J. Phys. Chem. A **1998,** *102,* 6503−6512

Remote Substituent Effects on the Reactivity of 9-Aryl- and 9,10-Diarylanthracene Radical Cations with Anions and Amines[1]

Mark S. Workentin*,†

The Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7

Vernon D. Parker¶

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-030

Tracy L. Morkin‡,§ and Danial D. M. Wayner*,‡

Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive Ottawa, Ontario, Canada K1A 0R6

Received: May 4, 1998

Radical cations of 9-aryl- and 9,10-diarylanthracenes with substituents on the 4 position of the aryl rings (PA-$X^{\bullet+}$ and DPA-$X^{\bullet+}$, respectively) have been generated by photoionization in acetonitrile. Their reactivity with *n*-butylamine (*n*-$BuNH_2$) and 1,4-diazabicyclo[2.2.2]octane (DABCO) and a number of anions ($CH_3CO_2^-$, Br^-, CN^-, N_3^-) has been studied using nanosecond laser flash photolysis. Reactions proceed by electron transfer and/or nucleophilic addition. Using PA-X and DPA-X as chemical probes, simple criteria are established that allow one mechanistic pathway to be distinguished from another. When electron transfer is thermodynamically feasible, this pathway dominates (e.g., DABCO and azide). For endothermic electron transfer, addition is not necessarily the preferred ultimate reaction pathway and an inner sphere process (addition/homolysis) can compete. In these cases other, criteria including steric factors and the strength of the incipient bond become important. Simple kinetic criteria and an approach to estimate the thermochemistry of the addition process are developed. It is clear from these studies that reactivity trends in the radical cation chemistry cannot be generalized as easily as those in carbocation chemistry. This has some implications concerning the development and utility of "clock" reactions in radical cation chemistry.

Introduction

The key role of radical cations as intermediates in electron transfer initiated processes and the increased interest in their use in synthetic strategies[2,3] has prompted a number of time-resolved studies of the dynamics of their reaction processes.[2a,4−16] An area of particular interest has been the investigation of the kinetic and mechanistic aspects of the bimolecular reactivity of radical cations with electron rich species,[4−6,13,14,16−20] as well as experimental and theoretical[21] comparisons of their reactivity to the reaction of carbonium ions with the same reactants. A reaction between a radical cation and an electron rich "nucleophilic" species, such as an anion or amine, can proceed by a number of possible competing processes including, nucleophilic addition, proton transfer, and electron transfer. Due to a general lack of information on the thermodynamic and kinetic factors that control the chemistry of radical cations, it is often difficult to predict a priori which of the reaction pathways, if any, will be favored for a particular radical cation−"nucleophile" combination.

Our interest is in developing molecular probes that will allow systematic studies of the dynamics of radical cation reactivity in order to better understand these factors. In this regard, we have found that 9-phenyl- and 9,10-diphenylanthracene derivatives are useful radical cation precursors to study the dynamics and mechanistic aspects of the initial interaction between an aromatic radical cation and a "nucleophilic" species by laser flash photolysis techniques.[5,6] In these systems proton transfer, when possible, has been shown to occur with rates of 10^3 M^{-1} s^{-1} or lower.[19g] Thus, these reactions are not commonly observed because the same base will generally also react by addition or electron transfer. These latter reactions can occur with rate constants approaching the diffusion controlled limit.[6,19] Delineating the competition between electron transfer and addition is complicated because the initial products of each process can be chemically linked or involve a common transition state. For example, an apparent addition process may occur in a single step or by a stepwise electron transfer followed by combination of the oxidized nucleophile with the neutral aromatic. Similarly, an apparent electron transfer reaction could result from an initial addition followed by dissociation of the σ-bonded radical product; a formal inner sphere ET (Scheme 1). Thus, product studies do not necessarily provide unequivocal evidence for any of the possible mechanisms. Furthermore, without a clear indication of the mechanism of the reaction, product studies cannot be used to assign rate constants determined by time resolved techniques to a particular reaction process or be used in competitive quenching experiments where product ratios are used to obtain absolute rate constants using

---

[†] The University of Western Ontario. Email: mworkent@julian.wwo.ca. Fax: (519) 661-3022.

