Rate–pH Profile for the Formation of 1-Hydroxy-8-acetylaminonaphthalene from 2-Methylnaphth[1,8-*de*]-1,3-oxazine in Aqueous Solution; Acid Catalysis and Inhibition and Comparison with the Reaction of 1-Amino-8-trifluoroacetylaminonaphthalene

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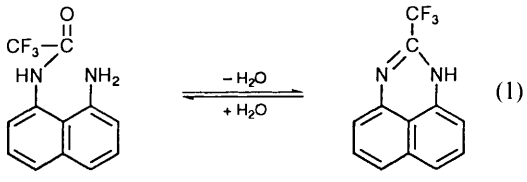
Formation of 1-hydroxy-8-acetylaminonaphthalene from 2-methylnaphth[1,8-*de*]-1,3-oxazine in aqueous solution shows a rate maximum at pH *ca.* 2. The results are compatible with a mechanism involving addition of solvent to the protonated oxazine to give a tetrahedral intermediate which collapses to product. In the range pH 6 to 2 the rate increases with acidity because an increasing fraction of the oxazine is converted into the more reactive protonated species (pK_a *ca.* 2). The unprotonated species is unreactive towards nucleophilic addition of water. Below pH 2 the reaction is inhibited by acid because collapse of the tetrahedral intermediate to the protonated oxazine is catalysed by acid. At pH > 12 the reaction is first-order in hydroxide ion showing that addition of hydroxide ion to the unprotonated oxazine occurs. The favourable reaction of 2-methylnaphth[1,8-*de*]-1,3-oxazine to 1-hydroxy-8-acetylaminonaphthalene contrasts with the behaviour of 1-amino-8-trifluoroacetylaminonaphthalene for which the preferred direction of reaction is the elimination of water in favour of the cyclic product 2-trifluoromethylperimidine.

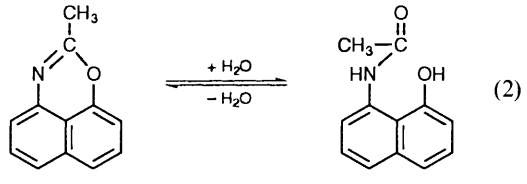
The formation of 2-trifluoromethylperimidine from 1-amino-8-trifluoroacetylaminonaphthalene, eqn. (1), occurs[1] to comple-



(1)

tion in 70% (v/v) Me_2SO–H_2O in the presence of hydrochloric acid and in buffers in the range pH 2.6 to 13.3. Reaction involves intramolecular nucleophilic addition of the amino group to the amide carbonyl followed by elimination of water. A biphasic Brønsted plot for catalysis by general acids has been explained[2] by a mechanism with rate-limiting protonation by buffer acids and hydronium ion of the zwitterionic intermediate formed in low concentration by the intramolecular addition of the amino group to the amide carbonyl.

In contrast, for the related interconversion between 2-methylnaphth[1,8-*de*]-1,3-oxazine and 1-hydroxy-8-acetylaminonaphthalene, eqn. (2), there is evidence to suggest that



(2)

reaction occurs in the direction of the acyclic species. It has been observed[3] that 2-methylnaphth[1,8-*de*]-1,3-oxazine is converted into 1-hydroxy-8-acetylaminonaphthalene on recrystallisation in ethanol although equilibrium and kinetic studies of the reaction were not carried out. In the present work we have found that the reaction in equation (2) occurs completely in the direction of 1-hydroxy-8-acetylaminonaphthalene in aqueous hydrochloric acid and in buffer solutions in the range pH 2.2 to 6.5 and in aqueous solutions of potassium hydroxide. We also report kinetic studies which provide evidence for the mechanism of the reaction.

