

Stabilities and Partitioning of Arenonium Ions in Aqueous Media

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Abstract: The phenanthrenonium ion is formed as a reactive intermediate in the solvolysis of 9-dichloroacetoxy-9,10-dihydrophenanthrene in aqueous acetonitrile and undergoes competing reactions with water acting as a base and nucleophile. Measurements of product ratios in the presence of azide ion as a trap and 'clock' yield rate constants $k_p = 3.7 \times 10^{10}$ and $k_{H_2O} = 1.5 \times 10^8 \text{ s}^{-1}$, respectively. Combining these with rate constants for the reverse reactions (protonation of phenanthrene and acid-catalyzed aromatization of its water adduct) gives equilibrium constants $pK_a = -20.9$ and $pK_R = -11.6$. For a series of arenonium and benzylic cations, correlation of $\log k_p$ with pK_a , taking account of the limit to k_p set by the relaxation of water (10^{11} s^{-1}), leads to extrapolation of $k_p = 9.0 \times 10^{10} \text{ s}^{-1}$ and $pK_a = -24.5$ for the benzenonium ion and $k_p = 6.5 \times 10^{10} \text{ s}^{-1}$ and $pK_a = -22.5$ for the 1-naphthalenonium ion. Combining these pK_a 's with estimates of equilibrium constants pK_{H_2O} for the hydration of benzene and naphthalene, and the relationship $pK_R = pK_a + pK_{H_2O}$ based on Hess's law, gives $pK_R = -2.3$ and -8.0 respectively, and highlights the inherent stability of the benzenonium ion. A correlation exists between the partitioning ratio, k_p/k_{H_2O} , for carbocations reacting in water and K_{H_2O} the equilibrium constant between the respective reaction products, i.e., $\log(k_p/k_{H_2O}) = 0.46pK_{H_2O} - 3.7$. It implies that k_p exceeds k_{H_2O} only when $K_{H_2O} > 10^8$. This is consistent with the proton transfer (a) possessing a lower intrinsic reactivity than reaction of the carbocation with water as a nucleophile and (b) being rate-determining in the hydration of alkenes (and dehydration of alcohols) except when the double bond of the alkene is unusually stabilized, as in the case of aromatic molecules.

Introduction

Carbocations¹ have been prominent in efforts over the past 20 years to establish the stabilities of high-energy intermediates of organic reactions in aqueous solution.² Equilibrium constants for hydrolysis (pK_R) or acid dissociation (pK_a) have been measured by combining rate constants for formation of the carbocations with the less easily accessible values for their reverse reactions, usually with solvent.^{3–11} The latter have been determined by two principal methods: (i) generating the

carbocation stoichiometrically by flash photolysis and monitoring its further reaction³ and (ii) measurement of product ratios from trapping of the carbocation by solvent in competition with a diffusion controlled reaction with azide ion, the so-called azide clock method.^{7,8}

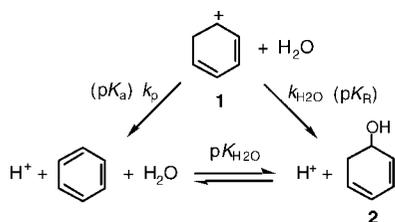
There is a third method applied by Richard to strongly basic carbanions,^{4,12} and also to the *t*-butyl carbocation.⁹ That is to measure the rate of formation of the carbocation under conditions for which its back reaction has reached the limit set by relaxation of the aqueous solvent molecules, namely, 10^{11} s^{-1} . This is applicable to highly unstable carbocations or to carbocations reacting to form unusually stable products. In this paper we report measurements for protonated aromatic molecules (arenonium ions), for which stabilization of the product from loss of a proton is so great that the relaxation limit is achieved even for relatively stable carbocations.

There have been a number of previous studies of arenonium ion equilibria. Values of pK_a and pK_R have been reported for 1-protonated naphthalene,¹⁰ 9-protonated anthracene and 3-protonated benzofuran,¹¹ pK_a 's have also been measured for protonation of relatively stable substituted benzenes^{13–15} and

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Scheme 1



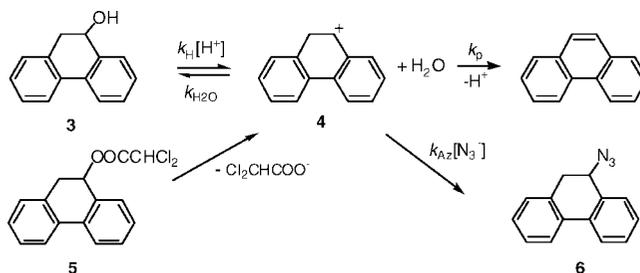
azulenes.¹⁶ Here, we describe application of the azide clock to measurements of pK_R and pK_a for 9-protonated phenanthrene and extrapolate tight limits (± 0.5 log units) for pK_a 's of protonated benzene and 2-protonated naphthalene.

In contrast to other carbocations, in water, arenonium ions, such as benzenonium or naphthalenonium, undergo loss of a proton rather than nucleophilic attack by solvent. This can be attributed to aromatic stabilization of the carbon–carbon double bond of the deprotonated product.^{5,17,18} However, in the case of phenanthrene, this stabilization is reduced and products from both reaction paths can be detected. As a result, trapping by azide ions yields rate constants for both reactions, and thence equilibrium constants pK_R and pK_a . The difference $pK_R - pK_a$ then gives the further constant pK_{H_2O} for hydration of the relevant carbon–carbon double bond based on the thermodynamic cycle illustrated for the benzenonium ion **1** in Scheme 1 (taking the single arrows to denote equilibria).

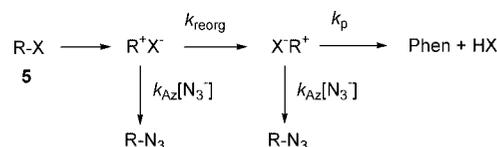
Cycles similar to Scheme 1 provide useful summaries of carbocation equilibria in aqueous solution.^{5,11} Where pK_R cannot be determined directly, as in the case of protonated benzene or naphthalene, pK_{H_2O} can be evaluated from the difference in free energies of formation of the aromatic molecule and hydrated product,¹⁹ and pK_R is obtained as $pK_a + pK_{H_2O}$.¹¹ The value of pK_R is important because the pK_a of arenonium ions strongly reflects the stability of the carbon–carbon double bond formed by loss of the proton. Measurements of pK_R represent more closely the inherent stability of the carbocation.

In this paper we compare values of pK_R and pK_a of arenonium and other carbocations and explore partitioning of the cations in water between the formation of hydrate or alcohol and arene or alkene products. This partitioning is expressed by a ratio of the rate constants k_p for deprotonation and k_{H_2O} for nucleophilic attack by water (Scheme 1). We show that a correlation exists between logs of ratios of these rate constants [$\log(k_p/k_{H_2O})$] and the relative stabilities of the products as expressed by pK_{H_2O} . The practical implications of this relationship, e.g., for the rate-determining step in the dehydration of alcohols (to form alkene) and the partitioning of the $Fe(CO)_3$ coordinated benzenonium ion in water between nucleophilic attack and deprotonation,²⁰ as well as its more fundamental implication for the intrinsic

Scheme 2



Scheme 3



reactivity of the carbocation toward reaction with water as a base and nucleophile, are discussed briefly.^{4,5,21}

Results

Phenanthrenonium Ion. The 9,10-hydrate of phenanthrene, 9-hydroxy-9,10-dihydrophenanthrene, **3**, may be prepared by reduction of the corresponding 9,10-epoxide.²² Reaction of the hydrate in dilute acid leads to dehydration to form phenanthrene with a rate constant $k_{de} = 3.4 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$.¹⁷ By analogy with other arene hydrates the reaction proceeds via 9-protonated phenanthrene **4** as an intermediate, as shown in the reaction at the top of Scheme 2. Expressed in terms of the rate constants in Scheme 3, $k_{de} = k_H k_p / (k_p + k_{H_2O})$, where k_H refers to formation of the carbocation and k_p and k_{H_2O} to its forward and backward reactions.

Reaction of **3** with dichloroacetyl chloride yields the dichloroacetate **5**, which solvolyzes in aqueous acetonitrile in the absence of acid to form a mixture of phenanthrene and the hydrate (**3**), conditions under which the hydrate does not react further. Measurements in a series of acetonitrile–water mixtures yield product ratios of phenanthrene/hydrate which are weakly dependent on solvent composition⁸ and give a ratio of rate constants for deprotonation and nucleophilic reaction of the carbocation with water $k_p/k_{H_2O} = 25$.

