K''/dm^3\ mol^{-1}$	$k_0/10^{-5}\ s^{-1}$	$k_1/dm^3\ mol^{-1}\ s^{-1}$	$k_2 dm^6\ mol^{-2}\ s^{-1}$
70	73 ± 8	5.9 ± 0.5	0.0106 ± 0.001	0.297 ± 0.01
80	258 ± 20	1.27 ± 0.15	0.0118 ± 0.002	2.53 ± 0.1
90	>2000	*ca.* 0	*ca.* 0	c

[a] Temperature 298.15 K and ionic strength 0.2 mol dm^{-3}. [b] Rate coefficients k_0, k_1 and k_2 and the equilibrium constant K'' refer to the reactions in Scheme 1. [c] $k_2/K'' = 0.0213 \pm 0.001\ dm^3\ mol^{-1}\ s^{-1}$ and $k_2 > 40\ dm^6\ mol^{-2}\ s^{-1}$.

reaction conditions the dianion is unreactive and the undissociated form of 1,8-bis(trifluoroacetylamino)naphthalene which is present at negligibly low concentration also does not contribute to the reaction. Eqn. (8) is deduced from Scheme 1

$$k_{obs} = (k_0 + k_1[OH^-] + k_2[OH^-]^2)/(1 + K''[OH^-]) \quad (8)$$

on the assumption that the proton transfer step is rapid and that there are three terms in the rate law for the hydrolysis of 1,8-bis(trifluoroacetylamino)naphthalene monoanion. These terms are a spontaneous reaction (rate coefficient k_0), a reaction first order in hydroxide ion (k_1), and a reaction second order in hydroxide ion (k_2).

Fits of eqn. (8) to the kinetic data in 70% and 80% (v/v) Me_2SO-H_2O were obtained using the separately measured values of K'' in the two solvents and best-fit values for k_0, k_1 and k_2. The data could not be fitted if any of the terms in eqn. (8) were excluded. Best-fit values for k_0 in the two solvents were obtained as the intercepts of plots of k_{obs} *vs.* $[OH^-]$ at low $[OH^-]$. Values of k_1 and k_2 were obtained by rearranging eqn. (8) to give eqn. (9) and the data were plotted in the form $\{k_{obs}$

$$\{k_{obs}(1 + K''[OH^-]) - k_0\}/[OH^-] = k_1 + k_2[OH^-] \quad (9)$$

$(1 + K''[OH^-]) - k_0\}/[OH^-]$ *vs.* $[OH^-]$ using the best-fit values of k_0. Linear regression analysis (correlation coefficients 0.994 and 0.999 for the results in 70% and 80% (v/v) Me_2SO-H_2O respectively) gave values for k_1 as the intercept and k_2 as the gradient. The results are shown in Table 1. Using the best-fit values of k_0, k_1 and k_2 and the experimentally determined values of K'' fits of eqn. (8) to the experimental results in 70% and 80% (v/v) Me_2SO-H_2O are shown as the lines in Fig. 1. For the results in 70% (v/v) Me_2SO-H_2O the average deviation of the experimental values (18 data points) from the fit is 3.1% and in 80% (v/v) Me_2SO-H_2O the average deviation of the 9 data points is 3.7%.

For the data in 90% (v/v) Me_2SO-H_2O, plots of k_{obs} *vs.* $[OH^-]$ at low $[OH^-]$ show that the k_0 term makes a negligible contribution to the rate. Equilibrium studies in 90% (v/v) Me_2SO-H_2O containing low concentrations of OH^- showed that the amide is practically fully dissociated into the dianion, eqn. (5), and it follows that $K''[OH^-] > 1$. With these approximations eqn. (8) reduces to eqn. (10) and a linear

$$k_{obs} = k_1/K'' + (k_2/K'')[OH^-] \quad (10)$$

regression fit of eqn. (10) to the kinetic results in 90% (v/v) Me_2SO-H_2O gave k_1/K'' *ca.* 0 and k_2/K'' 0.0213 $dm^3\ mol^{-1}\ s^{-1}$ with a correlation coefficient of 0.994 (10 data points). The line through the data in 90% (v/v) Me_2SO-H_2O in Fig. 1 is a fit of eqn. (8) using $k_0 = 0$, $k_1 = 0$, and k_2/K'' 0.0213 $dm^3\ mol^{-1}\ s^{-1}$ with the approximation $K''[OH^-] > 1$. The average deviation of the experimental values (ten data points) from the line is 5.9%. Using $K'' > 2000\ dm^3\ mol^{-1}$ estimated from equilibrium measurements, the result $k_2 > 40\ dm^6\ mol^{-2}\ s^{-1}$ is deduced for 90% (v/v) Me_2SO-H_2O.

