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Protonated Benzofuran, Anthracene, Naphthalene, Benzene, Ethene, and Ethyne: Measurements and Estimates of pK_a and pK_R

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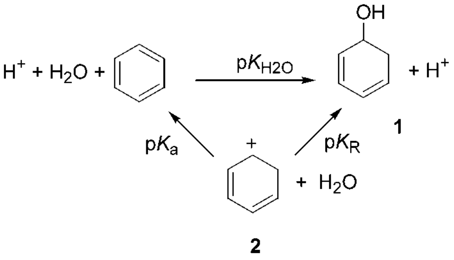
Abstract: Aqueous solvolyses of acyl derivatives of hydrates (water adducts) of anthracene and benzofuran yield carbocations which undergo competitive deprotonation to form the aromatic molecules and nucleophilic reaction with water to give the aromatic hydrates. Trapping experiments with azide ions yield rate constants k_p for the deprotonation and k_{H_2O} for the nucleophilic reaction based on the "azide clock". Combining these with rate constants for (a) the H^+-catalyzed reaction of the hydrate to form the carbocation and (b) hydrogen isotope exchange of the aromatic molecule (from the literature) yields $pK_R = -6.0$ and -9.4 and $pK_a = -13.5$ and -16.3 for the protonated anthracene and protonated benzofuran, respectively. These pK values may be compared with $pK_R = -6.7$ for naphthalene hydrate (1-hydroxy-1,2-dihydronaphthalene), extrapolated to water from measurements by Pirinccioglu and Thibblin for acetonitrile−water mixtures, and $pK_a = -20.4$ for the 2-protonated naphthalene from combining k_p with an exchange rate constant. The differences between pK_R and pK_a correspond to pK_{H_2O}, the equilibrium constant for hydration of the aromatic molecule ($pK_{H_2O} = pK_R - pK_a$). For naphthalene and anthracene values of $pK_{H_2O} = +13.7$ and $+7.5$ compare with independent estimates of $+14.2$ and $+7.4$. For benzene, $pK_a = -24.3$ is derived from an exchange rate constant and an assigned value for the reverse rate constant close to the limit for solvent relaxation. Combining this pK_a with calculated values of pK_{H_2O} gives $pK_R = -2.4$ and -2.1 for protonated benzenes forming 1,2- and 1,4-hydrates, respectively. Coincidentally, the rate constant for protonation of benzene is similar to those for protonation of ethylene and acetylene (Lucchini, V.; Modena, G. *J. Am. Chem Soc.* **1990,** *112*, 6291). Values of pK_a for the ethyl and vinyl cations (-24.8) may thus be derived in the same way as that for the benzenonium ion. Combining these with appropriate values of pK_{H_2O} then yields $pK_R = -39.8$ and -29.6 for the vinyl and ethyl cations, respectively.

Introduction

This paper reports measurements of equilibrium constants for the conversion of aromatic molecules and their water adducts (hydrates) to carbocations. The constants of interest, expressed as their negative logarithms, are pK_a and pK_R for the protonated aromatic species. These are related to the equilibrium constant pK_{H_2O} for hydration of the aromatic molecule by a thermodynamic cycle which is illustrated for benzene, benzene hydrate (**1**), and the benzenonium carbocation (**2**) in Scheme 1. As in the previous paper, the equilibria are represented by single arrows rather than double arrows to indicate the directions of reaction to which they refer.[1]

Scheme 1



The paper describes experimental measurements of pK_R for hydrates of benzofuran and anthracene. It draws on data from the literature[2−7] and the previous paper[1] to obtain pK_a values and to establish the corresponding equilibrium constants for two isomeric hydrates of naphthalene and, more speculatively, the isomeric hydrates of benzene. A pK_R value for one of the naphthalene hydrates, 2-hydroxy-1,2-dihydronaphthalene, has already been reported for 90% aqueous acetonitrile by Pirinccioglu and Thibblin.[2] An extension of these studies leads to estimates of pK_a and pK_R for alkyl carbocations and the vinyl cation.

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(1) Dey, J.; O'Donoghue, A. C.; More O'Ferrall, R. A. *J. Am. Chem. Soc.* **2002**, *124*, 8561 (preceding paper in this issue).

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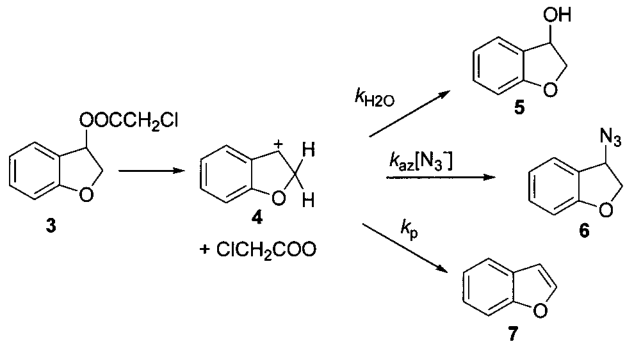
Scheme 2



The pK values in question are derived by combining rate constants for forward and reverse reactions in a manner that is now well-established for the formation of carbocations from alcohols.[2,8−14] For benzofuran hydrate (**5**), for example, a rate constant k_H for acid-catalyzed racemization of the hydrate[3] is taken as a measure of the rate of carbocation formation and combined with a rate constant for the reverse attack of water on the carbocation. The latter is measured by the azide clock method.[8−10] As shown in Scheme 2, solvolysis of a carboxylate ester of the hydrate **3** is presumed to yield a carbocation **4** which is partitioned between pathways leading to hydration, trapping by azide ion, and deprotonation. From the ratio of product concentrations of hydrate **5** and azide **6**, the rate constant for attack of water on the carbocation (k_{H_2O}) is derived by assuming that the reaction with azide ion approaches diffusion control ($k_{az} = 5 \times 10^9$ M^{-1} s^{-1}). Combining this rate constant with that for racemization (k_H) yields a value of pK_R.

Deprotonation of the carbocation **4** yields benzofuran **7**. A rate constant k_p for the deprotonation may be derived in the same manner as k_{H_2O}. This may be combined with a rate constant k_A for protonation of the aromatic molecule to form the carbocation. Since this carbocation is the reactive intermediate in aromatic hydrogen isotope exchange, k_A is obtained as the rate constant for acid-catalyzed exchange of 2-tritiobenzofuran corrected for a tritium isotope effect.

Results

Benzofuran-2,3-hydrate. Rate constants for acid-catalyzed dehydration of benzofuran hydrate **5** and for racemization of the chiral hydrate have been reported in an earlier paper as 1.5 × 10^{-3} and 4.5 × 10^{-3} M^{-1} s^{-1} respectively.[3] The smaller value for the dehydration indicates that formation of the carbocation is not fully rate-determining in this reaction. In this work measurements of azide trapping have been carried out using solvolysis of the chloroacetate of hydrate **3** as a source of carbocation **4**. In the absence of azide ion, benzofuran **7** and its hydrate are formed in a concentration ratio corresponding to the ratio of rate constants k_p/k_{H_2O} (Scheme 2). In the presence of azide ion, dihydrobenzofuranyl azide is also formed. Although this product was not isolated, HPLC analysis showed the appearance of a new peak with the expected difference in retention time between the peak assigned to the benzofuranyl azide and that of the alcohol (hydrate) based on studies of similar substrates.[8,11] Moreover, the dependence of the intensity of the azide peak upon the concentration of azide ion was consistent with its formation in the competing pathways shown in Scheme 2. In addition, the derived product ratios of azide to hydrate and azide to benzofuran were consistent with an independent measurement of the suppression of benzofuran product formed in the presence of azide ion determined spectrophotometrically.