Solvolysis of **5** in the presence of varying concentrations of sodium azide leads to formation of an azido product presumed to be 9-azido-9,10-dihydrophenanthrene, **6**. Attempts to isolate this product were unsuccessful, probably because of its low concentration in comparison with other products, but it could be identified by its HPLC retention time in relation to phenanthrene and hydrate products, the dependence of the intensity of its peak upon azide concentration and the growth of this intensity with a rate constant equal to that of the solvolysis reaction.^{7,8,11}

Figure 1 shows a plot of the ratio of concentrations of azide adduct to phenanthrene in the products based on the relationship of eq 1 (in which Phen denotes phenanthrene and RN_3 the azide-trapped product) and the usual assumption that the extinction

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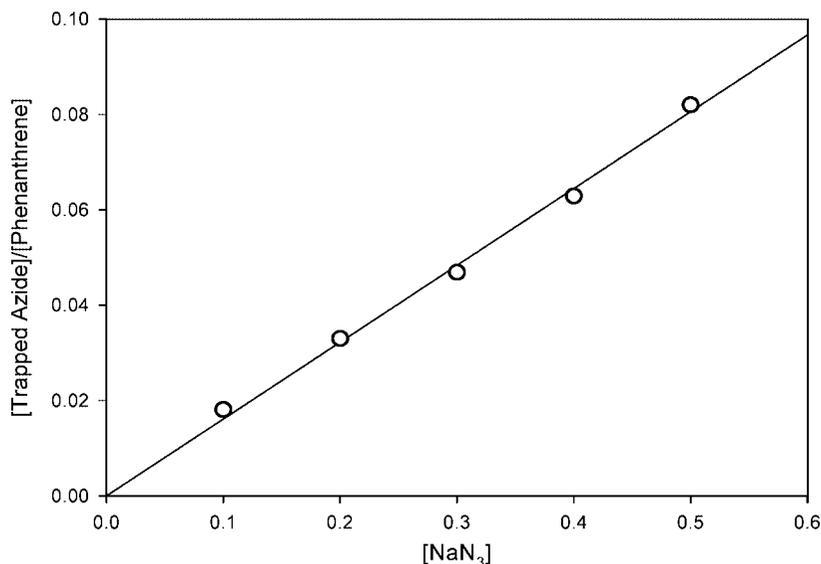


Figure 1. Ratios of concentrations of trapped 9-azido-9,10-dihydrophenanthrene and phenanthrene plotted against concentrations of azide ion in 50% aqueous MeCN at 25 °C.

coefficients of the azide and hydrate are the same.²³ From extrapolation of the slope of this and other plots for different solvent mixtures the ratio of rate constants for formation of the two products in water is $k_{Az}/k_p = 0.135$. Making the usual assumption of the azide clock method^{7,8} that trapping of the carbocation by azide ion is diffusion controlled with rate constant $k_{az} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ leads to $k_p = 3.7 \times 10^{10} \text{ s}^{-1}$ and, by combination of this value with $k_p/k_{H_2O} = 25$, to $k_{H_2O} = 1.5 \times 10^9 \text{ s}^{-1}$. Correction of the rate constant for dehydration of phenanthrene hydrate for the small degree of reversibility implied by the value of k_p/k_{H_2O} gives $k_H = 3.5 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, whence $K_R = k_{H_2O}/k_H = 4.3 \times 10^{11}$ and $pK_R = -11.6$ in aqueous solution at 25 °C.

$$\frac{[\text{RN}_3]}{[\text{Phen}]} = \frac{k_{Az}[\text{N}_3^-]}{k_p} \quad (1)$$

However, this analysis is oversimplified on three counts. The first is neglect of an explicit treatment of solvent relaxation as a limit on the rate of deprotonation of the phenanthrenonium ion. The influence of this limit has been considered by Richard in relation to the protonation of highly reactive carbanions by water¹² and is adapted to the deprotonation of carbocations in Scheme 3 below in which $k_{reorg} = 10^{11} \text{ s}^{-1}$ is a constant for solvent relaxation and R–X and Phen refer to the dichloroacetate **5** and phenanthrene, respectively.

The second simplification is neglect of ion pairs. In Scheme 3, deprotonation and attack of azide ion on the phenanthrenonium ion are shown as occurring on R^+X^- and X^-R^+ , which represent ion pairs before and after relaxation of the solvent, respectively. Richard²⁴ has estimated a rate constant for dissociation of an ion pair in water as $1.6 \times 10^{10} \text{ s}^{-1}$, and this will become significant if k_p is comparable with this value. However, if the ratio of k_p to the diffusion constant for the azide ion k_{Az} is unaffected by the ion pairing the kinetic expression based in Scheme 3 simplifies to that of eq 2.

$$\frac{[\text{R-N}_3]}{[\text{Phen}]} = \left\{ \frac{k_{Az}}{k_{reorg}} + \frac{k_{Az}}{k_p \{1 + (k_{Az}/k_{reorg})[\text{N}_3]\}} \right\} [\text{N}_3] \quad (2)$$

Taking $k_{Az} = 5 \times 10^9 \text{ s}^{-1}$ and $k_{reorg} = 10^{11} \text{ s}^{-1}$, the ratio $k_{Az}/k_{reorg} = 0.05$, and except at the highest concentrations of azide ion eq 2 is well approximated by eq 3.

$$\frac{[\text{R-N}_3]}{[\text{Phen}]} = k_{Az} \left\{ \frac{1}{k_{reorg}} + \frac{1}{k_p} \right\} [\text{N}_3] \quad (3)$$

This equation implies that when the rate constant for deprotonation is large the limiting product ratio = $[\text{RN}_3]/[\text{Phen}] = k_{Az}/k_{reorg} = 0.05$. Taking account of this limit leads to a minor modification of the value of k_p based on eq 1 from 3.7 to $5.9 \times 10^{10} \text{ s}^{-1}$.

It should be noted that it is also possible that reaction within the ion pair involves the dichloroacetate counterion rather than water acting as base. However, the rate of deprotonation is sufficiently close to the relaxation limit that it seems unlikely that k_p will be much affected by replacement of a water molecule in the solvation shell of the carbocation by a carboxylate anion.

A more serious limitation is that the analysis fails to take account of reaction by a preassociation mechanism. For solvolytic reactions of different charge types Richard has measured contributions from preassociation to values of $[\text{RN}_3]/[\text{solvolytic product}]$ in the range 0.2–0.7.²⁵ The value of $[\text{RN}_3]/[\text{Phen}] = 0.135$, which we find is below that range even before correction for a limiting value of 0.05.

In so far as the aim of this paper is to establish equilibrium constants we will not pursue these issues but simply note that by neglecting preassociation and trapping by azide of an unrelaxed ion (pair) the k_p determined represents a minimum value. Because the maximum value of k_p , $k_{reorg} = 10^{11} \text{ s}^{-1}$, is less than three times greater than the value of 3.7×10^{10} derived from the simple partitioning based in Scheme 2, the maximum error in $\log k_p$ and the derived value of $pK_R (= -11.6)$ is $\log 2.7$ or 0.4 log units, while the difference of $\log k_p$ from the value based in Scheme 3 is 0.2 units.

A value for the pK_a of the phenanthrenonium ion may be obtained by combining k_p with a rate constant k_A for protonation of phenanthrene. The latter may be derived from an isotope effect-corrected rate constant for protonation of the 1-position of naphthalene ($1.7 \times 10^{-11} \text{ M}^{-1} \text{ s}^{-1}$)²⁶ and a ratio of partial

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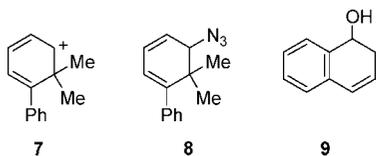
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rate factors for tritium exchange at the 9-position of phenanthrene²⁷ and 1-position of naphthalene.²⁸ From the derived value of $k_A = 5.0 \times 10^{-11}$, we find $K_a = k_p/k_A = 7.4 \times 10^{20}$ and $pK_a = -20.9$ in aqueous solution at 25 °C, with an estimated error of ± 0.5 .

The consistency of these pK_a and pK_R values is confirmed by the relationship $pK_a - pK_R = pK_{H_2O}$ implied in Scheme 1, in which pK_{H_2O} is the (negative log of) the equilibrium constant for hydration of the 9,10-double bond of phenanthrene. Comparison of the value $pK_a - pK_R = 9.3$ with a value of $pK_{H_2O} = 9.2$ estimated from the free energies of formation of phenanthrene and phenanthrene hydrate¹⁹ shows good agreement. Comparably good agreement is found between experimental and estimated values of pK_{H_2O} for hydration of the 1,2-double bond of naphthalene (13.7 and 14.2) and 9,10-hydration of anthracene (7.5 and 7.4).

