

High Relative Reactivities of Aromatic Cation Radicals Compared to Related Carbocations. Observation of an Unexpected Deuterium Kinetic Isotope Effect

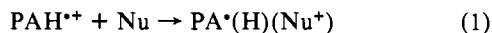
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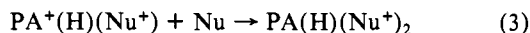
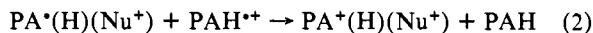
Abstract: The reaction between 9-phenylanthracene (PAH) cation radical and acetate ion was studied to probe for an electron-transfer pathway. The decomposition of acetoxy radical to methyl radical and carbon dioxide, accompanied by the regeneration of PAH, is the expected result of an initial electron transfer. Rate-determining attack of acetate ion on PAH^{•+} followed by rapid product-forming reactions could lead to a secondary α deuterium kinetic isotope effect. Neither of these results were observed. Attack by acetate ion on PAH^{•+} in acetonitrile at 293 K was observed to take place at nearly diffusion control. The slow step in the disappearance of acetate ion was observed to be the attack of acetate ion on PA⁺(H)(OAc), resulting from oxidation of the initial adduct: PA⁺(H)(OAc) + AcO⁻ → PA-OAc + HOAc (i). The proton abstraction reaction (i) resulted in a large (25 or greater) deuterium kinetic isotope effect for the reaction of the cation radical derived from 9-phenylanthracene-10-d. These observations show that nucleophilic attack on PAH^{•+} is more than 1 order of magnitude faster than reaction i and much faster than the attack of acetate ion on the carbocationic center of PA⁺(H)(OAc). This result is unexpected according to recent discussions of cation-radical reactivity.

The reactions of cation radicals derived from aromatic compounds are complex and often second-order in cation radical.¹ The propensity of cation radicals to take part in complex reaction schemes rather than simple combination reactions led to the proposal that they are of low intrinsic reactivity toward nucleophiles when compared to related carbocations.² This conclusion has been supported by theoretical considerations³ and challenged on the basis of kinetic⁴ and thermodynamic⁵ studies. A difficulty with the reactivity comparison² has been that kinetic data are not available for cation radicals and model carbocations under the same conditions.

In contrast to the reactions of 9,10-diphenylanthracene (DPA) cation radical with nitrogen-centered nucleophiles, which follow complex rate laws,¹ the corresponding reactions of the cation radical derived from 9-phenylanthracene (PAH) follow simple second-order kinetics.⁴ Rate constants ranging from about 10⁵ to 10⁹ M⁻¹ s⁻¹ were observed for reaction 1 where Nu represents



the nitrogen-centered nucleophile. Because this step is rate determining, further information on the rate of subsequent reactions cannot be obtained from kinetics based on the disappearance of the cation radical. Subsequent reactions leading to products include electron transfer 2 and and partitioning of the resulting



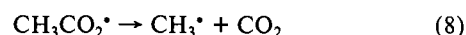
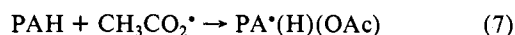
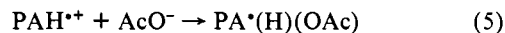
carbocation between nucleophilic attack 3 and proton transfer 4. An estimate of the relative rate constants, k_1/k_3 , would be of particular interest since this would give a direct measure of the relative reactivity of a cation radical and a closely related carbocation toward nucleophilic attack under identical experimental conditions. We now report kinetic data for this direct comparison.

Results and Discussion

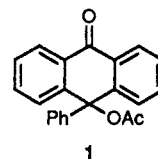
Theoretical Prediction of the Course of the PAH^{•+}-Acetate Ion Reaction. The configuration mixing (CM) model⁶ regards a single

electron shift (SES) as the fundamental event in most chemical reactions. The SES need not result in the formation of free radicals since unpaired electrons can remain coupled in the transition state. However, any factor such as extensive delocalization or steric effects that gives rise to "delayed coupling" can result in the formation of radical intermediates.⁶ The reaction of a cation radical with a nucleophile, or for that matter any reaction between open-shell and closed-shell reactants, could be regarded as an extreme case of delayed coupling where the SES necessarily results in electron transfer. Pross³ arrived at the conclusion that the reaction of a cation radical with a nucleophile would result in electron transfer and that bond formation between the reactants is a high activation energy "forbidden" process.