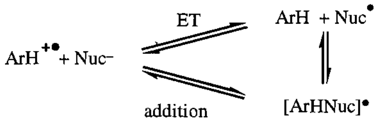
[‡] National Research Council (NRC).

[¶] Utah State University.

[§] NRC WES summer student 1994−95.

S1089-5639(98)02094-5 CCC: $15.00

SCHEME 1



"clock" reactions as has been done extensively in cation−nucleophile reactions.[22]

For a number of years, one of us has been involved in studies examining the reaction of anions and amines with the radical cations of anthracene derivatives by electrochemical techniques.[17−19] The electrochemical method is limited to studies involving those nucleophiles whose redox behavior does not interfere with the generation or observation of the radical cation of the anthracene species. Additionally, an evaluation of the kinetics of the reaction involved in the *initial* interaction between the nucleophile and the radical ion is difficult to evaluate because in the analysis one must consider that the intermediates formed are also electroactive and reactive species. In the majority of these studies, the mechanism for the bimolecular reactions of arylanthracene radical cations with nucleophiles and bases has been interpreted as proceeding through an initial π-complex followed by deprotonation or rearrangement to a σ-bonded complex (eqs 1 and 2). However, no direct evidence for the π-complex is available using the electrochemical methods.

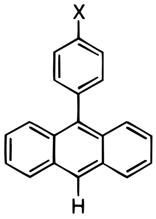
$$\mathrm{ArH}^{+\bullet} + \mathrm{Nuc}^{-} \rightleftharpoons \pi\text{-complex} \qquad (1)$$

$$\pi\text{-complex} \rightarrow [\mathrm{ArHNuc}]^{\bullet}\ \sigma\text{-complex} \qquad (2)$$

In an attempt to provide evidence for the π-complex and to extend the electrochemical studies, we began a time-resolved spectroscopic evaluation of the kinetics of these systems using nanosecond laser flash photolysis techniques. Our studies have shown that the radical cations of 9-phenylanthracene (PA-H) and 9,10-diphenylanthracene (DPA-H) are easily generated by photoionization methods allowing their reactivity with many electron rich species to be studied relatively simply.[5,6] In one of these earlier studies we examined the reactivity of these two radical cations with a number of primary, secondary, and tertiary amines.[6] Primary amines, which are more difficult to oxidize than PA-H and DPA-H, react with both radical cations by nucleophilic addition to the 10-position, forming the corresponding dihydroanthracenyl radicals with rates that depend on the basicity of the amine and steric factors. Tertiary amines, which were in general easier to oxidize than PA-H and DPA-H, react by electron transfer. Secondary amines, whose oxidation potentials were similar to the arylanthracenes, react by both nucleophilic addition and electron transfer with competitive rate constants. In the cases studied, we suggested that the partitioning between the reaction pathways was governed by the relative oxidation potential of the amines and PA-H and DPA-H and by the factors that affect the rates of nucleophilic addition. In none of the cases was direct evidence for a π-complex observed.

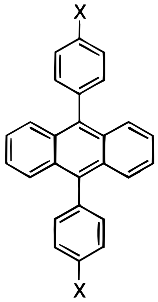
Using relative oxidation potentials to predict the reactivity of the same radical cations with anions is complicated by the lack of reliable standard potentials of anions in aqueous and organic solution, which, unlike the delocalized aromatic radical ions, are highly sensitive to solvent effects. In a preliminary communication we found that azide,[5] which is a nonselective nucleophile used as a clock in carbonium ion chemistry,[22] is a powerful *reducing agent* in its reactivity with PA-H$^{\bullet+}$ and DPA-H$^{\bullet+}$ (and indeed other radical cations) in acetonitrile and proceeds by electron transfer. In contrast, in 2,2,2-trifluoroethanol (TFE) the reaction of the same radical cations with azide is by nucleophilic addition as a result of a +500 mV shift (12 kcal mol^{-1}) in the oxidation potential of N_3^-.