Details of the HPLC product analysis for hydrate and azide and the derived azide/hydrate product ratios are given in the Experimental Section. From the dependence of the product ratios upon the concentration of sodium azide, we obtain the ratio of rate constants for attack of azide ion and water molecules on benzofuranyl carbocation **4** as $k_{az}/k_{H_2O} = 320$ M by use of eq 1 which is based on Scheme 2. The rate constant k_{H_2O} is first order with units s^{-1} at an ionic strength of 0.5 M.

$$\frac{[RN_3]}{[ROH]} = \frac{k_{az}[N_3^-]}{k_{H_2O}} \tag{1}$$

The independent measurement of k_{az}/k_{H_2O} was based on spectrophotometric determination of the intensity of the benzofuran chromophore formed in the products of solvolysis of dihydrobenzofuranyl chloroacetate in water in the presence and absence of added azide ion. For the same concentrations of chloroacetate reactant, the absorbance of the benzofuran product decreased with increasing concentration of azide ion (after correction for the absorbance of azide ion). The dependence of the absorbance on azide concentration may be expressed by eq 2, in which ΔA is the absorbance corresponding to a concentration of azide ion $[N_3^-]$, ΔA_o is the absorbance in the absence of azide ion, and the rate constants again correspond to those in Scheme 2. Both ΔA and ΔA_o are corrected for the absorbance of the reactant as described in the Experimental Section.

$$\frac{1}{\Delta A} = \frac{1}{\Delta A_o} + \frac{k_{az}[N_3^-]}{\Delta A_o(k_{H_2O} + k_p)} \tag{2}$$

From the slope divided by the intercept of the plot of 1/ΔA against $[N_3^-]$ the value of $k_{az}/(k_{H_2O} + k_p)$ is derived as 135. This may be converted to $k_{az}/k_{H_2O} = 214$ by taking the previously determined ratio $k_{H_2O}/k_p = 1.7$ based on either (a) a ratio of rate constants for acid-catalyzed racemization and dehydration of the benzofuran hydrate[3] or (b) the increase in the fraction of benzofuran product from further reaction with acid of the initially formed mixture of hydrate and benzofuran from solvolysis of the benzofuranyl chloroacetate. The value is in satisfactory agreement with the HPLC measurement ($k_{az}/k_{H_2O} = 320$ M) considering the lower ionic strength (0.01 M compared with 0.5 M) and the fact that there is interference from absorption by azide ion with the spectrophotometric measurements. Giving greater weight to the measurements at lower ionic strength the value k_{az}/k_{H_2O} is taken as 240.

The ratio k_{az}/k_{H_2O} may be converted to a rate constant k_{H_2O} for attack of water on the carbocation if the rate constant k_{az} can be assigned. In the azide clock analysis usually this is assumed to have the value for diffusion, 5 × 10^9 M^{-1} s^{-1}.

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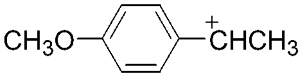
However for the benzofuranyl carbocation probably a better value is $k_{az} = 2.6 \times 10^9$ directly determined by McClelland et al. for reaction of azide ion with the 2-(4-methoxyphenyl)ethyl cation **8** generated by flash photosolvolysis from the alkyl chloride precursor.[12] We will see that the pK_R value (−9.4) derived for the benzofuranyl cation is close to that for **8**, which was measured as −8.6 in a 50:50 (v/v) trifluoroethanol−water mixture (and is expected to be about one unit more negative in pure water[13]).



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With this value of k_{az}, k_{H_2O} for the benzofuranyl cation is obtained as 1.1×10^7 s^{-1}. The rate constant k_p for deprotonation of the carbocation to form benzofuran, based on $k_{H_2O}/k_p = 1.7$, is 6.5×10^6 s^{-1}. Combining k_{H_2O} with a best value of $k_H = 4.1 \times 10^{-3}$ M^{-1} s^{-1} for the acid-catalyzed formation of the benzofuranyl cation from the hydrate[3] yields $K_R = k_{H_2O}/k_H = 2.6 \times 10^9$ and p$K_R = -9.4$.

Anthracene Hydrate. A rate constant for specific acid-catalyzed dehydration of anthracene hydrate (**9**) in acetic acid buffers at 0.5 M ionic strength was previously reported as 22.0 M^{-1} s^{-1}.[15] In this work we found reaction in dilute $HClO_4$ gave a rate constant 9.5 M^{-1} s^{-1}. Examination of the rate at different ionic strengths of sodium chloride confirmed that the discrepancy was substantially due to the difference in ionic strengths. These results are reported in Table S1 of the Supporting Information.

Anthracene hydrate **9** (Scheme 3) was acetylated[18] to give the acetate (**12**, X = OAc), which was solvolyzed in the same manner as the benzofuranyl chloroacetate to give a mixture of hydrate and anthracene (**11**). The ratio of hydrate to anthracene was determined from the fractional increase in absorbance of the anthracene on addition of sufficiently strong acid to induce acid-catalyzed dehydration of the hydrate. Because of the low solubility of the acetate and anthracene in water, these measurements were carried out in acetonitrile−water mixtures containing 33, 50, 67, and 80% acetonitrile (v/v). A ratio of $k_{H_2O}/k_p = 0.57 \pm 0.03$ with apparently no dependence on solvent composition was derived from the absorbance measurements. This corresponds to a product composition of 64% anthracene and 36% hydrate, which compares with 76% anthracene and 24% hydrate previously determined by NMR measurements in 40:60 aqueous acetone (v/v).[18]

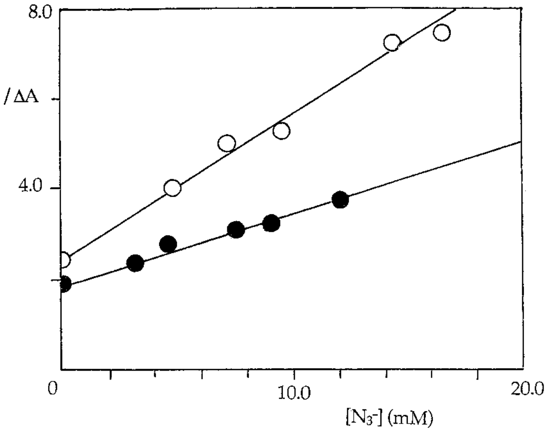
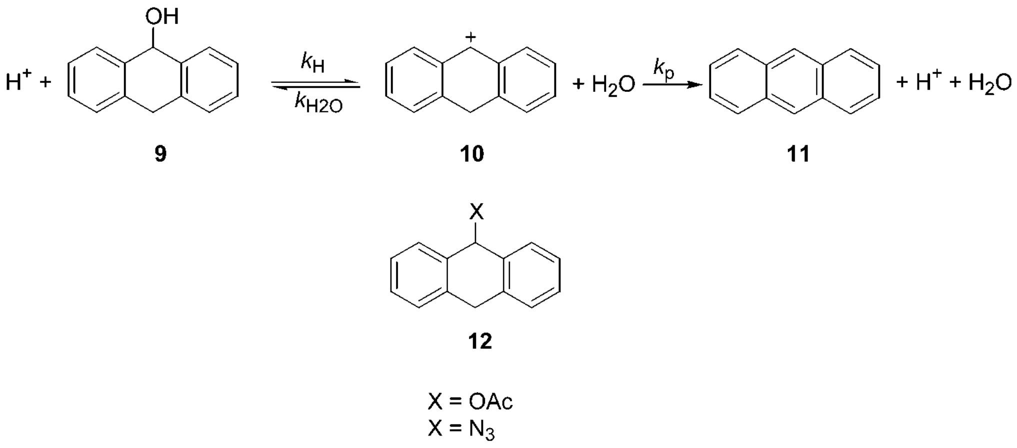


Figure 1. Plots of reciprocals of Δ*A* (final − initial absorbances) against concentration of azide ion for the solvolysis of 9-acetoxy-9,10-dihydroanthracene in aqueous acetonitrile at 25 °C (0, 20% CH_3CN; 50% CH_3CN).

