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Comparison of pK_R values of fluorenyl and anthracenyl cations[†]

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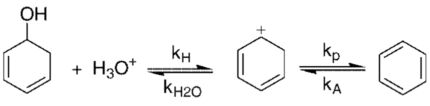
ABSTRACT: A value of p$K_R = -5.1$ for the anthracenonium ion in 50:50 (v/v) aqueous trifluorethanol is reported based on a ratio of measured rate constants k_H for acid-catalysed dehydration of the 9,10-hydrate of anthracene and k_{H_2O} for the reverse hydrolysis of the carbocation ($K_R = k_{H_2O}/k_H$). Comparison with p$K_R = -15.9$ for the fluorenyl cation indicates that the latter ion is less stable by more than 10 log units (15 kcal mol^{-1}). This difference is (a) considerably larger than that between the benzhydryl (p$K_R = -11.7$) and fluorenyl cations (Δp$K = 4.2$), which has been considered too small to indicate antiaromatic character for the fluorenyl cation, and (b) comparable to that between pK_as for the ionization (in DMSO) of fluorene (22.6) and diphenylmethane (32.2), which has been interpreted as implying aromatic character for the fluorenyl anion. It is shown that a difference in stability of anthracene hydrate and 9-hydroxyfluorene makes only a minor contribution to the difference in pK_R values and that the fluorenyl cation is destabilized by ca 10 kcal mol^{-1}. A smaller difference in pK_as for protonation of fluorenimine (5.85) and benzhydrylimine (7.0) is consistent with the expected moderating effect of an electron-donating substituent on relative carbocation stabilities. Evidence from calculations relating to the antiaromaticity of the fluorenyl cation is reviewed in the light of these measurements. An additional comparison between equilibrium constants for the ionization of aralkylazides (K_{az}) and alcohols (K_R) reveals the influence of differences in geminal σ-bond interactions for the hydroxy and azido groups in their respective reactants. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: pK_R; fluorenyl cations; anthracenyl cations

INTRODUCTION

It is now well established that the acid-catalysed aromatisation of aromatic hydrates and their methyl ethers occurs via formation of a carbocation intermediate.[1–7] The mechanism of these reactions is illustrated in Scheme 1 by the dehydration of benzene hydrate. In so far as it is a major factor controlling reactivity in these and other reactions the thermodynamic stability of carbocations continues to attract attention.[8,9]



Scheme 1

Methods for measuring the stabilities of reactive carbocations in aqueous solution are now reasonably well established. An equilibrium constant for formation of the carbocation from the hydrate (Scheme 1) can be derived from measurements of rate constants for the forward and reverse reactions. The rate constant k_{H_2O} for reaction of the carbocation with water may be obtained either (a) by generating stoichiometric concentrations of the cation by flash photolysis[10] or radiolysis[11] or (b) by competitive trapping of non-stoichiometric concentrations of solvolytically produced cations by water and azide ions based on the azide clock procedure.[2–4,8,12,13] The equilibrium constant pK_R ($-\log K_R$) is then obtained by combining k_{H_2O} with the rate constant k_H for acid-catalysed formation of the cation from the hydrate:

$$K_R = \frac{k_{H_2O}}{k_H} = \frac{[ROH][H^+]}{[R^+]} \qquad (1)$$

In the case of the hydrates of anthracene and naphthalene, the azide clock method also yields rate constants k_p for deprotonation of the cations.[2] Combination of these with rate constants k_A for protonation of the aromatic molecule derived from measurements of hydrogen isotope exchange[14] then yields a pK_a for the carbocation from the relationship $K_a = k_p/k_A$.[2]

The equilibrium constants pK_a and pK_R may be

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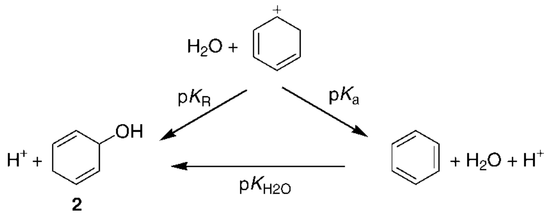
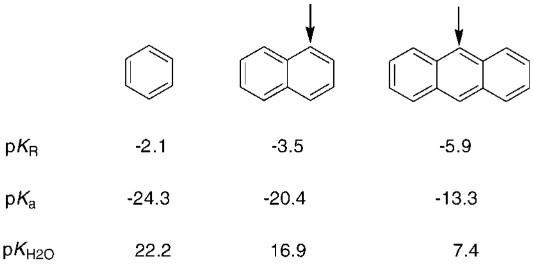
combined to yield a third equilibrium constant, pK_{H_2O}, for hydration of the aromatic molecule. This is also illustrated for benzene hydrate in Scheme 2, although Scheme 2 shows the 1,4-hydrate of benzene (**2**) rather than the 1,2-hydrate shown in Scheme 1.



Scheme 2

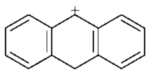
In practice, values of pK_{H_2O} are experimentally accessible for naphthalene, anthracene and benzofuran, for which both the rate constants k_{H_2O} and k_p have been measured.[2,3] More commonly, pK_{H_2O} is derived by estimating $\Delta G°_f$(aq) for the aromatic hydrate and combining it with values for the aromatic molecule and water.[15] This is particularly useful in the case of benzene where the carbocation is too unstable for trapping by azide ion but the pK_a can be estimated by combining a rate constant for isotope exchange of the tritiated aromatic molecule[14] with a rate constant for deprotonation that approaches the limiting value for relaxation of the aqueous solvent.[8,16] The latter value is assigned from consideration of this limit (10^{11} s^{-1}) and the dependence on pK_a of measured rate constants for deprotonation of carbocations for which measurements are available.[17]

Having established pK_a and pK_{H_2O} for benzene, the value of pK_R is obtained as the sum of pK_a and pK_{H_2O}.[2] This allows us to compare equilibrium constants for benzene, naphthalene and anthracene as shown in Scheme 3. In this scheme, the site of protonation of the aromatic molecule is shown by an arrow; the hydrates are the 1,4-hydrate for benzene and naphthalene and 9,10-hydrate for anthracene. It can be seen that there is a small variation in pK_R but that values of pK_{H_2O} exhibit large differences, reflecting the relative resonance stabilization energies of the aromatic molecules. These differences are also expressed in the pK_a values.



Scheme 3

The purpose of the present work was to compare pK_R values for the anthracenonium ion **3** and fluorenyl cation **4** as a contribution to recent discussions of whether or not the latter ion is antiaromatic.[18–21] On the basis of *ab initio* calculations and an experimental comparison between pK_R values for the fluorenyl and benzhydryl cations, Amyes *et al.*[18] concluded that, in contrast to the cyclopentadienyl and indenyl cations, the fluorenyl cation is not antiaromatic.