In so far as the rate constant k_H can be measured with a precision of a few percent the uncertainty in pK_R should be controlled by uncertainty in the magnitude of the rate constant for azide trapping (ca. ± 0.2 log units) and k_p/k_{H_2O} (± 0.1 log units). In principle pK_a is subject to greater uncertainty because of extrapolation and interpolation involved in determining k_A . However, this is mitigated in some degree by good agreement between experimental and estimated values of pK_{H_2O} . This suggests ± 0.4 log units as the likely error for pK_a .

Benzenonium and 1-Naphthalenonium Ions. Attempts to trap the benzenonium ion with azide ion following the procedure used by Pirincioglu and Thibblin for the naphthalenonium ion¹⁰ were unsuccessful. This must be partly because deprotonation of the ion is sufficiently fast that only a small amount of trapping occurs even at high azide concentrations. Thus if the rate constant of $9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ derived below is correct and the azide trapping is diffusion controlled with rate constant $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (which indeed is probably not the case), only 7% trapping would be observed at a 1 M concentration of NaN_3 . Moreover, McClelland has shown that the azide-trapped product from the structurally related dimethyl derivative of the 3-phenyl substituted benzenonium ion **7** solvolyzes with a half-life of 5 min.²⁹ If our estimate below that **1** is 10 times more stable than **7** is correct the half-life of the trapped azide (**8**, $X = \text{N}_3$) would be significantly less than this and would not be detectable by an HPLC method which at best takes several minutes per sample for analysis. Trapping of **7** was possible because the dimethylation precludes deprotonation as a reaction path and although solvolysis of the azide derivative is rapid the hydrate formed as the product of solvolysis (**8**, $X = \text{OH}$) exists in equilibrium with the azide.²⁹ The possibility of monitoring trapping of the benzenonium ion by UV under kinetic control, as proved effective in the case of the anthracenonium ion,¹¹ is precluded by the high absorption of azide ions and the much higher concentrations required for trapping in the case of benzenonium than anthracenonium ions.



The pK_a of the benzenoniumion, nevertheless, can be inferred from a correlation of rate constants (k_p) for deprotonation of carbocations with their pK_a values shown in Figure 2. Rate constants and equilibrium constants included in the figure are

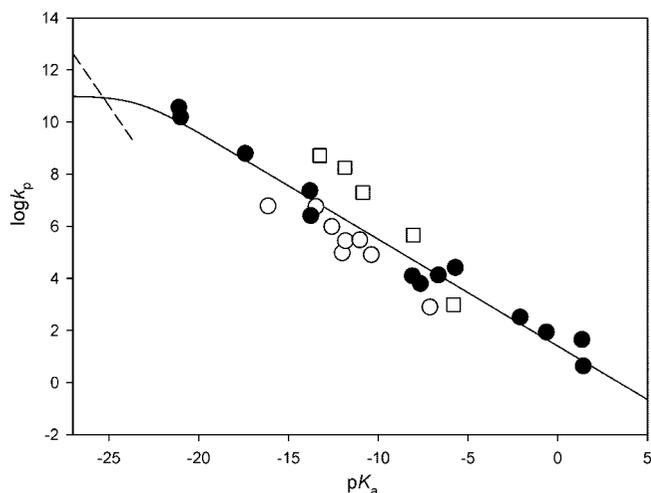


Figure 2. Plot of logs of rate constants for deprotonation of carbocations against pK_a in aqueous solution at 25 °C: filled circles, arenonium ions; open circles, secondary benzylic cations; squares, tertiary cations. The correlation line has a slope of -0.41 , changing to zero as relaxation of the solvent becomes rate-determining. The dashed line intersects the correlation line at the pK_a of the benzenonium ion (see text).

listed in Tables 1–3. The carbocations include arenonium ions^{10,11,13–17} and cyclic and noncyclic secondary^{5,30} and tertiary,^{5,9,31} usually benzylic, carbocations. The line drawn in the figure is based only on the arenonium ions, which are shown as filled circles. Measurements for the latter come from azide trapping of cations derived from protonation of naphthalene,^{10,11} 1-methylnaphthalene,³² anthracene,¹¹ phenanthrene, or benzofuran¹¹ and direct measurements of rate and equilibrium constants for more stable multiply substituted methyl-,^{15,33} methoxy-, or hydroxy-benzenonium ions^{13,14,34} and protonated azulenes.^{16,35–37} The line has slope -0.41 except at strongly negative pK_a values where the relaxation of water becomes rate controlling.

Measurements for carbocations other than arenonium ions are based on azide trapping.^{5,7,25,30} However, because reaction of the carbocation normally yields exclusively an alcohol as product the trapping leads to values of k_{H_2O} for nucleophilic reaction with water but not k_p for deprotonation. Combination of k_{H_2O} with measurement of the rate constant k_H for acid-catalyzed conversion of the alcohol to the carbocation then yields a value of pK_R . The value of k_H is obtained from racemisation or oxygen isotope exchange of the alcohol or by Richard's method⁷ of combining rate constants measured in water–trifluoroethanol (TFE) mixtures with a measurement of the partitioning of the carbocation between alcohol and trifluoroethyl

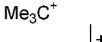
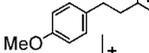
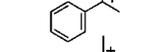
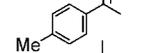
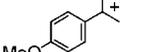
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Table 1. Rate Constants and Equilibrium Constants for Formation and Reaction of Carbocations in Aqueous Solution at 25 °C

| Carbocation | $k_H \text{ M}^{-1} \text{ s}^{-1a}$ | $k_{\text{H}_2\text{O}} \text{ s}^{-1b}$ | $k_A \text{ M}^{-1} \text{ s}^{-1c}$ | $k_p \text{ s}^{-1d}$ | pK_R^e | pK_a | $pK_{\text{H}_2\text{O}}^f$ | $\log(k_p/k_{\text{H}_2\text{O}})$ | Ref |
|---|--------------------------------------|--|--------------------------------------|-----------------------|----------|--------|-----------------------------|------------------------------------|-----------|
|  | 180 | 3.6×10^4 | 2.6×10^{-14} | 9.0×10^{10} | -2.3 | -24.5 | 22.2 | 6.60 | This work |
|  | 3200 | - | 2.3×10^{-9} | 6.0×10^8 | - | -17.4 | - | - | 32 |
|  | 240 | 7.6×10^5 | 6.8×10^{-11} | 1.6×10^{10} | -3.5 | -20.4 | 16.9 | 4.32 | 10,11,26 |
|  | 0.35 | 3.5×10^7 | 1.7×10^{-12} | 6.5×10^{10} | -8.0 | -22.5 | 14.5 | 3.27 | This work |
|  | 1.8 | 1.0×10^7 | 6.8×10^{-11} | 1.6×10^{10} | -6.7 | -20.4 | 13.7 | 3.20 | 10,11,26 |
|  | 3.4×10^{-3} | 1.0×10^9 | 5.0×10^{-11} | 2.9×10^{10} | -11.6 | -20.9 | 9.3 | 1.40 | This work |
|  | 14.9 | 1.3×10^7 | 5.7×10^{-7} | 2.33×10^7 | -6.0 | -13.5 | 7.5 | 0.25 | 30 |
|  | 7.4×10^{-3} | 1.55×10^7 | 4.5×10^{-10} | 6.1×10^6 | -9.3 | -16.1 | 6.8 | -0.41 | 30 |
|  | 2.8×10^{-3} | 3.8×10^9 | 1.95×10^{-7} | 5.84×10^6 | -12.1 | -13.5 | 1.4 | -2.81 | 30 |
|  | 1.7×10^{-3} | 1.6×10^9 | 9.45×10^{-8} | 9.45×10^4 | -12.0 | -12.0 | 0 | -4.23 | 30 |
|  | 2.0×10^{-4} | 6.0×10^9 | 4.3×10^{-7} | 4.3×10^5 | -13.5 | -12.0 | -1.5 | -4.15 | 30 |
|  | 3.2×10^{-3} | 1.6×10^9 | 3.4×10^{-6} | 1.23×10^5 | -11.7 | -10.6 | -1.1 | -4.12 | 30 |
|  | 6.0×10^{-3} | 2.3×10^9 | 2.6×10^{-7} | 9.8×10^5 | -11.6 | -12.6 | 1.0 | -3.37 | 30 |
|  | 5.25×10^{-4} | 3.30×10^9 | 2.9×10^{-6} | 4.6×10^5 | -12.8 | -11.2 | -1.60 | -3.86 | 5 |
|  | 6.9×10^{-2} | 5.50×10^7 | 8.77×10^{-5} | 1.21×10^3 | -8.9 | -7.34 | -1.56 | -4.65 | 5 |

^a Rate constant for H_3O^+ -catalyzed conversion of alcohol or aromatic hydrate to carbocation. ^b Rate constant for reaction of the carbocation with water. ^c Rate constant for protonation of a π -bond by H_3O^+ to give indicated carbocation. ^d Rate constant for deprotonation of carbocation by water. ^e $K_R = [\text{ROH}][\text{H}^+]/[\text{R}^+]$. ^f Equilibrium constant for addition of H_2O to the carbon-carbon double bond of conjugate base of carbocation. ^g Measurements in 50:50 (v/v) TFE-H₂O mixtures.