When the solvolysis was carried out in the presence of azide ion, the absorbance from the anthracene was suppressed with a linear dependence on the concentration of azide ion consistent with trapping of an anthracenonium ion intermediate **11** to give the azide (**12**, X = N_3). The azide adduct and anthracene were too insoluble for a product analysis to be carried out by HPLC. However, the analysis could be achieved spectrophotometrically by making measurements in the acetonitrile−water mixtures. Plots of the reciprocal of the absorbance against [N_3^-] gave linear plots consistent with eq 2, on the basis of which values of k_{az}/k_{H_2O} were determined as 344, 306, 225, and 198 in aqueous mixtures containing 33, 50, 67, and 80% acetonitrile, respectively, making use of the previously established value of k_p/k_{H_2O}. Reciprocal plots of limiting absorbances against azide concentration at two solvent compositions are shown in Figure 1 based on data recorded in Table S2 of the Supporting Information. Similar measurements with sodium acetate, up to 0.64 M concentration, showed no appreciable effect on the product absorbances, indicating that acetate ion does not catalyze proton abstraction from the anthracenonium ion to form anthracene. These measurements are in Table S3 of the Supporting Information.

Scheme 3

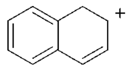


The ratio k_{az}/k_{H_2O} was extrapolated from acetonitrile−water mixtures to pure water by assuming that k_{H_2O} and k_{az} had the same dependence on solvent composition as that observed by McClelland for reactions with benzhydryl and trityl cations. Thus, k_{az} was found to be independent of solvent composition between water and 50% acetonitrile but increased by a factor of 1.25 in 67% and 1.5 in 80% acetonitrile.[11] The value of log k_{H_2O} was found to increase linearly with the volume fraction of acetonitrile with slope 0.14 between 0 and nearly 80% acetonitrile.[17] Our own values of log k_{az}/k_{H_2O} were corrected for these variations in k_{az} and plotted against the fraction of acetonitrile. A value of $k_{az}/k_{H_2O} = 375$ was extrapolated by drawing a best straight line with slope 0.14 through the points.

To obtain the value of K_R for the anthracenyl cation, k_{H_2O} must be combined with k_H, the rate constant for carbocation formation. The measured rate constant for acid-catalyzed dehydration corresponds to $k_Hk_p/(k_{H_2O} + k_p)$ as may be seen from inspection of Scheme 4

. From $k_{H_2O}/k_p = 0.57$ we obtain $k_H = 1.57 \times 9.5 = 14.9$ M^{-1} s^{-1}. Combining this with $k_{H_2O} = 1.3 \times 10^7$ gives $K_R = 8.9 \times 10^5$ and $pK_R = -6.0$ for the anthracenyl cation.

Naphthalene Hydrates. Measurements of rate constants for dehydration of naphthalene hydrates from a previous study[19] were combined with trapping experiments reported by Pirinccioglu and Thibblin[2] to obtain pK_R values of the naphthalenonium ion protonated at the 1-position. Pirinccioglu and Thibblin studied trapping of the 2-naphthalenonium ion **13**, generated from 1,2-dihydro-2-methoxynaphthalene (**14**, X = OCH_3), by azide ion to form 1,2-dihydro-2-azidonaphthalene (**14**, X = N_3) in competition with deprotonation to naphthalene and nucleophilic reaction with water to form the 1,2-naphthalene hydrate, 1,2-dihydro-2-hydroxynaphthalene (**14,** X = OH). Measurements were reported for 75% aqueous acetonitrile in the presence of 0.3 M sodium azide and gave a ratio of 2-azido product to naphthalene of 1:5. In the absence of azide ion the ratio of naphthalene to 1,2-naphthalene hydrate was 1600:1.



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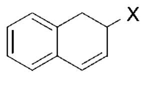

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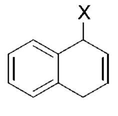
X = OCH_3, N_3, OH



15

X = N_3, OH

By assuming that azide trapping was diffusion-controlled, Pirinccioglu and Thibblin[2] derived $k_p = 1.6 \times 10^{10}$ s^{-1} and $k_{H_2O} = 1.0 \times 10^7$ s^{-1}. By combining k_{H_2O} and k_H for the acid-catalyzed reaction of the 2-hydrate, $pK_R = -7.8$ was obtained for the aqueous acetonitrile solvent.

We wished to obtain pK_R in H_2O and did so by using our own measurement of $k_H = 1.8$ M^{-1} s^{-1} in water[19] rather than the value for aqueous acetonitrile. Since McClelland found little change in values of k_{H_2O} between 75% aqueous acetonitrile and water,[11] this value of k_H was combined with Pirinccioglu and Thibblin's value of k_{H_2O} to give $K_R = 5.5 \times 10^6$ and $pK_R = -6.7$.

It should be noted that Toteva and Richard have argued that where a rate constant for reaction with solvent is as large as 1.6×10^{10} s^{-1}, it is difficult to exclude the possibility that a fraction of the azide reacts by a preassociation mechanism.[20,21] Ascribing all of the azide product formed to reaction of free carbocations ($k_d = 5 \times 10^9$ M^{-1} s^{-1}) then underestimates the rate constant for reaction with water and implies a more negative value of pK_R than is calculated (−6.7). However, as the limiting rate constant for solvent relaxation is probably 10^{11} s^{-1}, less than an order of magnitude larger than the derived value, the error introduced by the assumption of diffusion control is small.[21] Moreover, a correlation of log k_p with pK_a values for a range of carbocations suggests qualitatively that k_p might be closer to its (apparent) measured value than its upper limit.[22]

Aromatic Hydrogen Isotope Exchange. The carbocations derived from aromatic hydrates are conjugate acids of their parent aromatic molecules. This means that a rate constant for deprotonation of the carbocation (k_p) may be combined with a rate constant for protonation of the aromatic molecule (k_A) to obtain an acid dissociation constant of the protonated species as $K_a = k_p/k_A$.