As an extension of our two previous studies we now report absolute kinetic and spectroscopic data for the reactions of a number of anions ($CH_3CO_2^-$, CN^-, Br^-, and N_3^-) and amines (*n*-butylamine and 1,4-diazabicyclo[2.2.2]octane) with the radical cations of para-substituted 9-arylanthracenes (PA-X) and bis-para-substituted 9,10-diarylanthracenes (DPA-X) determined using nanosecond laser flash photolysis techniques. By varying the substituent at the 4-position of the phenyl group at the 9- and 9,10-positions of PA and DPA, we are able to modulate the redox properties of the radical cations in order to evaluate the remote electronic effects on their reactivity. The results of this study allow us to differentiate between nucleophilic addition or electron transfer in the initial interaction between these "nucleophiles" and the aromatic radical cations and provide important insights into the factors that control the reactivity and mechanisms of aromatic radical cations. This study complements other studies of the reactions of these and similar aromatic radical cations and provide important details for those utilizing radical cations in preparative reactions. In particular, we caution against using absolute rate constants obtained for the reaction of radical cations with nucleophilic species as the basis of radical cation clock reactions for competitive quenching experiments analogous to that used in carbocation chemistry.



PA-X

X = -OCH$_3$, -CH$_3$, H, CF$_3$, CN



DPA-X

X = -OCH$_3$, -CH$_3$, H, CN, NO$_2$

Results and Discussion

Generation of Radical Cations. Previously we demonstrated that irradiation of acetonitrile solutions of PA-H and DPA-H using 355 nm laser pulses of a nanosecond laser flash photolysis system generates the corresponding radical cations PA-H$^{\bullet+}$ and DPA-H$^{\bullet+}$ by photoionization (eq 3).[5,6] In the present study, the radical cations PA-X$^{\bullet+}$ and DPA-X$^{\bullet+}$ were generated from their corresponding aryl substituted anthracenes (PA-X or DPA-X) in the same way. This method is advantageous to study the spectroscopy and kinetics of the reactions of the radical cations. Because a sensitizing electron acceptor is not required, there is no interference from strongly absorbing radical anions of those acceptors commonly used as sensitizers (although the solvated electron is eventually captured to form the anthracene anion radical). Only DPA-NO$_2$ did not photoionize under these conditions (or with 266 nm excitation); however, DPA-NO$_2^{\bullet+}$ could be generated using chloranil as an electron-transfer sensitizer.

The transient absorption spectra of the radical cations measured using oxygen saturated acetonitrile (MeCN) solutions exhibit similar features: a relatively intense absorption band centered at 315−320 nm, a weak absorption centered near 420 nm, and a broad, structured absorption band in the 500−750 nm range. Representative spectra, obtained from 1×10^{-4} M

TABLE 1: Absorption Maxima of the Radical Cations of Para-Substituted 9-Aryl- ($PA\text{-}X^{\bullet+}$) and Bis-Para-Substituted 9,10-Diarylanthracene ($DPA\text{-}X^{\bullet+}$)[a] and the Oxidation Potentials[b] of the Corresponding Substituted Arylanthracenes (PA-X and DPA-X) and the Anions/Amines Used in This Study

compound	$E°$/V[c] vs SCE	FE° (kcal mol^{-1})	λ_{max}/nm[d]	nucleophile	$E°$/V vs SCE
PA-OCH_3	1.236	28.5	**315**, 550, 600, **655**	*n*-butylamine	$E_p > 1.6$[g]
PA-CH_3	1.268	29.2	**315**, 590, 645, **710**		
PA-H	1.300	30.0	**315**, 580, 650, **710**	DABCO	0.80[g]
PA-CF_3	1.352	31.2	**320**, 540, 575, 650, **715**		
PA-CN	1.386	32.0	**320**, 540, 580, 655, **715**	acetate, AcO^-	1.78[h]
DPA-OCH_3	1.183	27.2	**320**, 570, 635, **670**	cyanide, CN^-	1.65[i]
DPA-CH_3	1.237	28.5	**320**, 560, 600, **660**,700		
DPA-H	1.270	29.3	**320**, 550, 600, **650**, 720	azide, N_3^-	0.78[j]
DPA-CN	1.394	32.1	**320**, 550, 590, 655, **720**		
DPA-NO_2[e]	*f*		**310**, 600, **735**	bromide, Br^-	1.48[i]