Specifically, the CM model predicts that reaction 5 is "forbidden". The SES, in this case, is expected to result in electron transfer 6, giving rise to PAH and acetoxy radical. Attack of acetoxy radical on PAH (7) is not expected to compete with decomposition 8, which is known to have a rate constant in the liquid phase of the order of 10⁹ - 10¹⁰ s⁻¹.⁷ Thus, the overall result of the SES is expected to be the catalytic oxidation of acetate ion by PAH^{•+}. Therefore, this system represents an ideal experimental test of the CM model prediction of the results of ion-radical reactions.



Products of the Reaction of PAH^{•+} with Acetate Ion in Acetonitrile. The anodic oxidation of PAH in acetonitrile-acetic acid (3:1) containing sodium acetate (0.25 M) results in **1** in high yield.⁸



By constant-current coulometry⁹ with linear sweep voltammetry

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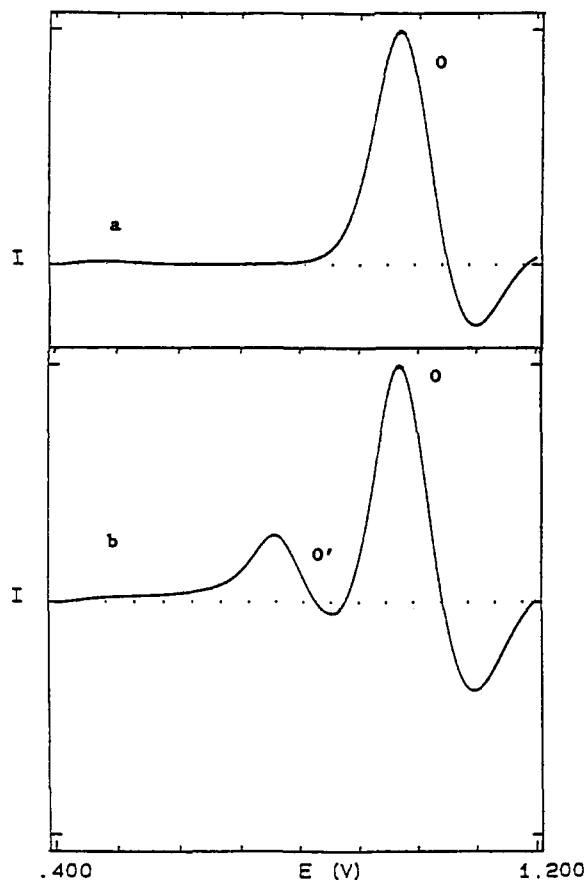


Figure 1. Derivative linear sweep voltammograms for the oxidation of PAH (1.0 mM) in $\text{CH}_3\text{CN}/\text{Bu}_4\text{NPF}_6$ (0.1 M) at 293 K with a voltage sweep rate of 100 mV/s in the absence (a) and the presence (b) of $\text{Bu}_4\text{N}^+\text{AcO}^-/\text{HOAc}$ (0.5 mM).

detection of the disappearance of PAH, we have confirmed that the oxidation in acetonitrile containing $\text{Bu}_4\text{N}^+\text{AcO}^-/\text{HOAc}$ involves the transfer of 4 faradays/mol accompanied by the formation of **1**. Gas-liquid chromatography (GLC) analysis after interruption of the oxidation before completion implicated 9-acetoxy-10-phenylanthracene (PA-OAc) as an intermediate on the pathway to formation of **1**. Voltammetric studies showed that PA-OAc and PAH are oxidized at very nearly the same potential. Constant-current coulometric oxidation of PA-OAc under the above conditions consumed 2 faradays/mol and resulted in **1** in high yield.