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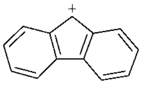

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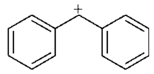

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More recently, Jiao *et al.* have characterized the fluorenyl cation as 'non-aromatic' on the basis of magnetic criteria. They drew attention to a compensation between the magnetic properties of the aromatic benzene rings and antiaromatic five-membered ring.[20] From a comparison with the anthracenyl cation they calculated a destabilization energy of 8 kcal mol^{-1} (1 kcal = 4.184 kJ) based on an orbital deletion procedure (ODP). This destabilization is similar to the 10 kcal mol^{-1} found by themselves and by Amyes *et al.* from isodesmic comparisons of the fluorenyl cation with a planarized benzhydryl cation. In so far as the experimental value of pK_R for the benzhydryl cations is affected by reduced resonance stabilization from the non-planarity of its rings, it seemed of interest to extend the experimental comparison to the planar anthracenyl cation.

The pK_R value for the anthracenyl cation in Scheme 3 cannot be compared directly with that for the fluorenyl cation because the latter refers to a 50:50 TFE–H_2O solvent mixture. Amyes *et al.*[18] reported a number of measurements of k_{H_2O} and pK_R for TFE–H_2O mixtures and noted that pK_R is approximately one unit greater in water than in the mixed solvent. However, few comparisons of pK_R values in H_2O and TFE–H_2O have been reported, and in this paper we describe an extension of the measurement of pK_R for the anthracenyl cation from water to the TFE–H_2O mixture. We also report a comparison of pK_as for protonation of benzhydrylimine and 9-fluorenimine. In their protonated forms these molecules may be considered as α-amino-substituted (benzhydryl and fluorenyl) carbocations.

Finally, it is worth noting, as recognized Jiao *et al.*,[20] that in principle pK_R values for the protonated benzene and protonated naphthalene forming 1,4-aromatic hydrates in Scheme 3 provide appropriate comparisons for pK_R measurements for the cyclopentadienyl and indenyl cations. So far, however, the only report of pK_R for these ions appears to be −40 for the cyclopentadienyl cation[22] based on a thermodynamic cycle linking pK_R to the pK_a of cyclopentadiene via oxidation potentials of the cyclopentadienyl anion determined by cyclic voltam-

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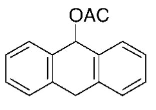
metry. As pointed out by the authors, this value is subject to considerable uncertainty.[22]

RESULTS

Anthracenyl cation

The principal experimental measurements required for evaluation of K_R for the anthracenyl cation in 50:50 (v/v) TFE–H_2O mixtures are rate constants for the acid-catalysed dehydration of the 9,10-anthracene hydrate, k_{de}, and for attack of water on the carbocation, k_{H_2O}. One difference from the reaction of the hydrate in water is that dehydration in TFE–H_2O occurs in the absence of added acid. Inhibition of the reaction by added hydroxide, azide or acetate ions indicates that the reaction involves specific acid catalysis arising from appreciable ionization of the trifluoroethanol rather than a general acid-catalysed reaction. Measurement of first-order rate constants under catalysis by $HClO_4$ gave the following values ($10^2\,k/s^{-1}$) at the indicated acid concentrations 2.46, 0.00058 M; 5.23, 0.00116 M; 7.64, 0.00163 M; 8.65, 0.00203 M; 10.0, 0.0029 M; 12.9, 0.0035 M; 1.85, 0.00464 M; and 2.63, 0.0059 M. These values yield a second-order rate constant $k_{de} = 37.3\ \text{M}^{-1}\,\text{s}^{-1}$, which compares with $9.5\ \text{M}^{-1}\,\text{s}^{-1}$ in water.[2] In the absence of acid the rate constant is $7.7 \times 10^{-3}\ \text{s}^{-1}$.

The rate constant for the reaction of the anthracenyl cation with water is based on two independent comparisons of the rate of attack by water with the rate of attack by azide ion. In the first, anthracenyl acetate (**6**) was solvolysed in 50:50 TFE–H_2O in the manner described previously for water.[2] Solvolysis occurred in the time taken to record the first measurement of absorbance following injection of a few microlitres of a 10^{-3} M stock solution in acetonitrile. This absorbance was depressed in the presence of azide ions in a manner consistent with nucleophilic trapping of the carbocation intermediate by azide ions in competition with deprotonation by water to form the main absorbing product anthracene. Ratios of rate constants for the reaction of the carbocation with azide ion, k_{az}, deprotonation, k_p, and nucleophilic reaction with water, k_{H_2O}, were evaluated by application of Eqn. (2) based on Scheme 4 (in which R^+ is the anthracenonium ion).



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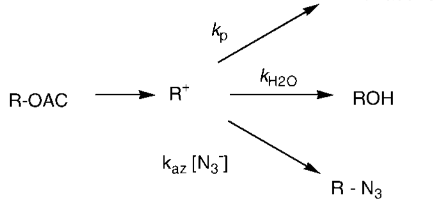

Scheme 4

$$\frac{1}{A_{az}} = \frac{1}{A_0} + \frac{1}{A_0}\frac{k_{az}[N_3]}{(k_p + k_{H_2O})} \tag{2}$$

The absorbances A_{az} and A_0 in Eqn. (2) correspond to limiting values at completion of the solvolysis in the presence and absence of sodium azide. The analysis is similar to that reported previously for solvolysis in acetonitrile–water mixtures[2] and it was assumed that the fraction of carbocation reacting with TFE to form a trifluoroethyl ether was small enough to be neglected. The ratio of rate constants $k_{az}/(k_p + k_{H_2O})$ was obtained as the ratio of slope to intercept from the plot of $1/A_{az}$ versus $[N_3^-]$ shown in Fig. 1. This plot is subject to considerably greater scatter than for aqueous acetonitrile mixtures, possibly because the azide product was not stable but itself underwent solvolysis.[3,4,23,24] The influence of this subsequent reaction was minimised by extrapolating absorbances to the time of injection of the anthracenyl acetate into the azide-containing TFE–H_2O mixture. From Fig. 1, a value of $k_{az}/(k_p + k_{H_2O}) = 240$ was obtained.