[a] Radical cations generated by 355 nm laser irradiation of *ca.* 1×10^{-4} M solution of PA-X or DPA-X in acetonitrile at 23 °C. [b] Measured in dry acetonitrile/Et_4NClO_4 (0.1 M) at 25 °C. [c] Oxidation potentials measured vs. ferrocene oxidation ($E°(Fc^+/Fc) = 0.448$V vs SCE) Error is ±0.005mV. [d] Error is ±5 nm. Values in bold face are the wavelengths of the absorptions with the highest extinction coefficients at the short and long wavelength bands and are the wavelengths where the kinetics where monitored. [e] Radical cation generated using chloranil as a sensitizer. [f] Oxidation potential not measured. [g] Reference 6. [h] Value from Eberson, L. *Acta Chem. Scand.* **1984**, *B38*, 439 with appropriate correction. See: Eberson, L. In *Electron Transfer in Organic Chemistry*; Springer-Verlag: New York, 1989. [i] Ref 20. Some of the values are reported in DMF and these are assumed to be similar in acetonitrile. In ref 20b, the value for $E°_{CN^\bullet/CN^-}$ is incorrectly listed; the value above is that determined by correcting the standard potential in water using the appropriate values given in the paper. [j] Reference 5.

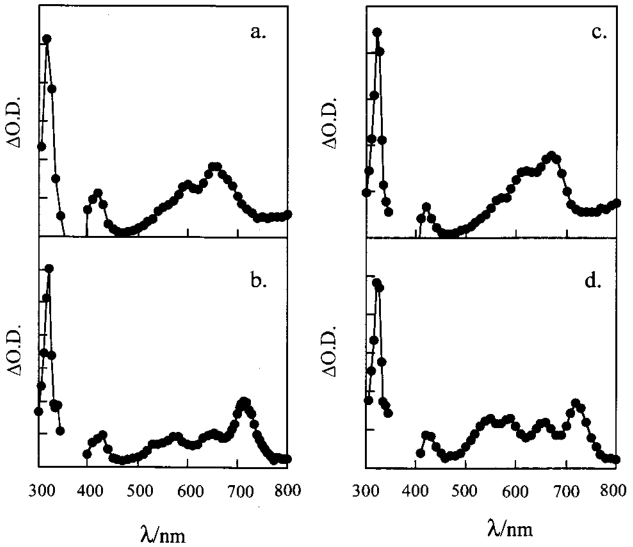


Figure 1. Transient absorption spectra recorded 200−300 ns after 355 nm excitation of 1×10^{-4} M solutions of (a) PA-OCH_3, (b) PA-CN, (c) DPA-OCH_3, and (d) DPA-CN in oxygen saturated acetonitrile solutions at 23 °C.

solutions of PA-OCH_3, PA-CN, DPA-OCH_3, and DPA-CN in MeCN, are shown in Figure 1. The region between 350 and 400 nm is not shown because it is an area of considerable bleaching (i.e., negative ΔOD) of the arylanthracene absorptions. The wavelengths of the absorption maxima of each of the bands observed for $PA\text{-}X^{\bullet+}$ and $DPA\text{-}X^{\bullet+}$ are summarized in Table 1. In nitrogen-saturated solution, the transient absorption spectra are essentially identical except for an increase in absorption intensity around 420−430 nm, which is attributable to a contribution from the triplet states of PA-X and DPA-X.[23] The absorptions at 420−430 nm are the only observable transients in nonpolar solvents, such as hexane (i.e., no photoionization occurs), and in all cases these absorptions are quenched by the addition of oxygen. The contribution to the absorption spectra from the triplet is substrate dependent, typically larger for PA-X than for DPA-X, consistent with the larger values for Φ_{isc} in the former.[24] To minimize interference from the triplet absorption, the kinetic studies described below were performed using air or oxygen saturated solutions, which has no observable effect on the kinetics or spectroscopy of the radical cations themselves.