Experimental

Preparations.—*1-Hydroxy-8-acetylaminonaphthalene.* A sample of 8-amino-1-naphthol was prepared in *ca.* 20% yield by fusion of 1,8-naphthosultam with a mixture of sodium hydroxide and potassium hydroxide and water.[4] The resulting crude product was extracted into water and a sufficient volume of 1 mol dm^{-3} HCl was added to bring the solution to pH 1. After filtering, the solution was adjusted to pH 7 by addition of saturated aqueous $NaHCO_3$ and the solid which precipitated was collected and dried under vacuum to give 8-amino-1-naphthol (m.p. 98 °C, lit.[5] 95 °C). The product was refluxed for 10 min with an equimolar quantity of acetic anhydride in the presence of a four-fold molar excess of acetic acid. After pouring into water the insoluble material was collected, recrystallised from ethanol–water (1:2) and dried under vacuum to give white crystals of 1-hydroxy-8-acetylaminonaphthalene (m.p. 160 °C, lit.,[6] 168 °C) in 45% yield: δ_H[$(CD_3)_2SO$, 360 MHz] 11.25 (br s, 1 H, OH), 11.09 (s, 1 H, NH), 8.42–6.88 (m, 6 H, Ar) and 2.15 (s, 3 H, CH_3); δ_C[$(CD_3)_2SO$, 90.5 MHz] 167.76 (CO), 153.42, 136.21, 135.64 and 115.15 (q, Ar), 126.35, 126.10, 122.93, 119.96, 114.72 and 110.16 (CH Ar) and 25.34 (CH_3); *m/z* (CI, NH_3) 403 (2M + 1, 6.6%), 385 (2M + 1 − H_2O, 48.7), 219 (M + NH_4^+, 18.1), 202 (M + 1, 7.9) and 184 (M + 1 − H_2O, 100).

2-Methylnaphth[1,8-de]*-1,3-oxazine.* Sublimation of 1-hydroxy-8-acetylaminonaphthalene at 180 °C under reduced pressure (*ca.* 2 mmHg) gave 2-methylnaphth[1,8-*de*]-1,3-oxazine in 76% yield and purity *ca.* 85% based on the NMR spectrum. A further sublimation at 70 °C and pressure 15 mmHg resulted in a pure off-white sample (m.p. 68 °C, lit.,[3] 72 °C); δ_H[$(CD_3)_2SO$, 360 MHz] 7.48–6.79 (m, 6 H, Ar) and 2.20 (s, 3 H, CH_3); δ_C[$(CD_3)_2SO$, 90.5 MHz] 157.94 (C=N), 149.20, 137.02, 133.79 and 117.85 (q, Ar), 128.76 127.93, 122.88, 120.72, 115.85 and 105.90 (CH Ar) and 20.71 (CH_3); *m/z* (CI, NH_3) 367 (2M + 1, 11.5%), 201 (M + NH_4, 3.4) and 184 (M + 1, 100).

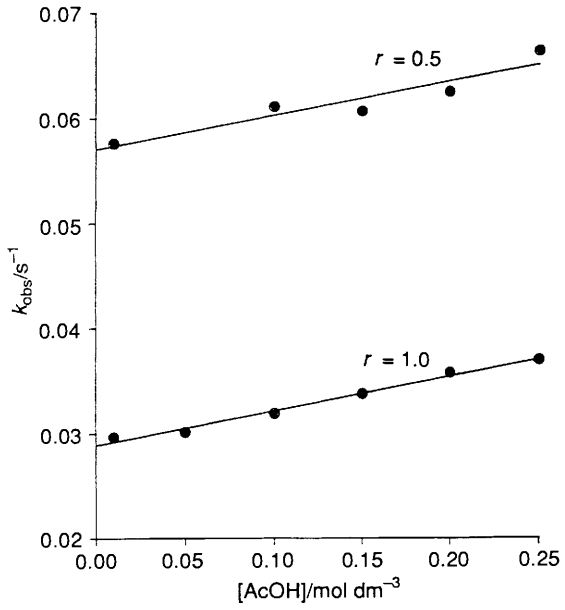


Fig. 1 Variation of the observed rate coefficient (k_{obs}) for the reaction in eqn. (2) in aqueous acetic acid buffer ratios r = [AcO$^-$]/[AcOH] = 0.5 and 1.0