A second value of $k_{az}/(k_p + k_{H_2O})$ was obtained from measurements of first-order rate constants for the relatively slow reaction ascribed to solvolysis of the anthracenylazide. Although this azide was not isolated its identity was inferred from its formation in the azide trapping measurements and the fact that the subsequent

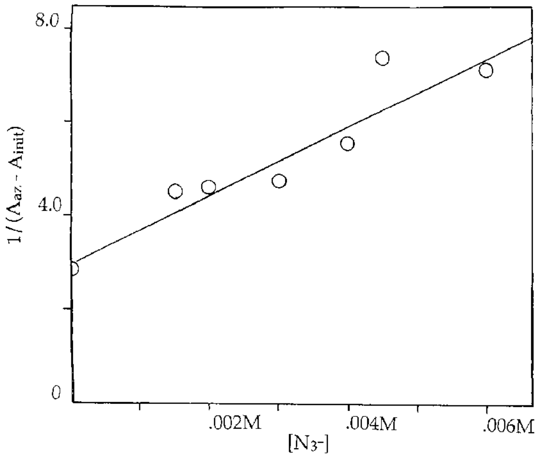

Figure 1. A plot of $1/(A_{az} - A_{init})$ against $[N_3^-]$ for the solvolysis 9-acetoxy-9,10-dihydroanthracene in 50:50 v:v TFE-H_2O mixtures at 25°; A_{init} and A_{az} are initial and final absorbances respectively

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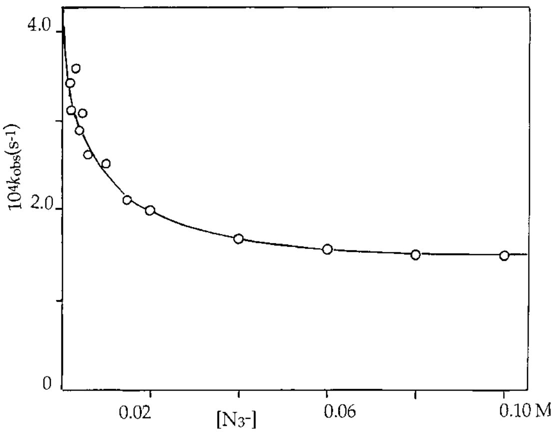
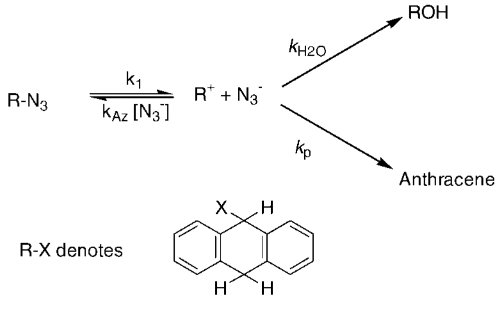


Figure 2. A plot of first order rate constants for the (presumed) solvolysis of 9-azido-9,10-dihydroanthracene against $[N_3^-]$ in 50:50 v:v TFE-H_2O at 25°

solvolysis formed anthracene and was subject to a characteristic common ion rate depression by added azide ions, as shown in the plot of first-order rate constants against $[N_3^-]$ in Fig. 2.

In addition, analysis of the rate depression by azide ions in Fig. 2 gave a ratio of rate constants $k_{az}/(k_p + k_{H_2O})$ consistent with that from the trapping measurements with anthracenyl acetate. The reaction scheme on which this analysis was based is shown in Scheme 5. The anthracenyl azide (RN_3) is subject to reversible ionization followed by attack of water to give a mixture of anthracene and anthracene hydrate. The rate-depressing influence of azide ion is expressed through the back reaction of the anthracenyl cation (R^+) to reform the azide reactant (RN_3).



Scheme 5

Inspection of Fig. 2 shows, however, that the rate of solvolysis of the azide reactant is not fully suppressed at higher azide concentrations but achieves a significant limiting value independent of further addition of azide ions. The magnitude of this limiting rate constant is too great to be consistent with attack of azide ion as a base on the free anthracenyl cation, and the behaviour is attributed to deprotonation of the anthracenyl cation by an azide ion within an ion pair. This is consistent with nucleophilic attack of azide ion on the anthracenyl cation being diffusion controlled, in so far as, in the reverse of the ionization reaction, re-formation of the azide will be faster than diffusive separation of an ion pair. Deprotonation within an ion pair is a commonly observed phenomenon[8,25] and it seems reasonable to suppose that the reaction competes, albeit inefficiently, with ion-pair return to the reactant.

The rate expression, based on Scheme 5, is given by the equation

$$k_{obs} = k_0 + \frac{k_1(k_{H_2O} + k_p)}{k_{az}[N_3] + (k_{H_2O} + k_p)} \qquad (3)$$

The line drawn through the points in Fig. 2 represents a best fit of this equation with $k_1 = 2.6 \times 10^{-4}\,M^{-1}\,s^{-1}$, $k_0 = 1.5 \times 10^{-4}\,s^{-1}$ and $k_{az}/(k_p + k_{H_2O}) = 155$. Although the last value agrees imperfectly with the value of 240 from the trapping experiments, it depends sensitively on measurements at high azide concentrations which may be influenced by a failure to keep the ionic strength constant. A good fit would also be obtained using a larger value of this ratio. Nevertheless, the values are probably within their error limits and an average of $k_{az}/(k_p + k_{H_2O}) = 200$ was assumed for the calculation of k_p and k_{H_2O}. The level of agreement between the two measurements is sufficiently good to provide further evidence for the validity of Scheme 4.

In the usual way, a value for $k_p + k_{H_2O}$ was derived by taking k_{az} as the diffusion-controlled value of $5 \times 10^9\,M^{-1}\,s^{-1}$.[12,13] This gave $k_p + k_{H_2O} = 2.5 \times 10^{-7}\,s^{-1}$. Separate values of k_p and k_{H_2O} could be obtained as before[2] by adding acid to the solvolysis product and observing the increase in absorbance from conversion of any anthracene hydrate formed in the k_{H_2O} pathway to anthracene. Indeed, in TFE–H_2O this occurs, as already noted, in the absence of acid. We thus obtained the ratio $k_{H_2O}/(k_p + k_{H_2O}) = 0.22$ and $k_{H_2O} = 5.4 \times 10^6\,M^{-1}\,s^{-1}$. The latter value is of a magnitude for which the assumption that the azide reaction is diffusion controlled is believed to be correct.[19]

We are now in a position to calculate K_R, the ionisation constant of anthracene hydrate, by using Eqn. (1). The rate constant k_{de} for dehydration of this hydrate in TFE–H_2O may be expressed in terms of the rate constant for formation of the carbocation k_H and $k_{H_2O}/(k_p + k_{H_2O})$ as in Eqn. (4), which is based on Scheme 6.

$$\mathrm{ROH} \underset{k_{H_2O}}{\overset{k_H[H^+]}{\rightleftharpoons}} R^+ + H_2O \xrightarrow{k_p} \text{anthracene}$$