Rate constants for protonation of aromatic molecules are available from measurements of hydrogen isotope exchange corrected for isotope effects. Normally measurements have been made in nonaqueous acidic media and must be extrapolated to water.[4−7] Thus, Cox[5] has extrapolated reported rate constants for deuterium or tritium exchange of a number of aromatic molecules, including benzene and naphthalene, in concentrated solutions of $HClO_4$ or H_2SO_4, by using the medium acidity function X[23,24] to correlate the dependence of the measured rate constants upon the acid concentration.[5] Although tritium and deuterium isotope effects have been fully evaluated in only a few cases, those that have provide a basis for estimating unmeasured isotope effects with a precision that is probably within that of the extrapolation. Thus, most values of k_H/k_D fall within a factor of 2 of each other and show a rather mild dependence on reactivity.[5]

In this way a rate constant for protonation at the 1-position of naphthalene in aqueous solution at 25 °C was obtained as 1.7×10^{-11} M^{-1} s^{-1}. If this is multiplied by a statistical factor of 4 to account for the number of equivalent positions, it may be combined with k_p from Pirinccioglu and Thibblin's data[2] to obtain $K_a = 2.3 \times 10^{20}$ ($pK_a = -20.4$).

The 2-naphthhalenonium ion is also the intermediate formed in the dehydration of the 1,4-hydrate of naphthalene (**15**, X = OH). Its pK_a therefore may be combined with $pK_{H_2O} = -16.9$ estimated in the previous paper as the equilibrium constant for conversion of naphthalene to its 1,4-hydrate, to obtain $pK_R = -3.5$ for this hydrate from the relationship $pK_R = pK_{H_2O} - pK_a$ (cf. benzene hydrate in Scheme 1).

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(25) A rate constant of 640 M^{-1} s^{-1} for the acid-catalyzed dehydration of the 1,4-naphthalene hydrate is considered more reliable than that previously reported (240 M^{-1} s^{-1}).[15]

Scheme 4

$$ArH^+ + H_2O \underset{k_H[H^+]}{\overset{k_{H2O}}{\rightleftharpoons}} ArHOH + H^+$$

$$K_R = \frac{[H^+][ArOH]}{[ArH^+]} \qquad pK_R = -\log K_R$$

For anthracene[6] and benzofuran,[4] measurements of tritium exchange have been reported by Taylor for CF_3COOH as solvent. For anthracene, $k_A = 3.27 \times 10^{-3}$ s^{-1} at 25 °C. This may be converted to a value in water by taking advantage of the fact that a rate constant for exchange of 1-tritionaphthalene has also been measured in CF_3COOH[7] and by assuming that the ratio of the two rate constants (for anthracene and naphthalene) is unaffected by the change in solvent. A basis for this approximation is the weak dependence of ratios of rate constants for substrates of not too different reactivity upon the composition of aqueous solutions of strong acids,[5] and the general presumption that partial rate factors are not sensitively dependent upon solvent.[26]

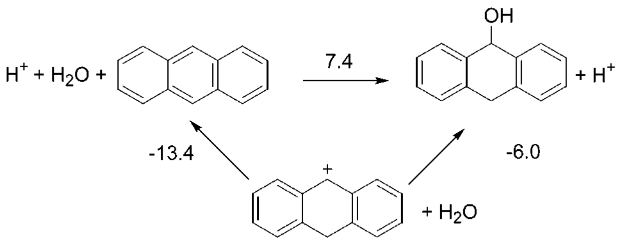
The rate constants for tritium exchange of naphthalene in CF_3COOH were measured at 70, 100.7, and 125 °C.[7] Extrapolation of these to 25 °C using an Arrhenius plot gives a rate constant 1.4×10^{-7} s^{-1}. From this value and the value in water we obtain $k_A = 3.27 \times 10^{-3} \times 1.7 \times 10^{-11}/(1.4 \times 10^{-7}) = 4.0 \times 10^{-7}$ M^{-1} s^{-1} for the protonation of anthracene by H_3O^+ in aqueous solution at 25 °C, if we make no correction for a difference in isotope effects for detritiation of anthracene and naphthalene (vide supra). Multiplying this rate constant by a statistical factor of 2 to allow for the two equivalent positions of protonation and combining with $k_p = 2.3 \times 10^7$ s^{-1} gives $K_a = 2.9 \times 10^{13}$ (p$K_a = -13.5$) for anthracene.

For benzofuran Katritzky and Taylor[4] have reported a partial rate factor for the 2-tritiated compound in CF_3COOH at 70 °C as 1.7×10^4. Following Baker et al., this may be corrected to 2.0×10^4 to allow for the unfavorable effect of hydrogen bonding by CF_3COOH upon exchange of oxygen or sulfur substituted substrates.[26] This partial rate factor may be combined with a value for 1-tritionaphthalene at 70 °C (1160) to give a ratio of rate constants for the two substrates which may be extrapolated to 25 °C by assuming that the difference in rates stems from a difference in activation energies only. Finally, this ratio may be combined with Cox's rate constant for 1-protonation of naphthalene in aqueous solution to give $k_A = 3.0 \times 10^{-10}$ for protonation at the 2-position of benzofuran. With $k_p = 6.5 \times 10^6$ M^{-1} s^{-1}, this gives $K_a = 2.2 \times 10^{16}$ (p$K_a = -16.3$).

Discussion

Equilibrium constants K_R measuring stabilities of carbocations derived from ionization of anthracene and benzofuran hydrates in aqueous solution at 25 °C have been measured. Rate constants k_H for the acid-catalyzed conversion of the hydrate (ArHOH) to the carbocation (ArH^+) are combined with rate constants k_{H_2O} for the reverse reaction of the cation with water measured by the azide clock method (Scheme 4). For the two carbocations, values of p$K_R = -9.4$ and -6.0 are obtained. For anthracene a pK_a can also be found by combining pK_R with an equilibrium constant pK_{H_2O} for hydration of the aromatic molecule, by taking advantage of the thermodynamic cycle illustrated for benzene hydrate and the benzenonium cation in Scheme 1. Evaluation of p$K_{H_2O} = 7.4$ for anthracene is described in the previous paper.[1] Combining this value with p$K_R = -6.0$ gives p$K_a = -13.4$. The cycle and relationship connecting these equilibrium constants are shown in Scheme 5 and eq 3.

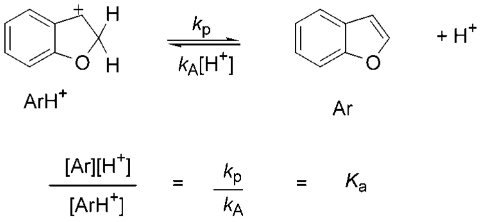
Scheme 5



$$pK_a = pK_R - pK_{H_2O} \qquad (3)$$

For benzofuran a value of pK_{H_2O} is not available. However, K_a may be obtained directly by combining a rate constant $k_p = 1.9 \times 10^7$ s^{-1} for deprotonation of the 2-protonated benzofuran **4** with a rate constant k_A for protonation of benzofuran at the 2-position, as shown in Scheme 6.

Scheme 6



In practice a rate constant for protonation of benzofuran in aqueous solution at 25 °C must be extrapolated from the measurement of a partial rate factor for isotope exchange of 2-tritiobenzofuran in trifluoroacetic acid solvent at 70 °C by Taylor.[4] The necessary corrections for an isotope effect and the changes in solvent and temperature have been described above. They yield a rate constant from which p$K_a = -16.3$ is obtained. If this pK_a is combined with p$K_R = -9.4$, we derive p$K_{H_2O} = 6.9$ by use of eq 3.

It is noteworthy that this value of pK_{H_2O} is less than p$K_{H_2O} = +7.4$ for anthracene.[1] This might suggest that the aromatic stabilization of the heterocyclic ring of benzofuran is somewhat smaller than that of the central ring of anthracene. However, the relative heats of hydrogenation of benzofuran and anthracene indicate that the benzofuran ring is the more stable by 2.6 kcal mol^{-1}.[27] It is possible that this discrepancy reflects the relative stabilities of the anthracene and benzofuran hydrates, and in particular destabilization of the benzofuran hydrate by an unfavorable repulsion between the endo- and exocyclic electronegative oxygen atoms.