Table 2. Rate and Equilibrium Constants for Formation and Reaction of Carbocations in Water or 50:50 Trifluoroethanol Water Mixtures at 25 °C^a

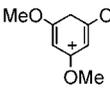
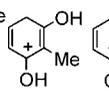
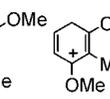
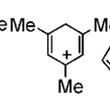
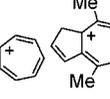
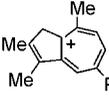
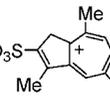
| Carbocation | $k_H (\text{M}^{-1} \text{s}^{-1})^b$ | $k_{\text{H}_2\text{O}} (\text{s}^{-1})^c$ | $k_A (\text{M}^{-1} \text{s}^{-1})^d$ | $k_p (\text{s}^{-1})^e$ | pK_R^f | pK_a | $pK_{\text{H}_2\text{O}}^g$ | $\log(k_p/k_{\text{H}_2\text{O}})$ |
|---|---------------------------------------|--|---------------------------------------|-------------------------|----------|--------|-----------------------------|------------------------------------|
|  | 4.0×10^{-4} | 1.0×10^{11} | 2.7×10^{-4} | 8.0×10^8 | -16.4 | -12.5 | -3.9 | -3.00 |
|  | 2.0×10^{-4} | 1.0×10^{11} | 3.2×10^{-5} | 1.6×10^9 | -16.7 | -13.7 | -2.95 | -1.80 |
|  | 7.5×10^{-3} | 1.5×10^{10} | 2.8×10^3 | 6.0×10^7 | -12.3 | -11.35 | -0.95 | -2.40 |
|  | 0.25 | 1.0×10^9 | 4.0×10^{-3} | 1.4×10^6 | -9.6 | -8.55 | -1.05 | -2.85 |
|  | 50.0 | 1.0×10^7 | 1.2×10^{-2} | 2.9×10^3 | -6.3 | -5.4 | -0.9 | -3.55 |

^a The *t*-butyl cation is in water, refs 5 and 30. The measurements for all other cations refer to 50% v/v TFE-H₂O mixtures, ref 5. ^b Rate constant for H_3O^+ -catalyzed conversion of alcohol or aromatic hydrate to carbocation. ^c Rate constant for reaction of the carbocation with water. ^d Rate constant for protonation of a π -bond by H_3O^+ to give indicated carbocation. ^e Rate constant for deprotonation of carbocation by water. ^f $K_R = [\text{ROH}][\text{H}^+]/[\text{R}^+]$. ^g Equilibrium constant for addition of H_2O to the carbon-carbon double bond of conjugate base of carbocation.

ether. If necessary k_H may be extrapolated from the mixed solvent to water,³⁰ or azide trapping may be carried out in the mixed solvent. The results for the cations in Tables 1 and 2 refer to water, whereas those for the tertiary cations in Table 3 are mainly for TFE-water mixtures.

The value of $pK_R = \log(k_H/k_{\text{H}_2\text{O}})$ so determined may be combined with a measured or estimated value of $pK_{\text{H}_2\text{O}}^{5,11}$ for the alkene corresponding to the conjugate base of the carbocation to provide pK_a .⁵ This in turn can be combined with a rate constant k_A for hydration of the alkene, for which

Table 3. Rate and Equilibrium Constants for Protonation of Methyl-, Methoxy-, and Hydroxy-Substituted Benzenes and Azulenes in Aqueous Solution at 25 °C

| |  |  |  |  |  |  |  |  | |
|---|---|---|---|---|---|---|---|---|-------|
| k_X^T (M ⁻¹ s ⁻¹) ^a | 6.2 × 10 ⁻³ | 2.3 × 10 ⁻⁴ | 7.95 × 10 ⁻⁶ | 1.07 × 10 ⁻⁵ | (2.4 × 10 ⁻⁸) ^b | 0.183 | 4.0 | 6.1 | 0.853 |
| $T_{k_H^T/k_T^c}$ | 20.3 | 20.3 | 20.3 | 20.3 | (9.5) ^d | 24.4 | 26.1 | 14.1 | 18.1 |
| k_A (M ⁻¹ s ⁻¹) | 1.53 × 10 ⁻² | 5.64 × 10 ⁻³ | 1.95 × 10 ⁻⁴ | 2.62 × 10 ⁻⁴ | 1.34 × 10 ⁻⁷ | 5.34 | 125.0 | 106.0 | 18.7 |
| k_p (s ⁻¹) | 2.80 × 10 ³ | 1.36 × 10 ⁴ | 1.30 × 10 ⁴ | 6.3 × 10 ³ | 2.55 × 10 ⁶ | 334.0 | 45.0 | 4.33 | 86.4 |
| pK_a | -5.23 | -6.35 | -7.80 | -7.35 | -13.28 | -1.76 | 1.65 | 1.42 | -0.63 |
| Ref | 13, 34 | 13, 14 | 13, 34 | 13, 14 | 15, 33 | 35, 36 | 37 | 37 | 36 |

^a Rate constant for H₃O⁺-catalyzed exchange of tritium from tritium-labelled substrate, except as indicated. ^b Rate constant for incorporation from tritiated acid solutions, TH₂O⁺/THO. ^c Isotope effect for partitioning arenonium intermediate. ^d Based on estimated value of $k_H/k_D = 4.8$ (see text).

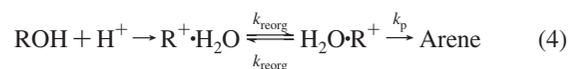
protonation of the alkene is normally the rate-determining step. Finally the rate constant k_p is obtained from the relationship $pK_a = \log(k_A/k_p)$.

For the correlation in Figure 2, rate and equilibrium constants have been corrected for statistical factors. Because k_p most commonly refers to proton abstraction from a methylene group no correction is made for the symmetry number 2 but rate constants for proton transfer from a CH₃ group are divided by 1.5 and from (CH₃)₃C⁺ by 4.5. The rate constants k_A (and hence the equilibrium constants K_a) are corrected for the number of equivalent positions for protonation, but without correction for the two faces of a double bond. Thus the symmetry correction for protonation of benzene is 1/6 and for protonation of a symmetrical alkene 1/2.

As indicated above, the correlation line in Figure 2 refers only to arenonium ions. Inclusion of a wider range of structures leads to significant scatter. However, this scatter appears to be systematic rather than random in character. Thus, negative deviations from the plot are associated with delocalization of carbocationic charge to an oxygen atom; positive deviations occur for tertiary cations, shown as squares. Further structures lead to similar systematic deviations (e.g., positive for vinyl ethers,³⁸ negative for enols or enolate anions^{39,40}) but there is no obvious increase in scatter or change in average slope.

Within the precision of the data, the correlation of arenonium ions is linear, except at the most negative pK_a values. At high reactivities and negative pK_a values, however, a best fit is expected to show curvature as a consequence of the deprotonation rate approaching a limit of 10¹¹ s⁻¹ for the rotational relaxation rate of water.^{24,41} The calculated correlation line is based on Richard's analysis of the protonation of enolate and related carbanions.¹² Applied to the deprotonation of arenonium ions it leads to the reaction scheme shown in eq 4 in which k_p

and k_{reorg} are the rate constants for deprotonation and relaxation, respectively. The rate expression based on this scheme is shown in eq 5 and the line drawn through the points in Figure 2 represents a best fit to this expression with $k_{reorg} = 10^{11}$ s⁻¹ and an optimized linear dependence of $\log k_p$ upon pK_a ($\log k_p = -0.41pK_a + 1.51$).



$$k_{obs} = k_{reorg} k_p / (k_p + k_{reorg}) \quad (5)$$

A pK_a for protonated benzene may be obtained from Figure 2 by combining the measured rate constant for protonation of benzene by H₃O⁺, based on measurements of hydrogen isotope exchange ($k_A = 2.6 \times 10^{-14}$ M⁻¹ s⁻¹),²⁶ with the simple relationship between rate and equilibrium constants, $K_a = k_p/k_A$. Substituting for k_A and taking logs gives $pK_a = -\log k_p - 14.36$. This expression is represented in Figure 2 by the dashed line of slope -1, which intercepts the $\log k_p - pK_a$ correlation line at $k_p = 9 \times 10^{10}$ and $pK_a = -24.5$ (after statistical correction of k_A by 1/6). These are the values for protonated benzene.