Kinetic Studies.—By following the changes in the UV–VIS spectrum over the range 250 to 450 nm it was established that the reaction in eqn. (2) occurs on introduction of 2-methylnaphth[1,8-*de*]-1,3-oxazine into aqueous solution. For a solution of 2-methylnaphth[1,8-*de*]-1,3-oxazine at an initial concentration of *ca.* 1 × 10^{-4} mol dm^{-3} in unbuffered aqueous solution and in an aqueous 1:1 dihydrogen orthophosphate monoanion/dianion buffer (pH 6.52), the spectral changes with time show an isosbestic point at 334 nm. The spectrum of the final product was found to be identical within experimental error with that of an authentic sample of 1-hydroxy-8-acetylaminonaphthalene under the same conditions. Similar conclusions were reached for the reaction in 0.1 and 1.0 mol dm^{-3} HCl and in 0.1 mol dm^{-3} KOH.

Kinetic measurements of the reaction in eqn. (2) were made in aqueous solution in the presence of hydrochloric acid, potassium hydroxide, and in carboxylic acid and phosphate buffer solutions. Solutions were prepared using double distilled water and buffers were made up by partial neutralisation of the buffer acid with standard potassium hydroxide solution. All measurements were made at 25.0 °C and at an ionic strength adjusted to 0.25 mol dm^{-3} by addition of potassium chloride. The reactions were followed by measuring the decrease in absorbance with time at *ca.* 350 nm except in the case of reactions in KOH which were followed by measuring the increase in absorbance at 341 nm. In aqueous potassium hydroxide and in buffer solutions with pH values > *ca.* 4, the reaction occurs with $t_{\frac{1}{2}}$ > 10 s and measurements of the change in absorbance with time were made using a conventional spectrophotometer. In buffer solutions of pH < *ca.* 4 and in solutions of hydrochloric acid the reaction occurs more rapidly and the change in absorbance with time was followed by stopped-flow spectrophotometry (Hi-Tech SF 51). For studies using conventional spectrophotometry, the reaction was begun by introducing 0.01 cm^3 of a solution of 2-methylnaphth[1,8-*de*]-1,3-oxazine in Me_2SO into 3 cm^3 of the reaction solution at 25.0 °C to give an initial concentration of *ca.* 1 × 10^{-4} mol dm^{-3}. For stopped-flow studies, the reaction was initiated by mixing equal volumes of an aqueous solution of 2-methylnaphth[1,8-*de*]-1,3-oxazine at a concentration of *ca.* 4 × 10^{-4} mol dm^{-3} with a buffer solution or a solution of HCl. The aqueous stock solution of 2-methylnaphth[1,8-*de*]-1,3-oxazine was used as soon as possible after making-up, since reaction to 1-hydroxy-8-acetylaminonaphthalene occurs with $t_{\frac{1}{2}}$ *ca.* 20 min in distilled water. The reaction in eqn. (2) was followed for 2–3 half lives and was found to be accurately first-order with respect to 2-methylnaphth[1,8-*de*]-1,3-oxazine. Values of the first-order rate coefficients (k_{obs}) were calculated as the gradients of plots of $\ln(A_t - A_\infty)$ against time where A_t is the absorbance at time t and A_∞ is the absorbance after complete reaction. Values of k_{obs} were reproducible to within ± 2%.

The values of the pH and hydrogen ion concentrations in buffers were calculated from the expression pH = $-\log$ [H_3O^+] = $-\log(K_{0.25}/r)$ where $K_{0.25}$ is the acid dissociation constant of the buffer acid under the conditions of the experiment (25 °C and ionic strength 0.25 mol dm^{-3}) and r is the buffer ratio (r = [buffer anion]/[buffer acid]). Values of $K_{0.25}$ were calculated from literature values[7] referring to infinite dilution (K_0) by means of the Debye–Hückel expression $pK_{0.25} = pK_0 - n \times 0.51 \sqrt{I}/(1 + \sqrt{I})$ in which I is the ionic strength (I = 0.25 mol dm^{-3}). For carboxylic acid buffers n = 2 and for orthophosphate monoanion/dianion buffers n = 4. The correction from infinite dilution to ionic strength 0.25 mol dm^{-3} is of limited accuracy and leads to a small uncertainty in the calculation of hydronium ion concentrations in carboxylic acid buffers and to a larger uncertainty for orthophosphate buffers.