For anthracene a pK_a can be estimated in the same way as for benzofuran based on measurement of a rate constant for exchange of 9-tritioanthracene in CF_3COOH at 25 °C.[6] This

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(26) Baker, R.; Eaborn, C.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1972**, 97. Taylor, R. *Electrophilic Aromatic Substitution*; Wiley: Chichester, U.K., 1990.

(27) Afeefy, H. Y.; Liebmann, J. F.; Stein, S. E. In *Natural Thermochemical Data in NIST Chemistry Webbook*, July 2001; Linstrom, P. J., Mallard, W. G., Eds.; NIST Standard Reference Base No. 69; National Institute of Standards and Technology: Gaithersburg, MD (http://webbook.nist.gov).

yields $pK_a = -13.5$ which agrees well with the value of -13.4 inferred from eq 3 and based on $pK_{H_2O} = 7.4$ from the previous paper.[1]

The level of agreement between measured and calculated values of pK_{H_2O} for anthracene implied by this comparison must be partly fortuitous. However, it suggests that the discrepancy between the differences in heats of hydrogenation and equilibrium constants for hydration of anthrancene and benzofuran probably does not arise from errors in the extrapolated rate constants for hydrogen isotope exchange.

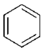
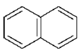
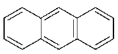
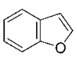
Naphthalene and Benzene. It is noteworthy that the conjugate acids of benzofuran and anthracene react in water at comparable rates by deprotonation to form the aromatic molecule and nucleophilic trapping to form the aromatic hydrates. This allows both pK_a and pK_R to be evaluated directly. For molecules with a greater aromatic stabilization, such as naphthalene or benzene, the deprotonation pathway normally dominates and the substitution reaction is not easily observed.[15] Nevertheless, Pirinccioglu and Thibblin have recently reported detectable nucleophilic trapping in competition with more rapid deprotonation for the 2-naphthalenonium ion **13**.[2] From a study of trapping by azide ion they obtained a value of $pK_R = -7.8$ in 75% aqueous acetonitrile. As described above, this value may be extrapolated to $pK_R = -6.7$ for a fully aqueous medium.

Pirinccioglu and Thibblin also deduced a rate constant for deprotonation of the 2-naphthalenonium ion as 1.6×10^{10} s^{-1}. If this is combined with $k_A = 6.9 \times 10^{-11}$ M^{-1} s^{-1} for the protonation of naphthalene,[5] a value of $pK_a = -20.4$ is obtained. From eq 3 this implies that $pK_{H_2O} = -13.7$, which is in satisfactory agreement with -14.2 from the preceding paper. The same pK_a may also be combined with $pK_{H_2O} = -16.9$ from the previous paper to obtain $pK_R = -3.5$ for formation of the 1,4-hydrate.

For benzene hydrate, derivations of pK_a and pK_R are more speculative. The data available are rate constants for carbocation formation from the 1,2-hydrate and for hydrogen isotope exchange of benzene extrapolated from strongly acidic media by Cox.[5] In addition, the equilibrium constant for hydration has been estimated in the preceding paper. To complete a thermodynamic cycle, one more rate constant is needed: for reaction of the benzenonium with water as either base or nucleophile.

It seems certain that we can make a good estimate of the rate constant for deprotonation of the benzenonium ion. The value from Pirinccioglu and Thibblin's study of the corresponding naphthalenonium ion cation (1.6×10^{10} s^{-1}) is close to that expected for rate limiting relaxation of the aqueous solvent, which provides a limiting value for deprotonation and which it seems likely the benzenonium ion will approach. For this limit, Richard et al. have suggested 10^{11} s^{-1} for nucleophilic attack by water, which is close to the rate constant for proton transfer between H_3O^+ and a water molecule.[20,21] Warkentin has recently measured a rate constant 2×10^{10} s^{-1} for reaction of an isopropyl cation to form 2-propanol in aqueous acetonitrile containing 10% (by volume) of water,[28] which implies a rate constant near this limit, especially if, as suggested, the value is partly influenced by the rate of loss of nitrogen from the diazonium ion precursor from which it is generated.

Table 1. Rate and Equilibrium Constants for Protonation and Hydration of Aromatic Molecules

Aromatic	Hydrate	pK_{H20}[a]	pK_R	pK_a	k_A[b] M^{-1}s^{-1}	k_p s^{-1}
	1,2	22.2	-2.1	-24.3	2.6×10^{-14}	(5×10^{10})[c]
	1,4	22.2	-2.1	-24.3		
	2,1	13.7[d]	-6.7	-20.4	6.9×10^{-11}	1.6×10^{10}
	1,4	16.9	-3.5	-20.4		
	9,10	7.5[e]	-6.0	-13.5	5.7×10^{-7}	9×10^{6}
	1,2	6.9[f]	-9.4	-16.3	6.4×10^{-9}	1.9×10^{7}

[a] From proceeding paper[1] unless indicated otherwise: the values of pK_{H_2O} for the 1,2- and 1,4-hydration of benzene are coincidentally equal. [b] Measurements taken or interpolated from refs 4, 5, and 26. [c] Estimated as described in text. [d] From difference in pK_a and pK_R, the calculated value is -14.2.[1] [e] From difference of pK_a and pK_R; the calculated value is 7.4.[1] [f] From the difference of pK_a and pK_R.

We have chosen a rate constant of 5×10^{10} s^{-1} for deprotonation of the benzenonium ion by recognizing that the thermodynamic driving force for this reaction must be greater than that for the 2-naphthalenonium ion but that the difference will not be large. This means that the constant should be between 1.6×10^{10} and 10^{11} s^{-1} and that the uncertainty in the chosen value should not be greater than a factor of 2 if that for the naphthalenonium ion is correct. Combining 5×10^{10} s^{-1} with the rate constant for protonation of benzene (2.6×10^{-14} M^{-1} s^{-1})[5] gives $K_a = 1.9 \times 10^{24}$ and $pK_a = -24.3$. This compares with $pK_a = -23$ estimated by Kresge from extrapolation of a correlation of pK_as and rate constants for aromatic hydrogen isotope exchange[29] and $pK_a = -25$ extrapolated from a similar correlation by Marziano et al.[30] The latter value is corroborated by further correlations between the aqueous pK_as and pK_as in HF or proton affinities of aromatic molecules in the gas phase.[30] Combining the $pK_a = -24.3$ with values of $pK_{H_2O} = 22.2$ from the preceding paper allows $pK_R = -2.1$ to be inferred for reaction of the benzenonium ion to form both the 1,2- and 1,4-benzene hydrates.

Values of pK_a, pK_R, and pK_{H_2O} for the molecules considered so far are summarized in Table 1. Values of pK_{H_2O} have been discussed in the preceding paper and show the expected dependence on the resonance stabilization of the parent aromatic molecule. For benzene, $pK_R = -2.1$ may be compared with the much more negative values of -16.4 for the *tert*-butyl,[20] -16.2 for the α-methyl benzyl,[13,31] and -9.6 for the benzofuranyl carbocations. From these comparisons it is clear that the highly unfavorable pK_as for protonation of benzene or naphthalene reflect the thermodynamic stability of the aromatic molecule rather than intrinsic instability of their conjugate acids (see also below).