A similar analysis may be used to obtain a pK_a for 2-protonated naphthalene, for which $\log k_A = -12.38 \pm 0.33$.²⁶ This leads to $k_p = 6.5 \times 10^{10}$ and $pK_a = -22.5$ (after statistical correction of k_A by 1/4). It may be noted that these high values of k_p imply a near absence of a primary isotope effect on isotope exchange reactions. The fact that in practice the reactions do show moderate isotope effects²⁶ is a consequence of the measurements being made in concentrated acid solutions in which the effective basicity of water, and hence the rate of proton transfer, is significantly less than in pure aqueous or dilute acid solutions.

Nucleophilic Reactions of Cations with Water. As described below, values of pK_a for benzenonium and naphthalenonium ions may be combined with pK_{H_2O} , the equilibrium constant for 1,2 addition of water across a double bond of the aromatic molecule,¹⁹ to obtain values of $pK_R = pK_{H_2O} - pK_a$ for hydrolysis of the ions. From pK_R we may then derive a rate constant k_{H_2O} for nucleophilic reaction of the ion with water.

Rate constants for the acid-catalyzed dehydration of the products of hydrolysis, namely the hydrates of benzene and naphthalene, **2** and **9**, have been reported previously.¹⁷ These correspond to the rate constants for rate-determining conversion of the hydrates to carbocations because the exceptional stability

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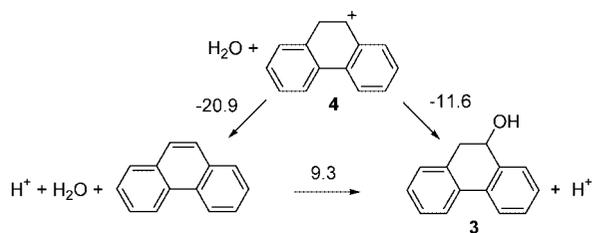
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Scheme 4



of the aromatic product renders deprotonation of the carbocations extremely fast as shown above. The rate constants k_{H_2O} for nucleophilic attack of water on the benzenonium ion and naphthalenonium ion to form the hydrates **2** or **9** can nevertheless be derived from the relationship $k_R = k_{H_2O}/k_H$.

An objective of this paper is to examine relative reactivities of carbocations toward deprotonation and nucleophilic attack by water. It is for this reason that values of k_{H_2O} are listed together with k_p in Tables 1 and 2. As discussed below, partitioning of the carbocations may be expressed as $\log(k_p/k_{H_2O})$, and is then well correlated by the equilibrium constant for hydration of the arene or alkene product arising from deprotonation, pK_{H_2O} . Values of pK_{H_2O} ¹⁹ are also included in the table therefore and, for completion, rate constants k_A and k_H and equilibrium constants pK_R . The combined data provide a comprehensive summary of rate and equilibrium constants for a wide range of structures of carbocations reacting in aqueous solution.

Discussion

The equilibrium constants pK_a , pK_R , and pK_{H_2O} for phenanthrene protonated at the 9-carbon atom (**4**) are summarized in the cycle of Scheme 4. The equilibria are represented by single arrows to emphasize the relationship between equilibrium constants implied by Hess's law, i.e., $pK_{H_2O} = pK_R - pK_a$. As described above, generation of the phenanthrenonium ion by solvolysis of the dichloroacetate precursor **5** in aqueous media leads to competing deprotonation to form phenanthrene and nucleophilic reaction to give the phenanthrene hydrate **3**. Application of the azide clock method^{7,8} leads to rate constants for both reactions and, by combination with values for the acid-catalyzed reverse processes, to evaluation of all the equilibrium constants shown in Scheme 4.

For protonated benzene trapping by azide ions is precluded by the high rate of proton loss to form benzene and probable rapid solvolysis of any small amounts of cyclohexadienyl azide formed. Nevertheless, a deprotonation rate constant can be derived from a correlation of logs of rate constants with pK_a values for deprotonation of other carbocations, especially arenonium ions, combined with the assumption that these rate constants are limited for highly acidic cations by the rate constant 10^{11} s^{-1} for rotational relaxation of water.^{5,9,41} This correlation is shown in Figure 2. It includes a wide range of structures of carbocations leading to a considerable scatter of points. However, the correlation is based on the filled circles representing arenonium ions, which are secondary cyclic allylic or benzylic cations. There are systematic deviations for tertiary carbocations, shown as squares, which appear to yield a separate correlation line and fall mainly above the line for the arenonium ions. Secondary carbocations containing oxygen or other electronegative substituents conjugated with the charge center, fall below the line.

Aside from these deviations, the linearity of the correlation line in Figure 2 outside the high reactivity limit is at first surprising. It can be attributed to modification of the 'normal' Marcus curvature, associated with a decrease in barrier to reaction arising from increased thermodynamic driving force, by a compensating effect of an increase in intrinsic barrier (i.e., barrier to a thermoneutral reaction).⁴² This compensation has been discussed by Richard for the formation of enolate anions.⁴³ The increase (in intrinsic barrier) arises from a decrease in resonance stabilization of a reactant or increase in resonance stabilization of a product.^{44,45} In the present instance both possibilities are likely⁴³ because the carbocation reactant and aromatic product are subject to extensive π -delocalization. It should be noted that, in addition to the compensation for Marcus curvature, the deviations from the correlation in Figure 2 can be attributed to variations in intrinsic barrier.

The rate constant $k_p = 3.7 \times 10^{10}$ for the phenanthrenonium ion determined in this work represents an important point on the correlation because of its close approach to the limit for rotational relaxation of water. It slightly exceeds the value of 1.6×10^{10} measured by Pirinccioglu and Thibblin for naphthalene protonated at the 1-position.¹⁰ A limiting rate constant (10^{11} s^{-1}) has been incorporated into the plot reflecting a change in rate-limiting step from deprotonation to solvent relaxation, and this leads to curvature of the plot, and eventually a lack of dependence of k_p on pK_a for sufficiently acidic arenonium ions. Although k_p for the benzenonium ion cannot be measured experimentally its value appears to be so close to the relaxation limit as to be accurately determinable. Because the rate constant available for benzene is that for protonation ($k_A = 4.4 \times 10^{-15}$ for a single carbon)²⁶ we make use of the relationship $K_a = k_p/k_A$ to derive a value of $k_p = 9 \times 10^{10} \text{ s}^{-1}$ and $pK_a = -24$ from the intersection of the line $\log k_p = \log k_A - pK_a$ (shown as the dashed line) with the correlation line in the figure.

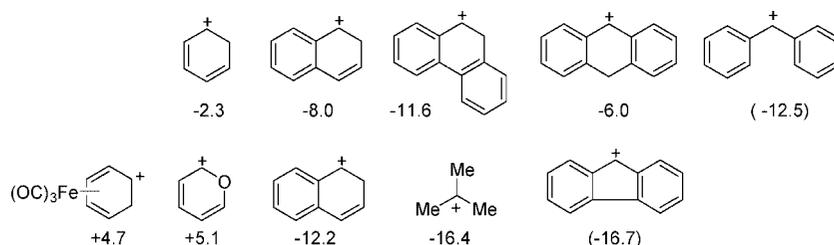
A value of $pK_a = -24$ for the benzenonium ion agrees surprisingly well with $pK_a = -23.5$ estimated by Kresge from oxygen substituent effects on the stabilities of protonated benzenes based on the pK_a values in Table 2 and similar measurements.¹³ It also agrees with that inferred by Marziano (reading from her graph) from a correlation of rate constants for hydrogen isotope exchange of aromatic molecules with pK_a values.¹⁵ Marziano's method is similar to our own, but the most acidic cation available to her was protonated mesitylene ($pK_a = -12.7$). Figure 2 contains measurements for a number of more acidic cations including the phenanthrenonium ion ($pK_a = -20.9$) and takes account of the limit on the rate constant represented by the relaxation of water. Moreover because of this limit, extrapolations of k_p , as in Figure 2, involve much smaller changes in rate constant than extrapolations based on rate constants for isotope exchange or protonation of the aromatic molecules (k_A) considered by Marziano. With respect to the last point, we previously estimated $k_p = 5 \times 10^{10} \text{ s}^{-1}$ for the benzenonium ion on grounds that it must lie between $1.6 \times 10^{10} \text{ s}^{-1}$ for the 1-protonated naphthalenonium ion and 10^{11} s^{-1} . This gave $pK_a = -24.3$. The correlation of Figure 2 suggests that k_p is significantly closer to its limiting value. However, the revised $pK_a = -24.5$, differs from the earlier value by less than the error of ± 0.26 log units estimated for the log of the rate

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Chart 1. pK_R Values of Carbocations

constant for the protonation of benzene k_A .²⁶ Since k_p is so close to 10^{11} , the uncertainty in pK_a corresponds to the combined errors in $\log k_A$ and the log of the relaxation limit.