Scheme 6

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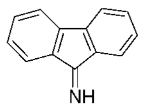
From the measured value of $k_{de} = 37.3\,\text{M}^{-1}\,\text{s}^{-1}$ we obtain a rate constant $k_H = 47.7\,\text{M}^{-1}\,\text{s}^{-1}$ for carbocation formation which may be combined with k_{H_2O} to obtain $K_R = 1.13 \times 10^5$ and $pK_R = -5.1$ as in Eqn. (1) (where ROH represents the anthracene hydrate).

$$k_{de} = \frac{k_H k_p}{(k_{H_2O} + k_p)} \tag{4}$$

It is not possible to evaluate an ionization constant K_a for the anthracenyl cation in TFE–H_2O because a rate constant for protonation of anthracene (from hydrogen isotope exchange measurements) is lacking for this solvent. However, one further equilibrium constant can be derived, for dissociation of the 9-azido-9,10-dihydroanthracene to form the carbocation and azide ion. This is obtained by combining the rate constant for solvolysis of the anthracenylazide, $k_1 = 2.6 \times 10^{-4}\,\text{M}^{-1}\,\text{s}^{-1}$, with the reverse rate constant for reaction of the cation with azide ion, which is assumed to have the diffusion value of $5 \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}$.[23,24] This yields $K_{eq} = 5.2 \times 10^{-14}$ and $pK_{eq} = 13.3$.

Fluorenimine

In addition to the study of the anthracenonium ion in H_2O–TFE mixtures, measurements of rate constants for the hydrolysis of 9-fluorenimine (**7**) to form fluorenone



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were undertaken to establish a pK_a for the protonation of its imino nitrogen atom. The hydrolysis was monitored in aqueous solution from changes in absorbance at 256 nm, and first-order rate constants were obtained for the reaction in dilute HCl, dilute NaOH and for buffer solutions in the pH range 4–9. For the more acidic acetic acid buffers (the most acidic buffer used) a mild buffer catalysis was observed, but for more basic buffers rate constants were independent of buffer concentration. A plot of logarithms of first-order rate constants against pH is shown in Fig. 3. The rate constants are extrapolated to zero buffer concentration for acetic and cacodylic acid buffers, but otherwise were based on measurements at a single buffer concentration. The ionic strength was maintained at 0.5 M with NaCl, except for measurements with HCl and NaOH, for which no salt was added.

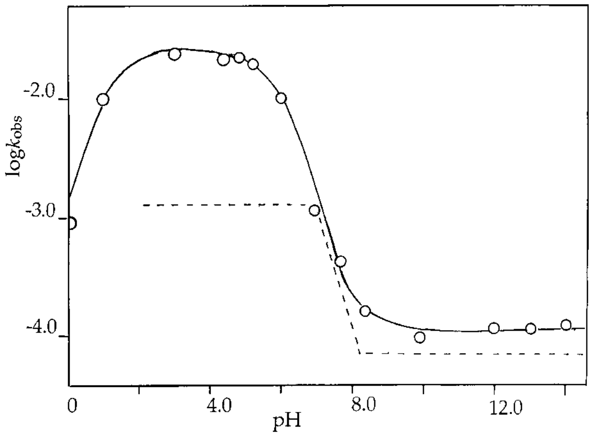
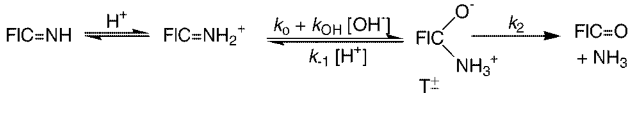


Figure 3. Logk_{OBS}-pH profile for the hydrolysis of 9-fluorenimine at 25°; the dashed line represents limiting values of logk_{OBS} for benzhydrylamine

The mechanism of hydrolysis of imines is well understood,[26,27] and the pH profile shows characteristic behaviour consistent with the reaction paths shown in Scheme 7 (in which fluorenimine is denoted by FlC=NH). At high pH the pH-independent reaction represents rate-determining attack of hydroxide ion upon the iminium ion. Between pH 1 and 10 the nucleophile is water rather than hydroxide. The pK_a of the iminium ion corresponds to the break in the pH profile close to pH 6. At low pH there is a further characteristic change from a pH-independent reaction to a reaction inversely dependent upon pH consistent with a change in rate-determining step from attack of water on the iminium ion to expulsion of the amine leaving group from a carbinolamine tetrahedral intermediate ($T^{\pm}$ in Scheme 7). The overall kinetic behaviour for the pH profile is summarized in Eqn. (5), which uses the same notation for rate constants as Scheme 7. The line drawn through the points in Fig. 3 represents a best fit of this equation to the measured first-order rate constants, with $k_{OH} = 1.01 \times 10^2\,\text{M}^{-1}\,\text{s}^{-1}$, $k_0 = 2.63 \times 10^{-2}\,\text{s}^{-1}$, $k_2/k_{-1} = 0.5\,\text{M}$ and $pK_a = 5.75$. These rate constants may be compared with the corresponding values for benzophenoneimine, $k_{OH} = 9.0 \times 10^2\,\text{M}^{-1}\,\text{s}^{-1}$, $k_0 = 1.3 \times 10^{-3}\,\text{s}^{-1}$ and $pK_a = 7.0$, measured by Koehler *et al.*[26] The limiting kinetic behaviour for this imine is shown by the dashed lines in Fig. 3.

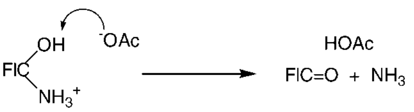
$$k_{obs} = \frac{k_0 + k_{OH}[OH^-]}{1 + K_a/[H^+]} + \frac{k_2}{(k_{-1}[H^+] + k_2)} \tag{5}$$

The main point of interest here is a comparison of the pK_as for fluorenone and benzophenone imines discussed below. However, it may also be noted that a possible interpretation of the buffer catalysis at low pH is that



Scheme 7

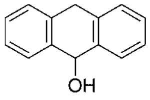
there is an increase in the rate of the partially rate-determining k_2 step of the reaction as a result of general base-catalysed formation of product from the T^+ tetrahedral intermediate as in the equation.



$$\mathrm{FlC(OH)(NH_3^+)} + {}^-\mathrm{OAc} \longrightarrow \mathrm{FlC{=}O + NH_3 + HOAc} \qquad (6)$$

DISCUSSION

The measurements described yield equilibrium constants for the ionization of 9,10-anthracene hydrate (**8**) and the corresponding adduct of anthracene with hydrazoic acid (**9**) in 50:50 (v/v) H_2O–TFE mixtures. In addition, we



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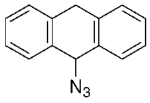