Kinetics of the Reaction of $\text{PAH}^{+\bullet}$ with Acetate Ion. Prepeak Method. The method¹⁰ is illustrated by the derivative linear sweep voltammograms shown in Figure 1. In the absence of an added nucleophile the electrode response for the reversible oxidation of PAH (1.0 mM) in $\text{CH}_3\text{CN}/\text{Bu}_4\text{NPF}_6$ (0.1 M) at 293 K consists of a single derivative peak (O) with a zero-crossing potential of +1.05 V vs the Ag/Ag^+ electrode (Figure 1a). The addition of $\text{Bu}_4\text{N}^+\text{AcO}^-/\text{HOAc}$ (0.5 mM) resulted in the observation of a prepeak (O') at less positive potentials (Figure 1b). The prepeak^{4,10} is due to the oxidation of PAH followed by the rapid combination with acetate ion and subsequent reactions. The concentration ratio, $[\text{PAH}^{+\bullet}]/[\text{PAH}]$, at the electrode surface determines the potential at which current flows according to the Nernst equation. The rapid consumption of $\text{PAH}^{+\bullet}$ brings about a kinetic potential shift, giving rise to the prepeak. Depletion of acetate ion in the diffusion layer limits the degree to which this reaction takes place and results in the observation of peak O for the reversible oxidation as well. The rate constant for the cation radical-acetate ion combination reaction 5 can be determined from the difference in zero-crossing potentials for the two processes by comparison with theoretical

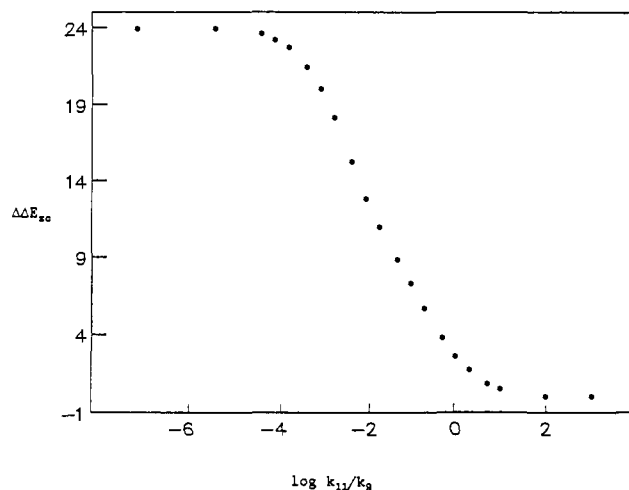
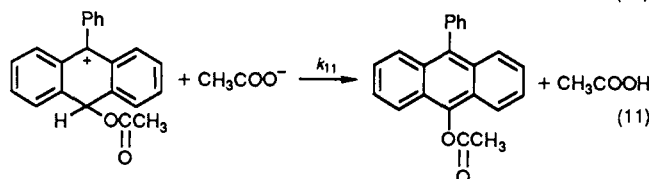
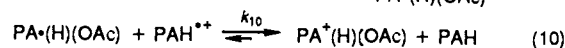
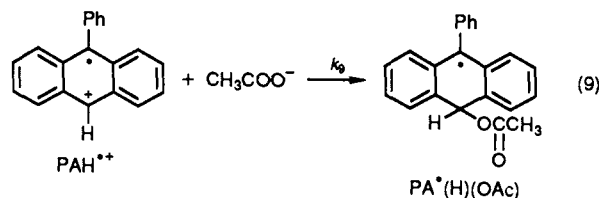


Figure 2. Theoretical prepeak data for the reaction sequence shown in eq 9-11. $\Delta\Delta E_{zc}$ is ΔE_{zc} for the case where $k_{11}/k_9 = \infty - \Delta E_{zc}$ for the rate constant ratio used in the calculation of the data point.

data obtained by digital simulation.

Theoretical Prepeak Data for Cation Radical-Nucleophile Combination Reactions. The derivative linear sweep voltammetry¹¹ response to the mechanism shown in eq 9-11 was calculated by



digital simulation¹² for limiting cases where $k_{11} = 0$ and where $k_{11}/k_9 = \infty$. The differences in zero-crossing potentials of peak O and the prepeak O', ΔE_{zc} (Figure 1), were observed to be 23.9 mV greater for the limiting case where $k_{11}/k_9 = \infty$ than for that where $k_{11} = 0$ with a [nucleophile]/[substrate] ratio of 0.5. Calculations carried out for k_{11}/k_9 ranging from 10^{-5} to 10 at intervals of 2 resulted in ΔE_{zc} values falling smoothly within the range defined by the two limiting cases. The results are plotted in Figure 2. The data for k_{11}/k_9 ranging from 0.000 02 to 2.0 were fit to a fifth-order polynomial equation that predicted ΔE_{zc} to better than 0.2 mV. This allowed the theoretical data to be expanded in order to estimate the deuterium kinetic isotope effect as described in the following section.