Following the same procedure as for the benzenonium a $pK_a = -22.5$ may be estimated for the 2-protonated naphthalenonium ion. Again this is based on the rate constant k_A for protonation extrapolated by Cox from measurements of hydrogen isotope exchange.²⁶

These pK_a 's for the benzenonium and naphthalenonium ions may be converted to hydrolysis constants pK_R by calling upon values of $pK_{H_2O} = 22.2$ and 14.6 , respectively, for the hydration of benzene and naphthalene.¹⁹ From the relationship $pK_R = pK_a + pK_{H_2O}$ we then obtain $pK_R = -2.3$ for the benzenonium ion and -8.0 for the 1-naphthalenonium ion.

Stabilities of Carbocations. For protonated benzene, naphthalene and phenanthrene it is evident that pK_R has a much smaller negative value than pK_a . This is because pK_R is influenced primarily by the stability of the carbocation, with only limited interaction between the reacting OH group of the alcohol (aromatic hydrate) and structural changes in the rest of the molecule, whereas the pK_a strongly reflects stabilization of the double bond in the aromatic molecule. This is particularly striking in the case of benzene for which $pK_a = -24.5$ and $pK_R = -2.3$. The reasonableness of the value for pK_R is confirmed by comparison with $pK_R = -3.5$ for the 2,2-dimethyl-4-phenyl benzenonium ion **7** measured by McClelland.⁴⁶

The more negative pK_a than pK_R for the benzenonium ion is also consistent with its reacting more readily with water as a base than a nucleophile. The rate constant for nucleophilic reaction with water can be estimated as $k_{H_2O} = 4.5 \times 10^4$ by combining pK_R with the rate constant for the reverse acid-catalyzed formation of the carbocation from benzene hydrate, $k_H = 180$.¹⁷ This is more than 10^6 times less than the rate constant for deprotonation.

It is noteworthy that while pK_R varies significantly between the benzenonium, naphthalenonium and phenanthrenonium ions, from -2.3 to -8.0 to -11.6 , the pK_a 's of these ion are rather similar, -24.5 , -22.5 , and -20.9 . This similarity is consistent with the uniformly large rate constants for deprotonation which fall in the range 10^{10} – 10^{11} s⁻¹. However, in the light of the very different stabilities of the aromatic products it is a first surprising. That stability is reflected in the values of $pK_{H_2O} = 22.2$, 14.6 , and 9.3 for benzene, naphthalene and phenanthrene, respectively. The reason for the uniformity of the pK_a 's and deprotonation rate constants is that it reflects compensation between the stability of the product and the stability of the carbocation as expressed in the relationship $pK_a = pK_R - pK_{H_2O}$.

A question remains: why do the stabilities of the arenonium cations vary as they do? It is clear that benzoannellation sharply

decreases pK_R and hence the stability of the cations, whereas for simple solvolysis reactions benzylic substrates are usually more reactive than allylic.¹⁷ However, we defer discussion of this question to a later paper.

Further comparisons of pK_R values are shown in Chart 1. Apart from the influence of benzoannellation they illustrate the stabilizing effects of an endocyclic oxygen⁴⁷ or π -bond, as well as coordination by an Fe(CO)₃ group.²⁰ The low stability of the fluorenyl cation⁴⁸ is also apparent and, by contrast, the stability conferred by addition of a methylene bridge¹¹ to the benzhydryl cation.²³ The value of $pK_R = -16.4$ for the *t*-butyl cation⁹ is included as a point of comparison. The pK_R values of -12.5 for the benzhydryl cation and -16.7 for the fluorenyl cation are shown in brackets because they have been adjusted by subtracting 0.8 from the measured values in 50:50 TFE–H₂O mixtures²³ to allow a better comparison with the other values in water.

Product Partitioning. The equilibrium constants pK_a and pK_R offer a guide to relative rates of reaction of a carbocation with water as a base and a nucleophile. This is indicated in Figure 3 in which the logs of ratios of rate constants for deprotonation and nucleophilic attack k_p/k_{H_2O} are plotted against $pK_R - pK_a = pK_{H_2O}$. For the arenonium ions and other secondary carbocations, which are shown as circles, a linear relationship is found with slope 0.42. Positive deviations from the correlation occur for tertiary carbocations shown as squares and are discussed below.

It is noteworthy that the line in Figure 3 does not pass through the origin. When pK_a and pK_R for a cation are equal ($pK_{H_2O} = 0$) the reaction with water as a nucleophile is favored by 1500-fold. This reflects a lower intrinsic barrier to the nucleophilic reaction, previously noted by Richard.^{4,5,21} The lower barrier probably arises because nucleophilic attack involves making of a single (O–C) bond, whereas deprotonation involves making and breaking of several bonds (O–H and C–H and a C=C π -bond).^{44,49}

The dashed line in the figure corresponds to $\log k_p/k_{H_2O} = 0$ and thus $k_p = k_{H_2O}$. From the point of intersection of the plot with this line, it is apparent that the pK_a of a carbocation should be seven or more units more negative than pK_R for elimination to be preferred over substitution. Since relative rates of deprotonation and nucleophilic attack control the rate determining step in the acid-catalyzed dehydration of alcohols (and reverse hydration of alkenes) it is not surprising that proton transfer is normally rate determining in these reactions. Only when the

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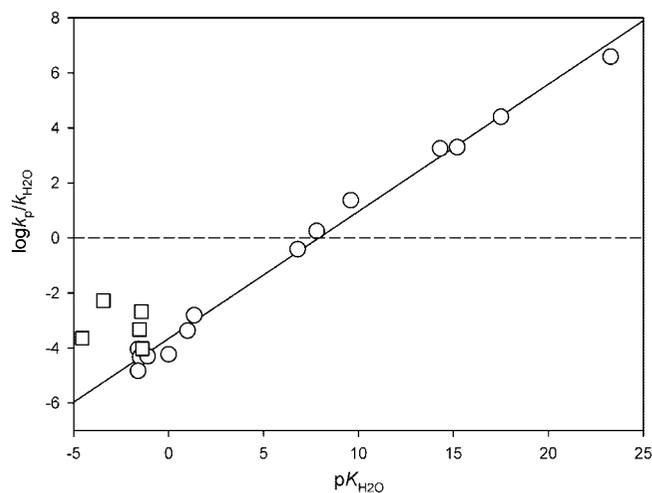


Figure 3. Plot of logs of k_p/k_{H_2O} for secondary (O) and tertiary (□) carbocations against pK_{H_2O} for hydration of the alkene conjugate base correlated by a best straight line $\log(k_p/k_{H_2O}) = 0.46pK_{H_2O} - 3.7$.

double bond of the product is unusually stabilized, e.g., by forming part of an aromatic system is carbocation formation rate-determining.

The simplest interpretation of the linearity of the correlation is that it represents a combination of free energy relationships between $\log k_p$ and pK_a on the one hand and $\log k_{H_2O}$ and pK_R on the other, as represented in eqs 6 and 7.

$$\log k_p = -m_a pK_a + c_a \quad (6)$$

$$\log k_{H_2O} = -m_R pK_R + c_R \quad (7)$$

The correlation of $\log k_p$ with pK_a is illustrated in Figure 2 of this paper. That between $\log k_{H_2O}$ and pK_R has been considered by McClelland who found linear correlations with only limited scatter for structurally homogeneous families of carbocations, such as diarylmethyl, triarylmethyl or aryldimethoxy.³ Equations 6 and 7 can be combined as $\log(k_p/k_{H_2O}) = m(pK_R - pK_a) + c$, provided that the slopes of the individual plots m_a and m_R are equal. This indeed seems to be the case. The slope of the plot in Figure 2 is -0.41 and that in Figure 3 is 0.46 . The slopes of McClelland's plots fall between -0.68 and -0.54 . However, McClelland studied tertiary or diarylmethyl cations whereas our cations are secondary benzylic or allylic. A plot of $\log k_{H_2O}$ against pK_R for the secondary cations of Figures 2 and 3 gives the lower slope of -0.44 (Figure S1). A steeper slope for tertiary than secondary cations is also characteristic of a correlation of $\log k_p$ with pK_a , as indicated by the squares in Figure 1, for which the slope is -0.62 .

It may be noted that there is a mild inconsistency between the correlations of secondary cations in that the slope of 0.46 in Figure 3 is greater than the (negative) slopes of its 'constituent' correlations of $\log k_p$ and $\log k_{H_2O}$ (-0.41 and -0.44). This difference is removed by restricting all three correlations to a common set of structures.