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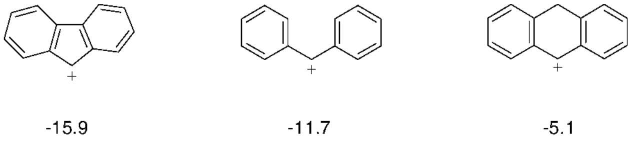
measured a pK_a for the protonation of 9-iminofluorene (in water). The results raise two distinct points for discussion. The first is the implications, if any, of the pK values for ionization of the hydrate and imine for the antiaromaticity of the fluorenyl cation. The second is the interpretation of the relative magnitudes of ionization constants of alcohols (or hydrates) and alkylazides and, more generally, of equilibrium constants for the formation of carbocations from precursors with different leaving groups. We consider first the question of antiaromaticity.

pK_R values for anthracenyl and fluorenyl cations

Ab inito calculations suggest by various criteria, including magnetic susceptibility exaltation, nucleus-independent chemical shifts (NICS)[20,21] and energetic and geometric comparisons with reference compounds,[18] that the cyclopentadienyl and indenyl cations are antiaromatic, whereas the fluorenyl cation is either non-antiaromatic,[18] 'non-aromatic'[20] or borderline in antiaromatic character.[21]

Amyes *et al.*[18] compared the stabilities of fluorenyl and benzhydryl cations and calculated energies, geometries and charge distributions using *ab initio* calculations at the 6–31G*/3–21G level. They also measured pK_R values for the two ions experimentally and found a difference (ΔpK_R) of 4.2 log units. Because their calculations were based on a planarized structure of the benzhydryl cation, a more appropriate structure for comparison with the calculations would appear to be the planar anthracenyl cation. Indeed this ion was later used for comparison in calculations by Jiao *et al.*[20]

The measurements in this paper show that the anthracenyl cation is significantly more stable than the benzhydryl cation with p$K_R = -5.1$ compared with -11.7. Comparison of the fluorenyl cation with the anthracenyl cation therefore increases the difference in pK_R values to 10.8 log units or 15 kcal mol^{-1}. These pK_R values are shown under the structures of the carbocations below.



It is noteworthy that the difference in pK_R values for the fluorenyl and anthracenyl cations is equivalent to the difference in pK_as for the ionization of fluorene and diphenylmethane to their respective anions. In DMSO these pK_as are 22.6 and 32.2, respectively.[28] Although a pK_a for dihydroanthracene appears not to have been reported, it can hardly be doubted that its value will be smaller than that for diphenylmethane. If the difference between fluorenyl and anthracenyl cations is not ascribed to antiaromaticity then the experimental energy difference adduced as evidence for the aromaticity of the fluorenyl anion is smaller than that on which the antiaromaticity of the cation is judged to be unimportant.

Comparison of experimental and calculated stabilization energies

The energy difference of 15 kcal implied by the pK_R values is close to the difference of 10 kcal in electronic energies calculated by Amyes *et al.*[18] for the fluorenyl and planarized benzhydryl cations, especially if account is taken of the stabilizing inductive effect of the methylene bridge of the anthracenyl cation. These authors were reluctant to ascribe the difference to a π-destabilization of the fluorenyl cation, however, because their calculations indicated a net π-stabilization of 50 kcal relative to the (planar) benzhydryl cation and revealed no other evidence of antiaromaticity. They suggested that either there might be a greater π-stabilization of the fluorenyl relative to the benzhydryl alcohol or that the energy difference derives from other sources.[18]

Experimentally it is not possible to distinguish π-stabilization from σ-stabilization or other energetic effects using pK_R measurements. However, it is possible to show that the stabilization arising from linking the benzene rings in fluorene (taken as a model for the 9-fluorenyl alcohol) is significantly less than the destabilization of the corresponding carbocation. The stabilization of fluorene relative to dihydroanthracene may be judged initially from the isodesmic reaction of Eqn. (7), for which $\Delta H = 7.6$ kcal mol^{-1} in the gas phase. Probably a better measure of this stabilization, however, is provided by Eqn. (8), in which the cyclohexane and

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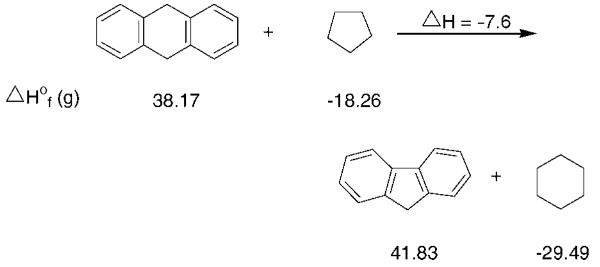
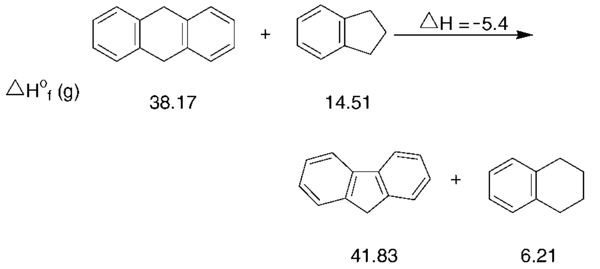
cyclopentane rings of Eqn. (7) are replaced by tetrahydronaphthalene and indane, in recognition of the benzo fusion of the five- and six-membered rings of fluorene and anthracene. Now the value of $\Delta H = 5.4$ kcal mol^{-1} is significantly smaller.[15,20] This is because benzoannelation is energetically more favourable for cyclopentane than cyclohexane. Indeed taking account of the double benzoannelation in fluorene and anthracene the true stabilization is probably smaller still, e.g. $\Delta H = 3$–4 kcal mol^{-1}.

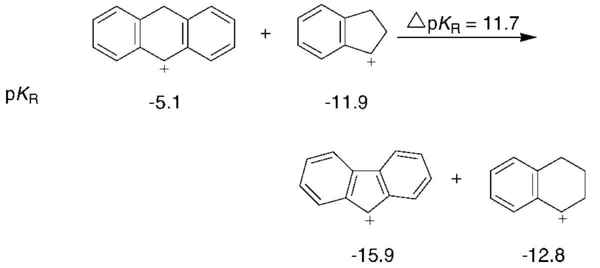


(7)



(8)

We can deduce the stabilization of the fluorenyl relative to the anthracenyl cation by considering the corresponding isodesmic relationship involving the indenyl and tetrahydronaphthyl cations shown in Eqn. (9). If we replace ΔH°_{f} (g) by pK_R values[17] we obtain a measure of the difference in stabilization of the carbocations relative to their alcohol reactants. This amounts to Δp$K_R = -11.7$, which is equivalent to 16 kcal mol^{-1}. If we suppose that stabilization of the alcohols may be approximated by ΔH in the gas phase for the corresponding hydrocarbons, i.e. 3–4 kcal mol^{-1}, we find that the fluorenyl cation is (isodesmically) destabilized relative to the anthracenyl cation by 12–13 kcal mol^{-1}.