Results and Discussion

Kinetic Studies in Buffer Solutions.—Measurements covering the range pH 2.22 to 6.52 were made in buffers of chloroacetic, acetic, and pivalic acid with the corresponding anion and in buffers of dihydrogen orthophosphate monoanion and monohydrogen orthophosphate dianion. In each buffer, values of the observed first-order rate coefficient (k_{obs}) where determined at several buffer concentrations in the range 0.01 to 0.25 mol dm^{-3} and at two buffer ratios r = 1.0 and 0.5. Results in acetic acid buffers ($pK_{0.25}$ 4.42 referring to 25 °C and ionic strength 0.25 mol dm^{-3}) are shown in Fig. 1. The intercepts of the plots in Fig. 1 correspond to a spontaneous reaction involving species derived from the solvent and the gradient corresponds to the effect of a change in buffer concentration on the rate, eqn. (3).

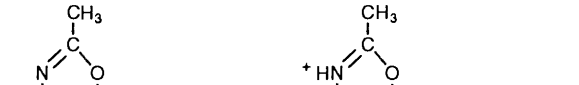
$$k_{obs} = k + k_{HA}[HA] \quad (3)$$

The spontaneous reaction (k) makes the predominant contribution to the rate. The solid lines in Fig. 1 are plots of eqn. (3) using the linear regression values k 0.029 s^{-1} and k_{HA} 0.032 dm^3 mol^{-1} s^{-1} at r = 1.0 and k 0.057 s^{-1} and k_{HA} 0.032 dm^3 mol^{-1} s^{-1} at r = 0.5. The two-fold increase in k as the buffer ratio is changed from r = 1.0 to r = 0.5 shows that the reaction is first order in hydronium ion at these concentrations which is confirmed by studies in solutions of hydrochloric acid described later. The increase in k_{obs} with buffer concentration amounts to *ca.* 25% at a buffer ratio of r = 1.0 and to *ca.* 15% at r = 0.5 as the concentration of acetic acid buffer is changed from 0.01 to 0.25 mol dm^{-3}. This could be interpreted as evidence for weak catalysis by the acidic component of the buffer. However it is more likely that the small change in k_{obs} is due to an electrolyte effect on the reaction brought about by the change in added anion from chloride to acetate ion as the concentration of buffer is increased and this is confirmed by the results in the other buffers. For buffers of the more weakly acid pivalic acid ($pK_{0.25}$ 4.69) and dihydrogen orthophosphate ($pK_{0.25}$ 6.52) the values of k_{obs} were independent of buffer concentration within experimental error and k was obtained as the average of the values of k_{obs} at different buffer concentrations. In pivalic acid the values were k 1.58 ± 0.05 × 10^{-2} and 3.03 ± 0.07 × 10^{-2} s^{-1} at buffer ratios of r = 1.0 and r = 0.5 respectively and in orthophosphate buffers the values were k 3.73 ± 0.2 × 10^{-4} and

$6.34 \pm 0.2 \times 10^{-4}$ s^{-1} at $r = 1.0$ and $r = 0.5$. In the more strongly acidic chloroacetic acid buffer ($pK_{0.25}$ 2.52) at a fixed stoichiometric buffer ratio, the hydronium ion concentration changes slightly as the buffer concentration is changed. For example as the stoichiometric buffer anion and buffer acid concentrations are changed from 0.05 to 0.25 mol dm^{-3} at a buffer ratio $r = 1.0$, the hydronium ion concentration changes from 2.71×10^{-3} to 2.95×10^{-3} mol dm^{-3}. Over this concentration range the value of k_{obs} changes from 1.31 to 1.33 s^{-1}. It follows that buffer catalysis is undetectable under the present conditions.