The simplest interpretation of the larger deviations of tertiary carbocations (squares) from the correlation of Figure 3 is that these represent nucleophilic reactions at or close to the limit set by solvent relaxation. This is true of the tertiary butyl cation for which the rate constant for deprotonation, $k_p = 8 \times 10^8 \text{ s}^{-1}$ is still short of this limit. Clearly if k_p continues to increase with increasing instability of the cation while k_{H_2O} remains constant k_p/k_{H_2O} will increase. In the limit that both k_p and k_{H_2O} achieve their limiting values the point should fall on the dashed

line corresponding to $\log k_p/k_{H_2O} = 0$. It is noteworthy that there is no pronounced negative deviation at the right-hand side of the plot where the rate of deprotonation of the benzenonium ion has reached its limit. However, this may be partly because the line drawn through the points masks a tendency to curvature for the more acidic protonated aromatic substrates.

Where nucleophilic and basic reactions of carbocations are not limited by water relaxation the correlation of Figure 3 implies that their relative rates simply depend on the equilibrium constant for hydration of the double bond, i.e., the relative stabilities of the alkene or arene and alcohol or hydrate products. In so far as an equilibrium constant for hydration is readily estimated even when pK_a and pK_R are unknown,¹¹ it is generally easy to predict which will be the faster reaction or rate-determining step. In an earlier paper²⁰ the fact that the benzenonium ion undergoes preferential deprotonation whereas its $\text{Fe}(\text{CO})_3$ complex is subject to substitution finds a straightforward explanation. An MP2 calculation of an equilibrium constant for hydration of the $\text{Fe}(\text{CO})_3$ coordinated benzene formed by deprotonation of the coordinated benzenonium ion yields a value of $pK_{H_2O} \approx -4$.⁵⁰ This value compares with $pK_{H_2O} = 22.2$ for benzene. Not only does it imply that the coordinated hydrate is thermodynamically more stable than coordinated benzene but that nucleophilic attack of water is much faster than deprotonation. According to Figure 3 we can expect $k_{H_2O}/k_p \approx 10^4$.

Summary. Measurements of rate and equilibrium constants give $k_p = 3.7 \times 10^{10} \text{ s}^{-1}$ and $pK_a = -20.9$ for deprotonation of the phenanthrenonium ion in water at 25°C . They help anchor a correlation between $\log k_p$ and pK_a for a range of protonated aromatic molecules, taking account of the limit for k_p set by the rotational relaxation of the solvent (10^{11} s^{-1}). From this correlation, pK_a 's for protonated benzene and naphthalene are inferred. Combining these with equilibrium constants pK_{H_2O} for addition of water to a double bond of the aromatic molecule furnishes hydrolysis constants pK_R . In contrast to pK_a , pK_R measures the stability of the arenonium ion independently of that of the aromatic molecule. In particular, $pK_R = -2.3$ for protonated benzene shows that it is a relatively stable carbocation. Values of pK_{H_2O} are also useful in predicting (a) ratios of rate constants k_p/k_{H_2O} for partitioning of carbocations between reactions with water as a base and a nucleophile and (b) the rate-determining step in a dehydration reaction.

Experimental Section

Instruments, Synthesis, Analytical Methods. ^1H and ^{13}C NMR spectra were measured on Varian 300 and 500 (Unity) MHz NMR spectrometers. UV-vis spectra and kinetic measurements were recorded on a Cary 50 spectrophotometer equipped with an automatic cell changer thermostatted at $25 \pm 0.1^\circ\text{C}$. HPLC measurements were made with a Waters 600 HPLC system with dual wavelength absorbance detection.

Phenanthrene hydrate (1-hydroxy-1,2-dihydrophenanthrene, **3**) was prepared by epoxidation of phenanthrene²² and reduction of the resulting 9,10-phenanthrene oxide with LiAlH_4 , as described previously.¹⁷ Its dichloroacetoxy ester derivative, 9-dichloroacetoxy-1,2-dihydrophenanthrene (**5**) was prepared by adding dichloroacetyl chloride (0.90 g) to an ice-cold stirred solution of the hydrate (0.10 g) in 10 mL of anhydrous dichloromethane containing 0.10 mL of pyridine. The solution was allowed to warm to room temperature and after two hours was quenched with 10 mL of saturated aqueous sodium bicarbonate. The organic layer was separated and washed

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with water (3×20 mL), dried over sodium sulfate and the solvent removed under reduced pressure. The crude product was triturated with cyclohexane to give a brown oil (0.15 g, 95%); ^1H (300 MHz, CDCl_3): δ 3.24 (2H, d, $J_{9,10} = 4.7$ Hz, H_{10}), 5.79 (1H, s, CHCl_2), 6.14 (1H, t, $J_{9,10} = 4.5$ Hz, H_9), 7.25–7.87 (8H, m).

Solvents used for kinetic measurements comprised distilled water or water mixed with HPLC grade acetonitrile. In a typical measurement 20 μL of a stock solution of substrate in acetonitrile (2×10^{-3} – 10^{-2} M) was injected into 2 mL of aqueous acid or aqueous acetonitrile in a silica cuvette. Reactions were initially surveyed by repetitive scans of UV–vis spectra and then monitored at a single wavelength.

HPLC measurements were used for product analysis and monitoring of kinetics where products trapped by azide ions were formed. Solvolysis of the dichloroacetate ester of phenanthrene hydrate (**5**) was initiated by injecting 25–30 μL of a stock solution of substrate into 0.25–0.5 mL of an acetonitrile–water mixture. Samples of 25 μL from the reaction were quenched in 500 μL of acetonitrile, which inhibited further solvolysis on the time scale of the analyses. Analyses were carried out by injection of 10 μL of this solution onto a Hichrome-5 C18 reverse phase column with aqueous acetonitrile as the mobile phase and a flow rate of 1 mL/min. Peaks for the ester reactant and the phenanthrene and phenanthrene hydrate (**3**) products were identified by comparison of their retention times with those of known samples. When the solvolyses were carried out in the presence of sodium azide a new peak appeared which was identified as 9-azidophenanthrene from the dependence of its intensity on the concentration of azide ions, the identity of its rate of appearance with that of other products and its retention time relative to that of the phenanthrene and phenanthrene hydrate (0.7 and 1.8) as compared with retention times for other azide–alcohol–hydrocarbon combinations.^{7,11,23}

Kinetic and Product Analyses. A rate constant for dehydration of phenanthrene hydrate had been determined previously as $3.40 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$.¹⁷ To derive k_{H} for carbocation formation this must be corrected for reversibility by measuring partitioning of the solvolytically generated carbocation between hydration and dehydration products under conditions that these are not equilibrated. The fraction of hydrate formed from solvolysis of ester derivatives of phenanthrene hydrates was previously estimated as ca. 15% from UV measurements.¹⁷ However, considerably more accurate values can be obtained by HPLC. Care must also be taken that part of the hydrate product does not come from hydrolysis of the ester function of the reactant, the contribution of which can be minimized by addition of a small amount of HCl (10^{-3} M) to the reacting solutions.

The solvolysis of 1-dichloroacetoxy-1,2-dihydronaphthalene in aqueous acetonitrile to form predominantly phenanthrene was monitored from an increase in absorbance at 250 nm; it gave rate constants 1.30, 4.13, and $16.3 \times 10^{-4} \text{s}^{-1}$ in 50%, 60%, and 74% (v/v) aqueous acetonitrile respectively. The ratios of phenanthrene/hydrate in the same solutions were determined as 24, 25, and 25, respectively. In the absence of HCl the corresponding values were 20, 21, and 16. An estimate of the contribution of uncatalysed hydrolysis based on the measured rate constant^{51,52} for hydrolysis of $\text{CH}_3\text{CH}_2\text{COOCHCl}_2$ and expected effect of a phenanthryl substituent (modeled as PhCHCH_2Ph with $\sigma^* \approx 0.3$)⁵³ indicated that this hydrolysis is very much slower than the observed rate of solvolysis. The lack of dependence of $k_{\text{p}}/k_{\text{H}_2\text{O}}$ on the composition of acetonitrile–water mixtures is consistent with a similar finding for the anthracenonium ion.¹⁷

The rate constant for dehydration of phenanthrene hydrate corresponds to $k_{\text{H}}/(1 + k_{\text{p}}/k_{\text{H}_2\text{O}})$ as implied in Scheme 2. The ratio $k_{\text{p}}/k_{\text{H}_2\text{O}}$ is given by the ratio phenanthrene to phenanthrene hydrate products in the solvolysis reaction, which was taken as 25. From

the rate constant for dehydration, $3.40 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$, we then obtain $k_{\text{H}} = 3.5 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$.