The existence in the rate law of a term for the spontaneous hydrolysis of the monoanion of 1,8-bis-(trifluoroacetylamino)-naphthalene in 70% (v/v) Me_2SO-H_2O can be demonstrated by setting $k_0 = 0$ as a result of which the plot of the function $\{k_{obs}(1 + K''[OH^-]) - k_0\}/[OH^-]$ *vs.* $[OH^-]$ as in eqn. (9) shows considerable departure from linearity and the function goes through a deep minimum as $[OH^-]$ increases. The contribution made by the k_0 term in 70% (v/v) Me_2SO-H_2O at a hydroxide ion concentration of 0.001 mol dm^{-3} accounts for over 80% of the reaction flux with *ca.* 15% contribution made by the k_1 term. At $[OH^-]$ 0.1 mol dm^{-3} the k_0 term is negligibly small compared with the other terms and the k_2 term accounts for 73% of the reaction. In 90% (v/v) Me_2SO-H_2O, contributions from the k_0 and k_1 terms are undetectable and the kinetic behaviour is accounted for entirely by the k_2 term. The value of k_2 increases with a change in solvent in the order 70% < 80% < 90% (v/v) Me_2SO-H_2O.

The kinetic behaviour observed for the hydrolysis of the monoanion of 1,8-bis(trifluoroacetylamino)naphthalene shows many of the features previously observed in the hydrolysis of amides. Terms first and second order in hydroxide ion are often found in amide hydrolysis and if the amide proton is acidic, it has been found previously that the rate of reaction is reduced by formation of the unreactive amide anion.[11] Thus the terms in k_1 and k_2 and the term involving K'' in eqn. (8) are consistent with the results for other amides. The first-order term is explained by reaction involving nucleophilic attack of hydroxide ion on the amide carbonyl to form an addition intermediate. The second-order term may be due to hydroxide ion catalysed decomposition of the addition intermediate or to rapid formation of the ionised form of the addition intermediate which then collapses to product.[12]

The data in Table 1 permit a limited discussion of the effect of solvent on the values of k_1 and k_2. In going from 70% to 80% (v/v) Me_2SO-H_2O the value of k_1 increases slightly but the value of k_2 increases *ca.* 9-fold and in 90% (v/v) Me_2SO-H_2O the value of k_2 is higher still. If the second-order term arises through a mechanism involving rapid ionisation of the first addition intermediate, the increase in basicity of hydroxide ion[13] with solvent in the order 70% < 80% < 90% (v/v) Me_2SO-H_2O would increase the extent of ionisation at a particular hydroxide ion concentration and would lead to an increase in the value of k_2. If the first-order term arises from rate-limiting addition of hydroxide ion at the amide carbonyl through a reactant-like transition state, the value of k_1 would increase with the increase in basicity of hydroxide ion in 70% compared with 80% (v/v) Me_2SO-H_2O but the increase would not be so great as in the case of k_2.

The k_0 term in eqn. (8) corresponding to spontaneous solvolysis of the monoanion of 1,8-bis(trifluoroacetylamino)-naphthalene is not usually observed in amide hydrolysis. The observation of significant spontaneous hydrolysis could arise through intramolecular base catalysis by the ionised amide group which assists the attack of water at the adjacent unionised amide. Similar intramolecular catalysis has previously been observed in the hydrolysis of the anions of 1-benzoylamino-8-dibenzoylaminonaphthalene[4] and 1-hydroxy-

8-acetoxynaphthalene[14] in which ionised amide and hydroxy groups respectively act as intramolecular base catalysts for the attack of water.

It is interesting to compare the magnitude of the rate coefficient (k_0 5.9 × 10^{-5} s^{-1}) for the intramolecularly catalysed attack of water at the amide carbonyl of 1,8-bis(trifluoroacetylamino)naphthalene with the value of the rate coefficient for reaction of the amide with hydroxide ion under the same conditions, k_1 0.0106 dm^3 mol^{-1} s^{-1}. After correcting k_0 for the concentration of water in 70% (v/v) Me_2SO–H_2O (*ca.* 17 mol dm^{-3}) the results show that the second-order rate coefficient for reaction of the amide monoanion with hydroxide ion is greater by a factor of *ca.* 3 × 10^3 than the second-order rate coefficient for reaction with water. In view of the difference in basicity of *ca.* 20 p*K* units between hydroxide ion and water in 70% (v/v) Me_2SO–H_2O a much greater difference in the rates of reaction with these nucleophiles would have been expected and the high value of k_0 for reaction with water points to substantial intramolecular catalysis by the ionised amide group. Previously it was observed[4] that the spontaneous solvolysis of the anion of 1-benzoylamino-8-dibenzoylaminonaphthalene in 70% (v/v) Me_2SO–H_2O occurred with a rate coefficient of 0.033 s^{-1}. After conversion to a second-order rate coefficient for reaction with water the value is a factor of *ca.* 200 below the value of the rate coefficient for reaction of 1-dibenzoylaminonaphthalene with hydroxide ion. In the aqueous hydrolysis of the ester group in the anion of 1-hydroxy-8-acetoxynaphthalene, intramolecular base catalysis of the attack of solvent by the ionised hydroxy group occurs with a second-order rate coefficient which is a factor of 2.1 × 10^4 below the value of the rate coefficient for reaction of 1-acetoxynaphthalene with hydroxide ion.[14]

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