Rate–pH *Profile*.—The values of the first-order rate coefficient (k) determined in solutions of hydrochloric acid at concentrations in the range 0.001 to 0.25 mol dm^{-3} at a total ionic strength of 0.25 mol dm^{-3} are given in the form of a log k–pH profile in Fig. 2. Rate coefficients for the reaction in the presence of 0.30, 0.40, 0.50 and 1.14 mol dm^{-3} HCl, though referring to different ionic strength, are also given. The values of k determined in buffer solutions are also included. In chloroacetic acid buffers at two buffer ratios the values of k are in reasonable agreement with the data in hydrochloric acid at the same hydronium ion concentrations.

The rate–pH profile can be explained by the mechanism in eqns. (4)–(6) for which the rate expression in eqn. (7) applies. To derive eqn. (7) it is assumed that the tetrahedral intermediate is present in low concentration and that the proton transfer in eqn. (4) occurs rapidly to an equilibrium position defined by the equilibrium constant K_1 = [protonated oxazine]/[oxazine]-[H_3O^+].



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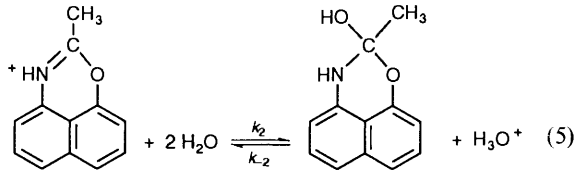

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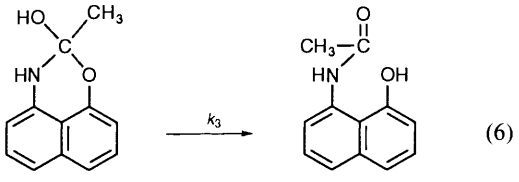

(6)

$$k = K_1k_2[H_3O^+]/(1 + k_{-2}[H_3O^+]/k_3)(1 + K_1[H_3O^+]) \quad (7)$$

$$k = K_1k_2[H_3O^+]/\{1 + (K_1 + k_{-2}/k_3)[H_3O^+] + (K_1k_{-2}/k_3)[H_3O^+]^2\} \quad (8)$$

$$k_{fit} = 851.4[H_3O^+]/(1 + 243.5[H_3O^+] + 1.14 \times 10^4[H_3O^+]^2) \quad (9)$$

$$1/k - 1/k_2K_1[H_3O^+] = (k_{-2}/k_2k_3)[H_3O^+] + (k_{-2} + K_1k_3)/k_2k_3K_1 \quad (10)$$

At low concentrations of hydronium ion for which the assumptions $K_1[H_3O^+] \ll 1$ and $(k_{-2}/k_3)[H_3O^+) \ll 1$ are valid, eqn. (7) predicts a direct dependence of k on $[H_3O^+]$ given by $k = K_1k_2[H_3O^+]$. The value K_1k_2 851 dm^3 mol^{-1} s^{-1} was obtained from a plot of the experimental values of k against $[H_3O^+]$ for the data obtained in pivalic acid and acetic acid buffer solutions. To evaluate the remaining constants, eqn. (7) was rearranged to give eqn. (10). Using the value K_1k_2 851 dm^3 mol^{-1} s^{-1} the data at higher concentrations of hydronium ion were treated according to eqn. (10) and $1/k - 1/k_2K_1[H_3O^+]$ was plotted against $[H_3O^+]$ to give a straight line from which values for k_{-2}/k_2k_3 and $(k_{-2} + K_1k_3)/k_2k_3K_1$ were obtained as gradient and intercept respectively. These values were used to evaluate the constants in eqn. (8) and the results are given in eqn. (9). The solid line in Fig. 2 was plotted using eqn. (9). The two data points at pH 6.52 and 6.22 refer to results in the presence of orthophosphate buffers and the small deviation of these points from the line is probably due to the error associated with the calculated pK value at ionic strength 0.25 mol dm^{-3}. The data at pH values below 0.60 also deviate from the theoretical plot produced from eqn. (9). This may be due to the effect of increased ionic strength on the rate of reaction in solutions of hydrochloric acid at concentrations above 0.25 mol dm^{-3}. A further term in the rate expression would be needed to improve the fit in this region and this possibility will be investigated further by studying oxazines for which the maximum in the plot of log k against pH occurs at higher pH values so that acid inhibition can be studied over a wide range of acid concentrations at constant ionic strength. If the data points in Fig. 2 at high and low pH are excluded, the values of k_{fit} calculated from eqn. (9) differ from the experimental values of k (23 data points) with an average deviation of 4.9%.