Trapping of the Phenanthrenonium Ion by Azide Ions. In principle the value of k_{H} may be combined with that of $k_{\text{H}_2\text{O}}$ to obtain $K_{\text{R}} = k_{\text{H}_2\text{O}}/k_{\text{H}}$. Normally, $k_{\text{H}_2\text{O}}$ would be obtained from solvolysis of the dichloroacetate ester **5** in the presence of azide ions and measurement of the ratio of azide-trapped product RN_3 (9-azido-9,10-dihydrophenanthrene) and phenanthrene hydrate (ROH). From the relationship $[\text{RN}_3]/[\text{ROH}] = k_{\text{AZ}}[\text{N}_3^-]/k_{\text{H}_2\text{O}}$, a value of $k_{\text{H}_2\text{O}}$ would then be obtained by assigning the value of k_{AZ} for reaction of the carbocation with azide ion as $5 \times 10^9 \text{M}^{-1} \text{s}^{-1}$, the rate constant for diffusion controlled reaction of oppositely charged ions in water. In practice, the ratio of azide to hydrate product, which should depend linearly upon the concentration of azide ions, is influenced by formation of excessive amounts of hydrate product which leads to downward curvature of a plot of $[\text{RN}_3]/[\text{ROH}]$ at high concentrations of azide ions. This behavior is understandable if hydrolysis of the ester to form the hydrate without intervention of the carbocation is catalyzed by azide ions acting as a nucleophilic or general base catalyst.^{30,54}

Rather than $k_{\text{AZ}}/k_{\text{H}_2\text{O}}$ therefore the rate constant ratio $k_{\text{AZ}}/k_{\text{p}}$ were determined by plotting $[\text{RN}_3]/[\text{phenanthrene}]$ against $[\text{N}_3^-]$. Measurements of product ratios by HPLC are listed in Table S1 and plots of product ratios against azide concentration similar to that in Figure 1 gave slopes 0.150, 0.156, and 0.21 in 50%, 60%, and 74% aqueous acetonitrile, respectively. The measurements in 74% water showed considerable scatter reflecting the insolubility of phenanthrene and consequently low concentrations of products analyzed. The slope in 74% H_2O was disregarded therefore and the other two values extrapolated to water on the assumption that the slope of a plot of $\log k_{\text{p}}$ against % acetonitrile had a slope of 0.14, as found for $k_{\text{H}_2\text{O}}$ for the reaction of benzhydryl cations with water by McClelland.⁸ This implies that the variation in $k_{\text{H}_2\text{O}}$ with solvent composition is opposite to that found here for 50% and 60% water. However, the discrepancy is small and again probably a symptom of the poor solubility of phenanthrene in the more aqueous solvent mixture. The extrapolated value of $k_{\text{AZ}}/k_{\text{p}}$ was 0.135 with a likely error of ± 0.015 (equivalent to ± 0.06 in derived $\text{p}K^{\text{r}}$ s). From $k_{\text{p}} = 5 \times 10^9/0.135 = 3.7 \times 10^{10}$ and $k_{\text{p}}/k_{\text{H}_2\text{O}} = 25$ we then obtain $k_{\text{H}_2\text{O}} = 1.5 \times 10^9 \text{M}^{-1} \text{s}^{-1}$. Combining $k_{\text{H}_2\text{O}}$ with $k_{\text{H}} = 3.5 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$ gives $K_{\text{R}} = k_{\text{H}_2\text{O}}/k_{\text{H}} = 4.3 \times 10^{11}$ and $\text{p}K_{\text{R}} = -11.6$.

The ionization constant K_{a} for the phenanthrenonium ion may be obtained by combining k_{p} with the rate constant k_{A} for protonation of phenanthrene. An approximate value for this rate constant may be derived from the comparison of the partial rate factor for hydrogen isotope exchange of 9-tritiated phenanthrene at 70 °C in trifluoroacetic acid (1610)²⁷ with that of 1-tritinationaphthalene (1160).²⁸ The isotope-corrected rate constant for protonation of 1-tritinationaphthalene in dilute aqueous sulfuric acid at 25 °C has been extrapolated from measurements in concentrated acid solutions as $1.7 \times 10^{-11} \text{M}^{-1} \text{s}^{-1}$.²⁶ If we assume that the exchange rate constants in trifluoroacetic acid show an Arrhenius dependence on temperature and differ only in activation energy we can derive a ratio of partial rate factors in trifluoroacetic acid at 25 °C as 1.46. If this ratio is unaffected by the change from trifluoroacetic acid to water as solvent, and the isotope effects for the two substrates (which have almost the same reactivity) are the same, then k_{A} for the protonation of phenanthrene is derived as $2 \times 1.46 \times 1.7 \times 10^{-11} = 5.0 \times 10^{-11}$ (where the factor of 2 takes account of equivalence of the 9- and 10-positions). We then find $K_{\text{a}} = k_{\text{p}}/k_{\text{A}} = 7.4 \times 10^{20}$ and $\text{p}K_{\text{a}} = -20.9$.

The values of k_{A} and k_{H} can be combined with an equilibrium constant $K_{\text{H}_2\text{O}}$ for hydration of phenanthrene to give an independent check on the value of $k_{\text{p}}/k_{\text{H}_2\text{O}}$. The equilibrium constant $K_{\text{H}_2\text{O}}$ can be written as a quotient of rate constants $k_{\text{A}}k_{\text{H}_2\text{O}}/k_{\text{H}}k_{\text{p}}$ as implied in Scheme 2 (from which, however, k_{A} is missing). A value for $K_{\text{H}_2\text{O}} = 6 \times 10^{-10}$ can be derived from free energies of formation of

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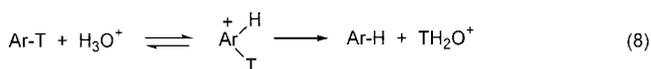
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phenanthrene and phenanthrene hydrate in aqueous solution if the latter value is estimated from the expected effect of a 9-hydroxyl substituent on the free energy of formation of 9,10-dihydrophenanthrene.²⁰ From the relationship $k_p/k_{H_2O} = k_A/k_H K_{H_2O}$ we then obtain from the values of k_A , k_H , and K_{H_2O} , $k_p/k_{H_2O} = 24$. This is in fortuitously good agreement with the value of 25 derived from measurements of phenanthrene/hydrate product ratios.

Treatment of Literature Data. Most of the data taken from the literature and listed in Tables 1–3 were used without modification. However, kinetic and equilibrium measurements for the oxygen substituted benzenonium ions in Table 3 were re-extrapolated from strongly acidic media to dilute aqueous solutions using the formalism of Cox and Yates.⁵⁵ This led to small changes in the values.

The kinetic measurements for all the substrates in Table 3 refer to hydrogen exchange of a tritium-labeled aromatic molecule (Ar-T). As shown in the reaction of eq 8 and derived kinetic expression of eq 9, to obtain the rate constant for protonation of the substrate (k_A) the measured rate constant k_x^T must be corrected for an isotope effect (k_H/k_T) from partitioning of the arenonium ion intermediate (ArTH⁺). Moreover, as indicated by the superscript T, the derived value of k_A^T must also be corrected for a secondary tritium isotope effect.



$$k_x = \frac{k_A^T}{1 + k_H/k_T} \quad (9)$$

Values of k_H/k_T are listed in Table 3. The values are quite large because they correspond to a primary tritium isotope effect amplified by a secondary effect. For the methoxy and hydroxybenzenes a common value of $k_H/k_T = 20.3$ measured for trimethoxybenzene

was used. Use of a common value is justified by the relatively mild dependence of isotope effects on reactivity and the fact that an error of a factor of 2 would fall within the range of scatter observed for the different substrates in the correlation of Figure 2. For mesitylene, for which an isotope effect measurement was also lacking, a primary isotope effect ($k_H/k_D = 4.8$) was inferred from a rough correlation of isotope effects with reactivity recorded by Cox.¹⁷ Derivation of k_H/k_T from the measured rate constant for uptake of tritium from the solvent required assignments of fractionation factors $l = 0.69$ ^{1.442} for tritium in H_2TO^+ and $\phi = 1.1$ ^{1.442} for tritium in the protonated intermediate (ArTH⁺), where the coefficient 1.442 is the exponent of the Swain–Schaad relationship relating deuterium and tritium isotope effects.⁵⁶ For all substrates studied the secondary isotope effect on k_A was taken as the value measured for trimethoxybenzene, ${}^H k_A^T/k_A = 1.15$.⁵⁷

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Supporting Information Available: Table S1 listing data from product analyses based on trapping experiments following solvolysis of ester **5** in aqueous acetonitrile–water mixtures containing sodium azide; Figure S1 showing a plot of $\log k_{H_2O}$ against pK_R for carbocations in Tables 1 and 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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