Deuterium Kinetic Isotope Effect for the Cation-Nucleophile Reaction. Attack by acetate ion at the 10-position of $\text{PA}^{+\bullet}$, 9-phenylanthracene-10-d cation radical, would be expected to be subject to an inverse secondary deuterium kinetic isotope effect (eq 9-11) by virtue of the sp^2 to sp^3 hybridization change.¹³ Our attempts to study this effect met with the surprising observation of a substantial difference in ΔE_{zc} values, 9.5 mV, during oxidation of PAH and PAD. These results indicate a primary kinetic isotope effect, $k_{\text{H}}/k_{\text{D}}$, of significant magnitude. Neither limiting case, $k_{11}/k_9 = \infty$ or $k_{11}/k_9 = 0$ (eq 9-11), is expected to be subject to a primary deuterium kinetic isotope effect. On the other hand,

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reactions in the transition region between the two limiting cases would be. This causes some uncertainty in the assignment of rate constants from the ΔE_{zc} measurements. For $\Delta E_{zc} = 9.5$ mV, the maximum value of k_{11}/k_9 consistent with the theoretical data for the reaction of $\text{PA}^{\text{D}\bullet+}$ is 0.036. A $k_{\text{H}}/k_{\text{D}} = 25$ is estimated from the theoretical data (Figure 2) if k_{11}/k_9 is assumed to be 0.0275. Assuming rate constant ratios either higher or lower than 0.0275 gives rise to larger values of $k_{\text{H}}/k_{\text{D}}$. For example, $k_{\text{H}}/k_{\text{D}}$ is estimated to equal 35 when the rate constant ratio is assumed to be either 0.126 or 0.0105. For this reason we estimate k_{11}/k_9 to be close to 0.0275 for the reaction of $\text{PAH}^{\bullet+}$ with AcO^- . Under this assumption, the rate constant for the reaction of $\text{PAH}^{\bullet+}$ with AcO^- , k_9 , in $\text{CH}_3\text{CN}/\text{Bu}_4\text{N}^+\text{PF}_6^-$ (0.1 M) at 293 K can be estimated to be $7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, reasonably close to the diffusion-controlled limit.

Mechanism of the Reaction between $\text{PAH}^{\bullet+}$ and Acetate Ion in Acetonitrile. The voltammetric, coulometric, and product studies of the oxidation of PAH in acetonitrile in the presence of acetate ion rule out electron transfer 6 as the initial step in the reaction between $\text{PAH}^{\bullet+}$ and acetate ion.¹⁴ Furthermore, the electron-transfer pathway cannot be detected during reactions of 9-nitroanthracene cation radical, formed at potentials about 600 mV more positive than $\text{PAH}^{\bullet+}$, under similar reaction conditions.

We conclude that steps 9–11 describe the mechanism of the cation radical–anionic nucleophile combination reaction. The formation of a carbon–oxygen bond between the cation radical and the nucleophile (9) is rate determining. The homogeneous electron-transfer reaction (10) is expected to have an equilibrium constant of 10^{10} or greater¹⁷ and must therefore be considered to be essentially irreversible. Reaction 11 then, *cannot* influence the rate of disappearance of the cation radical. On the other hand, it is important to note that acetate ion is the limiting reagent in the prepeak method, and its rate of disappearance will affect the value of ΔE_{zc} providing that reaction 11 is slower than reaction 9. The fact that we observe a primary kinetic isotope effect is indicative that k_{11} is less than k_9 .

Comparison of our experimental and theoretical prepeak data (Figure 2) indicates that the minimum value of $k_{\text{H}}/k_{\text{D}}$ that can be derived from the data is about 25, and this is obtained when k_{11}/k_9 is assumed to equal 0.0275. The ratio could be high as 0.126 and still be consistent with the data. Ratios lower than about 0.0105 require an excessively large deuterium kinetic isotope effect. Therefore, we regard 0.0275 as a reliable estimate of the rate constant ratio.