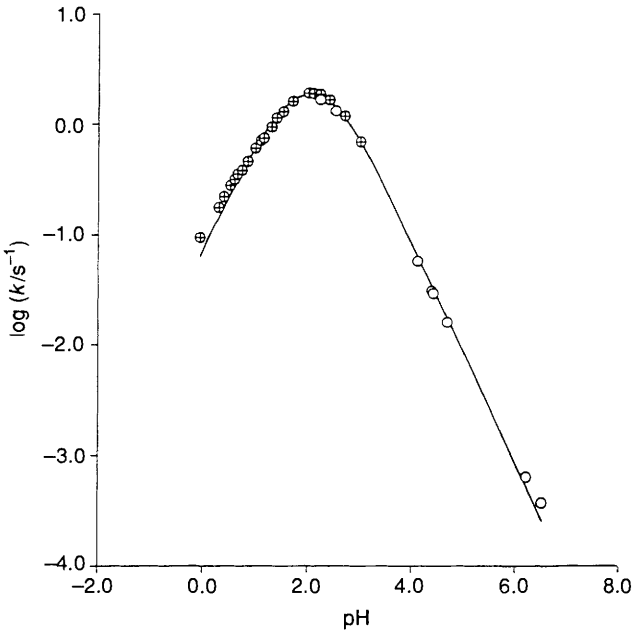

Fig. 2 Rate–pH profile for the reaction in eqn. (2); the points are values of the rate coefficients obtained in aqueous buffer solutions (○) and in solutions of hydrochloric acid (⊗)

Values for the individual rate coefficients for the steps in the mechanism in eqns. (4)–(6) and the value of the equilibrium constant K_1 cannot be deduced from the fit to the experimental data. The fit leads to two sets of values which will satisfy the observed dependence of log k on pH; k_2 13.4 s^{-1}, k_{-2}/k_3 180 dm^3 mol^{-1} and K_1 63.5 dm^3 mol^{-1} or k_2 4.73 s^{-1}, k_{-2}/k_3 63.5 dm^3 mol^{-1} and K_1 180 dm^3 mol^{-1}. The two possible values for K_1 give pK_a *ca.* 2 for acid dissociation of protonated 2-methylnaphth[1,8-*de*]-1,3-oxazine. There have been few direct measurements of the pK_a values of imines but pK_a 5.0 has been estimated[8] for PhC(OH)=NH. The reduction in pK_a of several

units expected for an *N*-phenyl substituent would give a value close to that estimated for 2-methylnaphth[1,8-*de*]-1,3-oxazine from the kinetic data.

It is likely that step (5) in the proposed mechanism is a combination of two steps: formation of the protonated form of the tetrahedral intermediate followed by equilibration to a low concentration of the unprotonated form which is formed rapidly and collapses to product as in eqn. (6). For this mechanism the form of the rate expression would be similar to that in eqn. (7) except that the rate coefficient k_{-2} would be replaced by the quotient of the rate coefficient for collapse of the protonated intermediate to the protonated oxazine and the equilibrium constant for deprotonation of the protonated tetrahedral intermediate.