(9)

It is likely that a further 3–4 kcal mol^{-1} of this difference reflects stabilization of the anthracenyl cation by the inductive effect of the methylene group. Nevertheless, the principal conclusion to be drawn from this analysis is that the magnitude of the experimental effect matches the value of $\Delta H = 10$ kcal mol^{-1} calculated by Amyes, *et al.*[18] and Jiao *et al.*[20] It is unlikely that this value needs correction for strain in the fluorenyl cation because this should be more than compensated by strain in the central ring of the anthracenyl cation. Thus there is more strain associated with replacing single bonds by one or two (conjugated) double bonds in a cyclohexane ring than a cyclopentane ring.[15]

This agreement between experiment and calculation supports the reality of the destabilization of the fluorenyl cation. It is possible that the origin of the destabilization lies in an accumulation of small effects arising from neglected contributions or approximations, such as the combination of ΔH values for the gas phase with ΔG in solution or the neglect of geminal interactions of the hydroxyl groups of the alcohols. However, the more obvious interpretation is that it represents a π-destabilization energy.

How could such a conclusion be reconciled with Amyes *et al.*'s calculation showing a greater π-stabilization of the fluorenyl than (planar) benzhydryl cation? As these authors pointed out, the antiaromaticity of simple molecules or ions such as cyclobutadiene or the cyclopentadienyl cation is unambiguous and is revealed by characteristically degenerate highest occupied molecular orbitals in their planar configurations. For the indenyl cation the antiaromatic ring is fused to an aromatic ring and the degeneracy (and simplicity) of the cyclopentadienyl cation is lost. Nevertheless, it is generally agreed that the indenyl cation is subject to antiaromatic destabilization.

In the case of the fluorenyl cation the electronic characteristics of the central five-membered ring are overlain by the influence of the two benzene rings.[20] Jiao *et al.*[20] noted agreement of their own calculations with those of Amyes *et al.*[18] in implying a net 'nonaromatic' character for the fluorenyl cation. However, they estimated a delocalization energy in a different manner from Amyes *et al.* They compared the effect on fluorenyl and anthracenyl cations of excluding from the energy calculation the p-orbital that would accommodate the positive change if it were fully *localized* at the 9-position of the two cations. By this means they estimated a reduced delocalization energy for the fluorenyl relative to the anthracenyl cation of 8 kcal mol^{-1}. This is in reasonable agreement with the experimental measurements and calculations of overall energy differences and suggests that by the ODP criterion these may be regarded as mainly antiaromatic in origin.

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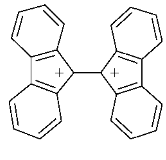
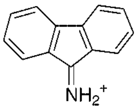
Stabilization and NICS values

An interesting suggestion by Mills[21] is that the degree of antiaromaticity of the fluorenyl cation is influenced by the electronegativity of substituents at the formal charge-bearing carbon atom, i.e. the 9-position of the fluorenyl ring. By the criterion of NICS values and proton chemical shifts a fluorenyl cation with sufficiently electron-withdrawing substituents such as CF_3 or, most strikingly, another 9-fluorenyl cation (**10**), is found to be unambiguously antiaromatic, based on NMR measurements and high-level Gaussian (including DFT) calculations.

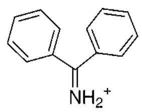


10

Our own measurement of pK_a for the protonated 9-iminofluorene (**11**), although not strictly comparable to the measurements of pK_R values, reveals a difference of 1.25 log units from the pK_a (= 7.0) for protonated benzhydrylimine (**12**). This small difference is consistent with extensive delocalization of charge from the carbocation centre by the strongly electron-donating amino susbstituent and a reduction in the difference in stability compared with the parent ions. An even smaller difference in pK_as has been reported[30] for protonation of fluorenone (−6.65) and benzophenone (−6.16). As expected, the pK_a = −5.10 for anthrone is less than that for benzophenone.[30]



11



12

Strictly, these results only show that differences in stabilities of fluorenyl and benzhydryl or anthracenyl cations are, as expected, saturated by electron-donating substituents. Nevertheless, formally, they complement the calculations of NICS values for more unstable cations.

In so far as there have been good correlations between NICS values and energy differences in recognized examples of antiaromatic molecules, it seems reasonable to suppose that the energy difference between the parent fluorenyl and anthracenyl cations in part reflects the same phenomenon as is responsible for the trend in NICS values. Mills[21] interpreted the trend in NICS values with 9-substituent for the fluorenyl cation as indicating that the unsubstituted cation is close to the borderline of magnetically detectable antiaromaticity. However, Jiao *et al.*[20] emphasized that polycyclic aromatic hydrocarbons show a less clear correlation between magnetic properties and stabilization energies than monocyclics. Moreover, as implied above for polycyclic aromatic molecules showing borderline antiaromatic behaviour, it may be difficult to assign clearly the origin of electronic contributions to the destabilization, especially where the rings are non-equivalent. It seems fair to conclude, therefore, that the possibility of a mild antiaromatic destabilization of the fluorenyl cation is not excluded by the calculated NICS values.[20,21]

Ionization of 9-azido-9,10-dihydroanthracene

The measurement of an ionization constant K_{az} for 9-anthracenylazide is of interest in the context of a comparison of the ionization constants of azides and alcohols. There have been a number of reports of equilibrium constants for the ionisation of azide derivatives, notably of arylalkylazides and azido methyl ethers.[23,24] These have been based on measurements of a common ion rate depression by azide ion accompanying solvolysis of the azide susbstrate. These substrates either have been synthesized directly or have been formed *in situ* by trapping of a carbocation generated from a more reactive solvolytic precursor.[3,24] Equilibrium constants have been obtained by combining a rate constant for the ionization step with a rate constant for the reverse reaction of the carbocation with azide ion. For relatively unstable cations this reaction is diffusion controlled.[13]