An apparent deuterium kinetic isotope effect of 25 or greater at 293 K can only be explained by quantum mechanical tunneling.¹⁸ An even greater isotope effect has been observed in an ion–radical reaction involving hydrogen atom abstraction from acetonitrile solvent by diazodiphenylmethane anion radical.¹⁹

Comparing the structures of $\text{PAH}^{\bullet+}$ and $\text{PA}^+(\text{H})(\text{OAc})$ (eq 9–11) gives some insight as to why the former is more reactive toward acetate ion. The cation radical is essentially unhindered toward nucleophilic attack at the 10-position. On the other hand attack by acetate ion at the 9-position of $\text{PA}^+(\text{H})(\text{OAc})$ is severely hindered by the phenyl group and apparently does not take place since a substantial deuterium kinetic isotope effect is observed. Our estimate of 0.0275 for k_{11}/k_9 , along with the deuterium kinetic

isotope effect of 25, indicates that $\text{PAH}^{\bullet+}$ reacts with acetate ion (5) about 10^3 times ($25/0.0275$) as fast as acetate ion removes a deuteron from $\text{PA}^+(\text{D})(\text{OAc})$. This means that nucleophilic attack of acetate ion on $\text{PA}^+(\text{D})(\text{OAc})$, a process that we did not observe, has a rate constant no more than $10^{-4} k_9$. We have previously⁴ found that $\text{PAH}^{\bullet+}$ is 500–7000 times as reactive toward nitrogen-centered nucleophiles as is $\text{DPA}^{\bullet+}$, a comparison eminently relevant to the one discussed here. This leads to the conclusion that the carbocations, $\text{PA}^+(\text{H})(\text{OAc})$ or $\text{PA}^+(\text{D})(\text{OAc})$, are no more reactive toward nucleophilic attack by acetate ion than is $\text{DPA}^{\bullet+}$.

A further detail of our results requires comment. Our source of acetate ion for our kinetic experiments was the homoconjugate salt $\text{Bu}_4\text{N}^+\text{AcO}^-/\text{HOAc}$. The equilibrium constant for the dissociation of AcO^-/HOAc in acetonitrile has been reported to be equal to 0.000 213 at 298 K.²⁰ Under our reaction conditions this corresponds to about 50% dissociation to free acetate ions when the salt concentration is 0.5 mM. As acetate ion is depleted in the diffusion layer, the percent dissociation is expected to increase. Thus, the rate constant we obtain without taking into account incomplete dissociation of the salt, $7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, is a minimum value, and the real value is expected to be somewhere between this and $1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

The results reported here support our earlier view that cation radicals do not exhibit unusually low reactivity toward nucleophiles. It seems highly likely that the reason why some cation radicals react slowly with some neutral nucleophiles originates in unfavorable equilibria for the initial step. This conclusion is supported by the fact that the relative equilibrium constants for the reactions of DPA dication with water and methanol are of the order of 10^{20} times those for reactions of the corresponding cation radical.⁵

Experimental Section

Materials. Reagent-grade acetonitrile was distilled from P_2O_5 before it was passed through a column of active neutral alumina to remove water and protic impurities. Tetrabutylammonium hexafluorophosphate (Aldrich) was recrystallized from dichloromethane–ether before use. Tetrabutylammonium hydrogen diacetate²⁰ was recrystallized from ethyl acetate. 9-Phenylanthracene (Aldrich) was used without further purification and 10-phenyl-10-acetoxy-9-anthrone (**1**) was available from a previous study.⁸ 9-Acetoxy-10-phenylanthracene was prepared according to a published procedure.²¹

Instrumentation and Data Handling Procedures. Other than the potentiostat, a JAS Instrument Systems Model J-1600-B, the instrumentation was similar to that described previously.²² The current–voltage response to a linear potential sweep driven by a Hewlett-Packard HP 3314A function generator was recorded on a Nicolet 310 digital oscilloscope interfaced to a PC. Digital filtering was carried out with a fast Fourier transform routine followed by numerical differentiation.²³ Digital simulation¹² was carried out in Fortran written for the IBM-AT personal computer with the integrated form of the second-order rate law corresponding to the reactions shown in eq 9–11. The electrode potential differences, ΔE_{zc} , were reproducible to ± 0.5 mV corresponding to an uncertainty of the order of 5% in the derived rate constants due to experimental error.

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(14) The recent claim¹⁵ that the reaction between acetate ion and tris(4-bromophenyl)aminium ion is an electron-transfer process has been refuted.¹⁶

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