Reaction with Hydroxide Ion.—In solutions of potassium hydroxide at concentrations in the range 0.05 to 0.25 mol dm^{-3} and a total ionic strength of 0.25 mol dm^{-3}, the observed first-order rate coefficient (k) varies directly with the concentration of hydroxide ion, eqn. (11), to give a second-order rate coefficient k_{OH} 7.1 × 10^{-3} dm^3 mol^{-1} s^{-1}. Under these conditions 2-methylnaphth[1,8-*de*]-1,3-oxazine is protonated to a negligible extent and the first-order dependence of k on hydroxide ion concentration can be explained by a mechanism involving rate-limiting attack by hydroxide ion on 2-methylnaphth-[1,8-*de*]-1,3-oxazine. In acidic solution the preferred mechanism in eqns. (4)–(6) involves nucleophilic attack by water on the protonated oxazine. A term for the reaction of the unprotonated oxazine with water could not be detected.

$$k = k_{OH}[OH^-] \quad (11)$$

Comparison with Related Reactions.—A mechanism similar to that in eqns. (4)–(6) has been proposed[9] for the reaction of 2-methylbenzoxazole to 2-hydroxyacetanilide in aqueous solution, eqn. (12). General acid catalysis by buffer acids was

(12)

undetectable and the values K_1 2.3 dm^3 mol^{-1}, k_2 0.0162 s^{-1} and k_{-2}/k_3 181 dm^3 mol^{-1} corresponding to the same mechanistic steps as in eqns. (4)–(6) were obtained from a best fit to the kinetic data. For 2-trifluoromethylbenzoxazole the conclusion was also reached that at high pH values the rate increased due to reaction of the neutral form with hydroxide ion although quantitative measurements were not made. Reaction of 2-methylbenzoxazole with hydroxide ion was not detected. In comparison with 2-methylnaphth[1,8-*de*]-1,3-oxazine, protonation of the imino nitrogen in 2-methylbenzoxazole requires higher acid concentrations and also attack of water on the protonated species occurs with a rate coefficient which is at least 300-fold lower than for 2-methylnaphth[1,8-*de*]-1,3-oxazine. The lower basicity of the imino nitrogen in 2-methylbenzoxazole may arise because of better conjugation with the aromatic ring in this case than in the case of 2-methylnaphth[1,8-*de*]-1,3-oxazine. The lower reactivity of protonated 2-methylbenzoxazole towards nucleophilic attack by water can be explained by the greater increase in strain on formation of the tetrahedral intermediate as part of a five-membered ring in 2-methylbenzoxazole compared with the six-membered cyclic tetrahedral intermediate formed from protonated 2- methylnaphth[1,8-*de*]-1,3-oxazine.

In contrast to the finding that the ring opening of 2-methylnaphth[1,8-*de*]-1,3-oxazine proceeds to 1-hydroxy-8-acetylaminonaphthalene in aqueous solution, eqn. (2), it has been found previously[1] that 1-amino-8-trifluoroacetylaminonaphthalene cyclises to give 2-trifluoromethylperimidine as in eqn. (1) over the range pH 3 to 14 and in the presence of 0.002 to 0.25 mol dm^{-3} hydrochloric acid in 70% (v/v) Me_2SO–H_2O. Similarly it has been observed[10] that elimination of water from 2-aminoacetanilide to give 2-methylbenzimidazole is the preferred direction of reaction, in contrast to the thermodynamically favourable addition of water to 2-methylbenzoxazole as in eqn. (12). The unprotonated forms of 2-trifluoromethylperimidine and 2-methylbenzimidazole are stabilised by tautomerisation which is not possible in the case of 2-methylnaphth[1,8-*de*]-1,3-oxazine or 2-methylbenzoxazole and this may partly account for the difference in behaviour. There are however examples of –NH–C(R)=N– systems such as 3,4-dihydroquinazoline in which addition of water to give the acyclic species (2-amino-*N*-formylbenzylamine) is the thermodynamically preferred direction.[11] We are carrying out further studies to understand the reasons for these differences.

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