Vinyl Cation. Lucchini and Modena have measured rate constants for acid-catalyzed hydrolysis of acetylene in aqueous sulfuric acid using NMR to monitor the reaction.[32] On the basis of measurements of an isotope effect $k_{H_2SO_4}/k_{D_2SO_4} = 2.2-2.5$ and an analysis of solvent and substituent effects, they concluded

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(28) Pezacki, J. P.; Shukla, D.; Lusztyk, J.; Warkentin, J. *J. Am. Chem. Soc.* **1999**, *121*, 6589.

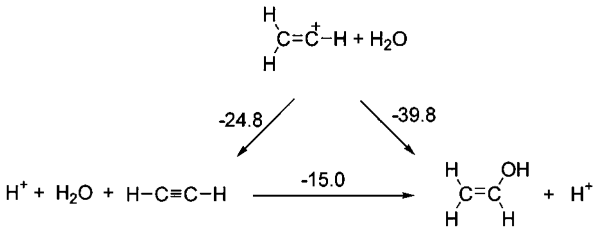
(29) Kresge, A. J.; Mylonakis, S. G.; Sato, Y.; Vitullo, V. P. *J. Am. Chem. Soc.* **1992**, *114*, 8032.

(30) Marziano, N. C.; Tortato, C.; Bertani, R. *J. Chem. Soc., Perkin Trans. 2* **1992**, 955.

(31) A value of pK_R in H_2O is estimated as one log unit less than the measurement in 50:50 (v/v) water–trifluorethanol in ref 13.

(32) Lucchini, V.; Modena, G. *J. Am. Chem. Soc.* **1990**, *112*, 6291.

Scheme 7



that the reaction occurs with rate-determining protonation of the acetylene to form a vinyl cation intermediate. Coincidentally the rate constant extrapolated to water is similar to that for the protonation of benzene. This suggests that a pK_a for the vinyl cation may be derived by assigning a rate constant near the limit for solvent relaxation to the reverse reaction. If this rate constant is taken to be the same as that for the benzenonium ion (5×10^{10} s^{-1}), then a similar value of p$K_a = -24.8$ is obtained. Despite its large magnitude this rate constant is not inconsistent with the measurement of a hydrogen isotope effect and proton transfer being rate-determining. This is partly because nucleophilic attack of water on the vinyl cation may occur *at* the relaxation limit for the solvent, which has the larger value of $\sim 10^{11}$ s^{-1}, and partly because the effective basicity of the water molecule will be reduced in the strong acid media of the isotope measurement and the difference in rates between deprotonation and nucleophilic attack by water may be enhanced.

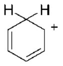
The pK_a for the vinyl cation may be converted into pK_R by using a thermodynamic cycle similar to that of Schemes 1 and 5 and combining pK_a with pK_{H_2O}, the equilibrium constant for hydration of acetylene. As shown in Scheme 7, the hydrate of acetylene is the enol of acetaldehyde. A value of p$K_{H_2O} = -15.0$ was estimated for this reaction in the previous paper. We thus obtain p$K_R = -39.8$ for the vinyl cation.

Remarkably, although the vinyl cation and benzenonium ion have practically the same acidities, their K_R values differ by 37 orders of magnitude. Thus, the similar acidities do not imply similar thermodynamic stabilities but that a large difference in stabilities of the cations is offset by a corresponding difference in the acetylenic and aromatic π-bonds subject to protonation.[32]

Recently Okuyama has argued that a vinyl cation is not involved as a discrete intermediate in nucleophilic substitution at a primary vinyl carbon atom, even when this bears a "super-leaving group" such as the phenyliodonium ion.[33] This is consistent with the extreme energetic inaccessibility of the vinyl cation from a functionalized vinyl alcohol, as implied by p$K_R = -39.8$. On the other hand, the instability of the double bond of acetylene favors access to the carbocation from this precursor.

Alkyl Cations. In addition to acetylene Lucchini and Modena studied the acid-catalyzed hydration of ethylene, butene, and methylacetylene.[32] For ethylene Tidwell et al. have summarized arguments that this reaction proceeds with rate-determining formation of an ethyl cation.[34] The rate constant is again nearly the same as for benzene and acetylene, and a similar value of p$K_a = -24.8$ may be derived by the method already described. Combination with p$K_{H_2O} = -4.8$ for the hydration of ethylene to ethyl alcohol yields p$K_R = -29.6$, a value intermediate between that of the vinyl and benzenonium carbocations.

Table 2. Rate and Equilibrium Constants for Protonation and Hydration of Carbon−Carbon Double and Triple Bonds[a]

Congugate acid	k_A[b] $M^{-1}s^{-1}$	k_p[c] s^{-1}	pK_a	pK_{H_2O}	pK_R
	2.6×10^{-14}	5×10^{10}	-24.3	22.2	-2.1
$H_2C{=}CH^{\cdot}$	8.5×10^{-15}	5×10^{10}	-24.8	-15.0	-39.8
$H_2C{=}C^{-}$- CH_3	4.5×10^{-10}	1×10^{10}	-19.3	-13.4	-32.7
$CH_3CH_2^{+}$	8.5×10^{-15}	5×10^{10}	-24.8	-4.8	-29.6
$(CH_3)_2CH^{-}$	2.4×10^{-9}	7×10^{9}	-18.5	-4.23	-22.7
$(CH_3)_3C^{-}$	3.1×10^{-4}	8×10^{8d}	-12.5	-3.9	-16.4

[a] The benzenonium ion is included for comparison. [b] Measurements from the literature; see text for references. [c] Measured experimentally only in the case of the *tert*-butyl cation.[20,41] [d] Includes a statistical factor of 9: $\sim 10^8$ per H atom would be appropriate therefore.

For propene and methylacetylene rate constants for hydration are considerably greater than for ethylene, acetylene, or benzene and closer in value to that for 2-protonation of naphthalene, i.e., $\sim 10^{-9}$ M^{-1} s^{-1}.[32] Approximate pK_as were evaluated therefore by combining these rate constants with reverse rate constants based on short extrapolations from the value for naphthalene using a correlation[22] of log k_p and pK_a for other carbocations[21] and protonated aromatic molecules.[35] The derived pK_a values, estimated values for pK_{H_2O} and resultant values of pK_R are collected in Table 2 together with values for the *tert*-butyl cation based on Richard's assignment of p$K_R = -16.4$ [20] and for the benzenonium, vinyl, and ethyl cations discussed above. Although the correlation of log k_p with pK_A is subject to significant deviations between subgroups of carbocation structures, it offers some support for the minor corrections of limiting rate constants on which the pK_as for the isopropyl and methylvinyl cations are based.

Inspection of Table 2 shows a parallel and chemically reasonable influence of methyl substituents upon the stability of vinyl and ethyl cations. This offers further support for the inference of Lucchini and Modena that like their homologues acetylene and ethylene do indeed undergo hydration with the formation of discrete carbocation intermediates. Lucchini and Modena presented a similar argument based on a correlation of rate constants for hydration of double and triple carbon−carbon bonds. The results in Table 2 not only convert the correlation of kinetic measurements to equilibria but allow comparison of pK_R as well as pK_a values. The pK_R values reflect explicitly the difference in stability of alkyl and vinyl cations and support the interpretation provided by Modena et al. of the surprising similarity in reactivity of alkenes and alkynes,[36] i.e., that this is a consequence of compensating differences in stability between the carbocations and carbon−carbon π-bonds in the reactants.