The equilibrium constants to be compared are the ionization constant pK_{az} for the azide and pK_R for the alcohol. Strictly, pK_R is a hydrolysis constant for the carbocation. A more appropriate equilibrium constant for comparison with K_{az} therefore is that for ionisation of the alcohol (i.e. for the equilibrium $ROH \rightleftharpoons R^+ + OH^-$), denoted K_c. Thus $1/K_{az}$ and $1/K_c$ measure respectively the affinities of the azide ion and hydroxide ion for the carbocation. However, as discussed elsewhere, K_c is inversely related to K_R through the relationship $K_c = K_w/K_R$ where K_w is the autoprotolysis constant of water.[31] Because K_R is used more widely than K_c, it is

$$R^+ + H_2O \overset{K_R}{\rightleftharpoons} ROH + H^+$$

$$RN_3 \overset{K_{az}}{\rightleftharpoons} R^+ + N_3^-$$

$$K_R = \frac{[ROH][H_3O^+]}{[R^+][H_2O]}$$

$$K_{az} = \frac{[R^+][N_3^-]}{[RN_3]}$$

$$K_{az}K_R = \frac{[ROH]}{[RN_3]}\frac{[N_3^-][H_3O^+]}{[H_2O]}$$

Scheme 8

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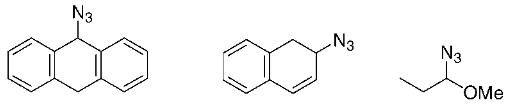

	13	14	15
pK_{az}	13.3	13.0	13.2
pK_R	-5.1	-7.8	-10.0
Solvent	TFE-H_2O	CH_3CN-H_2O	H_2O

Scheme 9

convenient to quantify comparisons in terms of the product $K_{az}K_R$ rather than the ratio K_{az}/K_c. Scheme 8 summarizes expressions for K_{az}, K_R and $K_{az}K_R$.

The relevant measurements for comparison are shown in Scheme 9. Values of pK_{az} and pK_R are compared for three substrates in (different) mixed or pure aqueous solvents. The main point of interest for the present discussion is that whereas pK_{az} for the three substrates remains practically the same (13.1 ± 0.2), pK_R varies from -5.1 to -10, i.e. changes by five powers of ten.

At first sight this behaviour is surprising because the relative magnitudes of K_{az} and K_R (strictly the product $K_{az}K_R$) should be independent of the stability of the carbocation. The origin of the behaviour is best assessed if $K_{az}K_R$ is rewritten in terms of two further equilibrium constants, $K_a^{HN_3}$, the ionization constant of hydrazoic acid (HN_3), and K_{bond}, the equilibrium constant for the 'bond exchange reaction' between OH and N_3 leaving groups shown in Scheme 10. The latter constant is a measure of the relative strengths of bonds between oxygen and nitrogen and hydrogen on the one hand and oxygen and nitrogen and carbon on the other. By comparing Schemes 8 and 10, it can be seen that the relationship between the two pairs of equilibrium constants is $K_{az}K_R = K_{bond}K_a^{HN_3}$.

$$HN_3 \overset{K_a^{HN_3}}{\rightleftharpoons} H^+ + N_3^-$$

$$RN_3 + HOH \overset{K_{bond}}{\rightleftharpoons} ROH + HN_3$$

Scheme 10

Before focusing on the bond exchange equilibrium, it may be recalled that the equilibrium constants in Scheme 9 were measured in different solvents, specifically aqueous trifluoroethanol, aqueous acetonitrile and water. Although the value of $K_{az}K_R$ is independent of the nature of the carbocation, it is not necessarily independent of the solvent.

However, while a change in solvent does change pK_{az} and pK_R it appears that the effects on the two equilibrium constants may be compensating. Thus between water and 50:50 TFE–H_2O, pK_R for the anthracenonium cation increases from -5.9 to -5.1, whereas for the same solvent change pK_{az} decreases. This is implied by the lack of solvolysis of the azide in water (and the supposition that the rate constant for the reverse reaction remains unchanged at the diffusion value). The less polar acetonitrile has the opposite effect on pK_R as is indicated by a decrease from -6.7 to -7.8 for 2-hydroxy-1,2-dihydronaphthalene on admixture of 25% acetonitrile with water.[2,3] On the other hand, solvolysis of the alkylazide must occur more readily in the aqueous medium (**13**) (kinetically and presumably thermodynamically), as has been well established, for example, for the comparable solvolysis of the anthracenyl acetate (**6**).[2]

If the change in solvent is not the main factor causing the discrepancy between changes in K_R and K_{az}, then the differences arise chiefly from variation in K_{bond}, rather than the solvent sensitive but substrate independent ionisation constant of hydrazoic acid, $K_a^{HN_3}$. Hence they arise from differences in stabilities of the substrates RN_3 and ROH. If we consider first the highly negative value of pK_R for the ionization of propionaldehyde hemiacetal (**15**), it seems clear that this must arise from the stabilising geminal interaction between the two oxygen atoms of the reactant. This stabilization amounts to about 7 kcal mol^{-1} and would contribute 5 log units to a difference between pK_R and pK_{az}.[32] Although the magnitude of the geminal interaction of OMe and N_3 in **15** is not certainly known, such interactions can vary widely and that between OH and CN (for example) is *un*favourable by 7 kcal mol^{-1}.[32] What evidence there is is consistent with the N_3–MeO interaction being considerably less favourable than MeO–MeO.[33]

Turning to the difference of 2.7 log units between pK_R values for anthryl and naphthyl substrates (**13** and **14**), we may draw on recent estimates of the energy difference between substitution of a hydroxyl group for a hydrogen atom at the appropriate carbon atoms of 9,10-dihydroanthracene and 1,2-dihydronaphthalene.[15] A difference of $\Delta G(aq) = 1.8$ kcal mol^{-1} was estimated in favour of the 2-hydroxy-1,2-dihydronaphthalene, reflecting a more favourable hydroxyl–alkyl than hydroxyl–phenyl interaction. This is consistent with the direction of the observed difference in pK_Rs. Again, little is known of the corresponding geminal interactions of an azido group but we may speculate that the interaction of an azide with the phenyl groups in 9-azido-9,10-dihydroanthracene is more stabilizing than with a hydroxyl group.

One objective of the above analysis was to explore the possibility of using measurements of pK_{az} to derive values of pK_R for alcohols for which direct measurements are lacking. The issues discussed are pertinent to the

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general problem of interrelating pK values for ionisation reactions involving different leaving groups. The attraction of establishing such relationships is that in favourable cases equilibrium constants can be derived from solvolysis measurements in aqueous solution in the same way as for the azides discussed above,[24] i.e. by combining the solvolysis rate constant with a rate constant for the reverse reaction which is assumed to be diffusion controlled.[34] Then if an equilibrium constant for one leaving group becomes available, others may be deduced. However, in the absence of relevant thermodynamic measurements, more information on (equilibrium constants for) σ-bond interactions of the leaving groups will be required to make the necessary interpolations. In principle this information may be accessible from calculations.[35]

EXPERIMENTAL

Instrumentation and reagents. NMR measurements were made with a Jeol JNMGX270 spectrometer operating at 270 MHz for ^{1}H NMR and 68 MHz for ^{13}C NMR. UV–Vis spectra were recorded using Phillips PU 8600, Bausch and Lomb Spectronic and Perkin-Elmer Hitachi 124 spectrophotometers, with thermostatting of cell compartments at 25.0 ± 0.1 °C for kinetic measurements. Reagents, including the solvent trifluoroethanol, were normally purchased from Aldrich and used without purification; acetonitrile was of HPLC grade. Water for kinetic measurement was doubly distilled.