In conclusion, two further points deserve comment. The first is the derivation of rate constants for carbocation formation in water based on measurements in concentrated solutions of strong acids. This does not imply that in practice the mechanism or reaction in water is the same as in the more concentrated acid solutions, but that the extrapolated rate constant refers to the

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(33) Fujita, M.; Sakanishi, Y.; Okuyama, T. *J. Am. Chem. Soc.* **2000**, *122*, 8787.

(34) Nowlan, V. J.; Tidwell, T. T. *Acc. Chem. Res.* **1977**, *10*, 252. Chwang, W. J.; Nowlan, V. J.; Tidwell, T. T. *J. Am. Chem. Soc.* **1977**, *99*, 7233.

(35) Kresge, A. J.; Mylonakis, S. G.; Sato, Y.; Vitullo, V. P. *J. Am. Chem. Soc.* **1971**, *93*, 6181. Kresge, A. J.; Chen, H. J.; Hakka, L. E.; Kouba, J. E. *J. Am. Chem. Soc.* **1971**, *93*, 6174.

(36) Modena, G.; Rivetti, F.; Scorrano, G.; Tonellato, U. *J. Am. Chem. Soc.* **1977**, *99*, 3392.

process occurring in the acidic media. An alternative mechanism would have a larger rate constant.

Also noteworthy is that the extrapolated rate constants yield values of pK_a and not pK_R. In principle pK_R for the ethyl cation, for example, might have been derived by combining a rate constant for acid-catalyzed oxygen exchange of ^{18}O-labeled ethanol with a rate constant for nucleophilic reaction of the carbocation with water corresponding to the limit for solvent relaxation (10^{11} s^{-1}). In practice the exchange reaction would be expected to proceed by a concerted S_N2 mechanism.

By contrast reactions involving protonation of π-bonds presumably proceed by a "stepwise" mechanism because, despite the high energy of the reactive intermediate, the alternative concerted reaction is less favorable. For electrophilic aromatic substitution indeed it is doubtful if a concerted mechanism exists at all. Even for addition reactions, such as the hydration of ethylene, according to Dewar concerted mechanisms are less favorable than for (S_N2) nucleophilic substitution because they require coupling of bond-making and bond-breaking over four bonds rather than two.[37]

Experimental Section

The preparation of the 2,3-hydrate of benzofuran and its chloroacetyl derivative 3-chloroacetoxy-2,3-dihydrobenzofuran have been described.[3] The 9,10-hydrate of anthracene[38,393] and its acetoxy derivative[18] have also been reported. However, improved preparations are given below.

9-Hydroxy-9,10-dihydroanthracene. Anthraquinone (2 g, 9.6 mmol) and zinc dust (4 g, activated with 5% hydrochloric acid) were dissolved in aqueous ammonia (12 mL) and deionized water (8 mL) to give a red solution which was heated at 60−70 °C for 3.5 h to give a yellow-grey precipitate. This precipitate was filtered from the hot solution and washed with two 10 mL portions of hot CH_2C1_2. The filtrate was then cooled and separated and the aqueous layer extracted with 2 × 10 mL of CH_2C1_2. The CH_2C1_2 extracts were combined and dried with Na_2SO_4. The solvent was evaporated to give a yellowish solid which was recrystallized from 40 to 60 petroleum spirits to give white needles (1.7 g, 87%): ^1H NMR ($CDC1_3$) δ 2.17 (d, 1H), 2.95 (d, 1H), 4.15 (d, 1H), 5.64 (d, 1H), 7.3−7.5 (m, 6H), 7.7 (br s, 2H).

9-Acetoxy-9,10-dihydroanthracene. 9-Hydroxy-9,10-dihydroanthracene (1.6 g, 8 mmol) was dissolved under nitrogen in a minimum volume of dry pyridine. Acetic anhydride (0.98 g, 9.6 mmol) in dry pyridine (1 mL) was added dropwise using a syringe. The solution was left stirring under nitrogen overnight, and 20 mL of $CC1_4$ was added. It was dried with Na_2SO_4 and evaporated to give a white solid that was recrystallized from 40 to 60 petroleum spirits to give a white/yellow solid (0.84 g, 53%) which was stored in a freezer: ^1H NMR ($CDC1_3$) δ 2.00 (s, 2H), 3.92 (d, 1H), 4.26 (d, 1H), 6.96 (s, 1H), 7.25−7.37 (m,6H), 7.53 (m,2H).

NMR spectra of the products were recorded on a JEOL JNMGX270 instrument operating at 270 MHz for proton NMR and 68 MHz for ^{13}C NMR. HPLC analyses were carried out using a Waters 600E system with a Waters 486 tunable UV detector and reverse-phase 10 μm octadecylsilane column in a radial compression unit. Peak areas were integrated using Millenium 2000 software and a 286 PC. Kinetic measurements made use of a Phillips PU 8600 single beam UV−vis spectrophotmeter or a Hitachi-124 double beam instrument. Water for kinetic measurements was doubly distilled, and other reagents and solvents were normally AR or HPLC grades.

For kinetic and product analyses based on UV−vis measurements stock solutions of 10^{-2}−10^{-4} M in (ester) substrate were freshly prepared in methanol or acetonitrile solvents and 20 μL injected into a cuvette containing 2 mL of aqueous or mixed aqueous solvent with or without added sodium azide. The change in absorbance accompanying or at completion of the reaction was monitored.

3-Chloroacetoxy-2,3-dihydrobenzofuran. For product analyses from aqueous solvolysis of 3-dichloroacetoxy-2,3-dihydrobenzofuran, 6 μL of a 0.055 M stock solution in acetonitrile were injected into 1 mL of water or solution of sodium azide to give a final concentration of 3.3×10^{-4} M. Aliquots of 25 μL were injected from the product mixture to the HPLC column. Separation of components was achieved by isocratic elution of aqueous solvent mixtures with 50−65% methanol (v/v) and a flow rate of 1 mL/min. The analytical wavelength was maintained at 600 nm for 4 min (to avoid overloading of the UV detector during elution of azide ion) and at 220 nm for the remaining elution time. The following ratios of peak areas for products 3-azido- and 3-hydroxy-2,3-dihyrobenzofuran ($[RN_3]/[ROH]$) were observed for the indicated concentrations of sodium azide for reactions conducted at 20 ± 0.2 °C and ionic strength $\mu = 0.05$ ($NaClO_4$): 0.28, 1.0 mM; 0.55, 2.0 mM; 1.5, 5.0 mM; 2.7, 8.0 mM.

For the product analysis by spectrophotometry limiting absorbances at 243 nm were measured for the reaction solution (a) before solvolysis (or from complete conversion of the ester to alcohol by the addition of sodium hydroxide), A_{init}; (b) after solvolysis in water, A_o; and (c) after solvolysis in the presence of sufficient acid to convert the benzofuran hydrate product to benzofuran, A_{max}. The absorption at 243 nm arises mainly from the benzofuran. The ratio of benzofuran to hydrate in the solvolysis products is given by $(A_o - A_{init})/(A_{max} - A_o)$. The ratio is unaffected by partial conversion of the reactant solutions to benzofuran.

Addition of sodium azide to the reactant solution led to a reduction in the limiting absorbance A_o to A_{lim}. Reactions were carried out for concentrations of sodium azide in the range 0−0.01 M at 0.1 M ionic strength. At higher concentrations, the absorbance of the azide ion swamped that of the benzofuran and the amount of benzofuran formed in the product was small. Assuming that the drop in absorbance in the presence of N_3^- is due to formation of azide trapped product, the ratio of rate constants for trapping of the benzofuranyl carbocation intermediate by azide ion (k_{az}) to those for elimination to benzofuran (k_p) and nucleophilic trapping by water (k_{H_2O}) is given by eq 2, in which $\Delta A = A_{lim}$ - A_{init} and ΔA_o is the limiting absorbance in the absence of azide ion (A_o) corrected for A_{init}. For a substrate concentration 1.65×10^{-4} M and $A_{init} = 0.264$, the following limiting absorbances were obtained at the indicated concentrations of NaN_3: 0.0 M, 0.738; 0.001 M, 0.66; 0.003 M 0.565; 0.005 M, 0.503; 0.007 M, 0.445; 0.009 M, 0.360. The value of A_{max} for complete conversion to benzofuran by H^+ in the absence of azide ion was 1.53. The ratio of slope to intercept of a plot $1/\Delta A$ ($\Delta A = A_{lim} - A_{init}$) versus $[N_3^-]$ (disregarding a 10% deviation of A_{lim} from the correlation at 0.009 M) gave $k_{az}/(k_{H_2O} + k_p) = 135$. The ionic strength was 0.01 M (NaCl).

9-Hydroxy-9,10-dihydroanthracene (kinetics). Kinetic measurements of the acid-catalyzed dehydration of this substrate to anthracene were based on measurements of the increase in absobance at 251 nm. The low solubility of the product necessitated use of very dilute solutions, $<10^{-6}$ M, leading to absorbance changes of ∼0.2 accompanying reaction. The following first-order rate constants (10^2k, s^{-1}) were measured in aqueous solution at 25 °C at the indicated concentrations of $HClO_4$: 0.0008 M, 1.34; 0.00116 M, 2.24; 0.00252 M, 2.68; 0.00363 M, 3.56; 0.00503 M, 5.22; 0.00725 M, 7.43.

Measurements at ionic strengths 0.1 and 0.5 M (NaCl) showed a 2-fold increase in rate constant at the higher ionic strength, which was confirmed by systematic measurements in this range summarized in Table S1. The dependence of the rate constant for the acid-catalyzed reaction upon sodium chloride concentration was given by $1.32(1 + a[Cl^-])$ M^{-1} s^{-1}, where $a = 1.25$ M^{-1} and the concentration of $HClO_4$ was 0.002 43 M. Suprisingly no increase in rate with buffer concentration was observed in acetic acid buffers if the buffer ratio was kept constant despite the fact that in the absence of buffer deprotonation of the protonated anthracene is partially rate determining. Apparently the

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Bronsted exponent for the reaction is quite small or water is a more efficient base than expected from its equilibrium basicity. These results are shown in Table S4. Absence of catalysis of deprotonation by acetate is confirmed below.

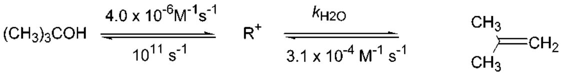
9-Acetoxy-9,10-dihydroanthracene (kinetics). The solvolysis of this substrate was studied in acetonitrile−water mixtures as its low solubility precluded measurements in pure water. Rate constants for solvolysis decrease with increasing fraction of CH_3CN as indicated by the following first-order rate constants (10^3k, s^{-1}) measured at 25 °C by monitoring the increase in absorbance of the anthracene product at 251 nm at the indicated volume percentages of acetonitrile: 142, 20%; 39.2, 30%; 10.7 40%; 3.37, 50%; 1.61, 60%; 0.60, 70%; 0.177, 80%.

Measurements of the ratio of hydrate to anthracene were based on measurements of an initial absorbance, the absorbances on completion of the solvolysis reaction, and the absorbance following addition of acid to convert the hydrate formed to anthracene. The following absorbances (in the order indicated above) were measured at 25 °C at the volume percentages of CH_3CN indicated: 0.269, 0.653, 0.87, 33%; 0.358, 0.89, 1.144, 50%; 0.269, 0.637, 0.861, 67%; 0.358, 0.767, 1.062, 80%. These yield values of $k_p/k_{H_2O} = 0.565$, (0.48), 0.61, and 0.59, respectively. The value of 0.48 for 50% acetonitrile was disregarded. Six further measurements in dilute acetic acid buffers at 25 °C in 33% acetonitrile gave $k_p/k_{H_2O} = 0.55$.

Measurements of trapping by azide ion were also carried out in acetonitrile−water mixtures in the same way as for the dihydrobenzofuranyl acetate. The measured absorbances are reported in Table S2 of the Supporting Information for aqueous acetonitrile solutions with 20, 33, 50, and 67% acetonitrile, and plots of $1/\Delta A$ ($\Delta A = A_{\mathrm{lim}} - A_{\mathrm{init}}$) versus $[N_3^-]$ for 20 and 50% acetonitrile are shown in Figure 1. Similar measurements were carried out with sodium acetate and showed that acetate ion did not appreciably increase the proportion of anthracene in the product up to a concentration of 0.5 M. These results are reported in Table S3 and are consistent with the kinetic measurements for dehydration of the anthracene hydrate in acetic acid buffers mentioned above. Both of these results indicate no contribution or a very minor contribution from deprotonation of the anthracenonium ion by acetate ion.

Equilibrium Constants for Dehydration. The equilibrium constant for dehydration of the enol of acetone to form methylacetylene given in Table 2 was based on free energies of formation in aqueous solution taken from compilations by Guthrie: $\Delta G^o{}_f(\mathrm{aq}) = -27.02$ kcal mol^{-1} ($CH_2{=}C(OH)CH_3$)[40] and 47.93 kcal mol^{-1} ($CH_3C{\equiv}CH$).[41] For liquid water $\Delta G^\circ{}_f(\mathrm{aq})$ was taken as -56.69 kcal mol^{-1}.

In the hydration of isobutene a rate constant for deprotonation of the *tert*-butyl cation (k_p) was evaluated by combining the equilibrium constant for hydration,[1,42] $K_{H_2O} = 9.9 \times 10^3$, with rate constants for H^+-catalyzed ^{18}O exchange of *tert*-butyl alcohol, hydration (protonation) of isobutene, and a value of $k_{H_2O} = 10^{11}$ s^{-1} proposed by Toteva and Richard[20] for nucleophilic reaction of the carbocation with water. These values are summarized in eqs 4 and 5 and yield $k_{H_2O} = 8 \times 10^8$ s^{-1}, a value which is preferred to that derived by Richard et al. (3×10^9 s^{-1})[21] based on different experimental data.[42]



(4)

$$k_{H2O} = \frac{10^{11} \times 3.1 \times 10^{-4}}{9.9 \times 10^{3} \times 4.0 \times 10^{-6}} = 8 \times 10^{8}\ \mathrm{s}^{-1} \qquad (5)$$

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Supporting Information Available: Tables S1−S4 listing kinetic data and limiting absorbances for the dehydration of 9-hydroxy-9,10-dihydroanthracene and solvolysis of its acetoxy derivative. This material is available free of charge via the Internet at http://pubs.acs.org.

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