Synthesis. The preparation of 9-hydroxy-and 9-acetoxy-9,10-dihydroanthracene has been described previously.[2] Fluorenimine was prepared by the method of Hilbert and Pinck,[36] with the variations described below.

Fluorenimine (7). Fluorenone (50.0 g, 0.278 mol) was heated slightly above its melting-point (82 °C) and gaseous ammonia, dried by passage through a calcium oxide tower, bubbled through the melt for 7 days, using a bubbler with a sintered-glass end to give a large gas–liquid surface area. Formation of the imine was detected by thin-layer chromatography on silica [chloroform: R_f(ketone) = 0.8; R_f(imine) = 0.3] although extensive hydrolysis occurred (even on neutral alumina plates). The reaction could be crudely monitored by the increase in bath temperature necessary to maintain the melt in the molten state, since the melting-point of the imine product (124 °C) is higher than that of fluoreneone (82 °C). Completion of the reaction was difficult to attain because of accumulation in the melt of water produced during the reaction and because the solubility of the ammonia falls with increasing temperature.

The melt was allowed to solidify and then dissolved in chloroform and shaken with dilute hydrochloric acid. The fluorenimine hydrochloride precipitated as an orange solid, leaving the unreacted fluorenone in solution. Neutralization of the hydrochloride with aqueous ammonia yielded the imine, which was crystallized from tolnene–methanol to give yellow needles (22.5 g, 41% yield): m.p. 123.5–124.5 °C (lit.[36] 124 °C); ^{1}H NMR ($CDCl_3$), δ 7.14–8.27 (m, 8H, fluorenyl rings), 10.32 (s, 1H, NH).

Kinetic and equilibrium measurements. Kinetic methods for the measurement of rate constants for dehydration of anthracene hydrate and solvolysis of 9-acetoxy-9,10-dihydroanthracene in water or water–acetonitrile mixtures have been described, as have product analyses and trapping experiments with azide ion.[2] Similar methods were used for the TFE–H_2O solvent mixtures.

Determination of the ratio of aromatic product to hydrate formed from solvolysis of 9-acetoxy-9,10-dihydroanthracene was based on differences in absorbance at 251 nm between the beginning of the solvolysis reaction (estimated from injection from a stock solution of the substrate into non-solvolysing acetonitrile), A_{init}, the absorbance at the completion of the reaction, A_0, and the absorbance following addition of a small amount of a strong acid to effect conversion of anthracene hydrate to anthracene, A_{max}. In principle, some trifluorethyl ether would also be formed in the solvolysis but inspection of the dependence of the product ratio of alcohol and trifluoroethyl ether upon pK_R for the carbocation in previous studies suggested that the amount would be small enough (<5%) to be neglected.[18] The ratio of anthracene to hydrate in the solvolysis products (and thus k_p/k_{H_2O}) is then given by $(A_0 - A_{init})/(A_{max} - A_0)$ and was based on the following measurements of A_0 and A_{max}: 0.45, 0.53; 0.46, 0.53; and 0.48, 0.54. In each case A_{init} was 0.16.

Addition of sodium azide to the solvolysis reaction led to a reduction in absorbance of the product from A_0 to A_{az}. As described above, a ratio of rate constants for trapping the solvolytic intermediate (presumed to be the anthracenonium ion) by azide ion and water is obtained from a plot of $1/(A_{az} - A_{init})$ against $[N_3^-]$, as shown in Fig. 1. The measured values of A_{az} at the indicated concentration of azide ion were: 0.51, 0 M; 0.38, 0.0015 M; 0.38, 0.0020 M; 0.37, 0.0030 M; 0.34, 0.0040 M; 0.295, 0.0045 M; and 0.30, 0.0060 M. In all cases A_{init} was 0.16.

Following the trapping by azide ion a further increase in absorbance was observed which was attributed to solvolysis of the azide trapped product 9-azido-9,10-dihydroanthracene. Rate constants for this process ($10^4 k_{obs}$ s^{-1}) were measured at the indicated concentrations of azide ion and plotted against $[N_3^-]$ in Fig. 2: 3.42, 0.0015 M; 3.12, 0.002 M; 3.59, 0.003 M; 2.86, 0.004 M; 3.09, 0.0045 M; 2.60, 0.006 M; 2.51, 0.010 M; 2.10, 0.015 M; 1.99, 0.020 M; 1.66, 0.040 M; 1.57, 0.060 M; 1.52, 0.080 M; and 1.52, 0.1 M.

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The hydrolysis of fluorenimine was monitored spectrophotometrically from the increase in absorbance at 256 nm, λ_{max} for the fluorenone product. First-order rate constants were measured in aqueous HCl, sodium hydroxide and acetate, cacodylate, *N*-methylmorpholine and trimethylamine buffers. For the buffers the ionic strength was maintained at 0.5 M with NaCl but no NaCl was added to the HCl or NaOH solutions. For the acetate and cacodylate buffers rate constants were extrapolated to zero buffer concentration. The following first-order rate constants ($10^3 k$ s^{-1}) were measured at the indicated pHs: 0.97, pH 0; 11.2, pH 1; 24.7, pH 2; 23.0, pH 4.22; 24.0, pH 4.83; 21.0, pH 5.30; 11.6, pH 5.98; 1.23, pH 7.12; 0.47, pH 7.63; 0.178, pH 8.35; 0.115, pH 9.89; 0.98, pH 12; 0.87, pH 13; and 1.12, pH 14.

Weak buffer catalysis in 4:1 AcOH–AcO$^-$ buffers (ionic strength 0.5 M, pH 4.22) was indicated by measurements of first-order rate constants (10^2 k s^{-1}) at the indicated acetate ion concentrations: 2.63, 0.04 M; 2.74, 0.06 M; 2.96, 0.08 M; and 3.0, 0.1 M. These give an apparent second-order rate constant with respect to acetate ion of 0.08 M^{-1} s^{-1}. Corresponding rate constants in 1:1 and 1:4 AcOH–AcO$^-$ buffers were 0.06 and 0.03 M^{-1} s^{-1}.

Acknowledgements

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