$$\text{PA-X (DPA-X)} \xrightarrow{h\nu} \text{PA-X}^{\bullet+}\ (\text{DPA-X}^{\bullet+}) + e^-_{\text{solvated}} \quad (3)$$

The para-substituents on the 9- and 10-aryl rings of PA-X and DPA-X affect the relative redox properties. The reversible oxidation potentials ($E°$) of PA-X and DPA-X measured in dried MeCN/Et_4NClO_4 (0.1M) solution measured versus an internal ferrocene (Fc/Fc^+) couple at 298 K are summarized in Table 1; when available they agree with those previously reported.[19f] As expected, the $E°$ values correlate with the Hammett σ^+ parameter. Plots of $(F/2.303RT)E°$ vs σ^+ (for substituents on the 9- and 10-aryl rings) give ρ^+ values of 1.65 ($r = 0.981$) and 1.24 ($r = 0.989$) for PA-X and DPA-X, respectively, suggesting that there may be some saturation of the substituent effects in the DPA-X system.

The kinetics for decay of the radical cations are most easily monitored at wavelengths where the absorptions are most intense (highlighted in boldface in Table 1). In the absence of any added reactant, radical cations decay with approximately second-order kinetics having half-lives of several microseconds. In the less nucleophilic solvent, 2,2,2-trifluorethanol, the lifetimes of the radical cations are increased by a factor of 10 or more. Upon addition of the anions or amines to the solution, the lifetime of the long wavelength absorptions are shortened and the decays become first order. The lifetime of the short wavelength band (320 nm) is also decreased under these conditions (as expected for an absorption due to the same species); however, in some cases the decay kinetics do not appear first order due to the concomitant growth and subsequent decay of product absorptions that overlap with the decay of the radical cation in this region (vide infra).

Bimolecular rate constants for the reaction of $PA\text{-}X^{\bullet+}$ and $DPA\text{-}X^{\bullet+}$ with a number of anions, which include bromide (Br^-), acetate ($CH_3CO_2^-$), cyanide (CN^-), and azide (N_3^-) and the amines *n*-butylamine (*n*-$BuNH_2$) and 1,4-diazabicyclo[2.2.2]-octane (DABCO) were obtained by measuring the pseudo-first-order rate constants for decay (k_{obs}) of the radical cation (typically monitoring the decay of the long wavelength band) as a function of the concentration of added reactant. The observed rate constants for decay increased linearly according to eq 4, where k_0 is the sum of the rate constants for decay of the radical cation in the absence of quencher. The slopes of the plots yield bimolecular rate constants (k_R) for reactions of $PA\text{-}X^{\bullet+}$ and $DPA\text{-}X^{\bullet+}$ (summarized in Table 2). Rate constants for reaction of DPA-NO_2 were not determined since many of

TABLE 2: Second-Order Rate Constants for the Reaction of PA-X$^{\bullet+}$ and DPA-X$^{\bullet+}$ with a Variety of Anions and Amines[a]

	$k_R/10^9$ M^{-1} s^{-1}					
	n-butylamine	DABCO	$CH_3CO_2^-$	CN^-	Br^-	N_3^-
PA-OCH_3	0.66	14	16	8.5	0.035	34
PA-CH_3	1.0	13	18	12	0.06	31
PA-H	1.8	15	20	22	0.075	28
PA-CF_3	1.7	14	25	25	0.11[b]	32
PA-CN	2.2	14	25	24	0.12[b]	38
DPA-OCH_3	0.0060	11	0.044	0.04	0.001	28
DPA-CH_3	0.013	12	1.7	1.6	0.0044	29
DPA-H	0.029	14	2.8	3.1	0.011	25
DPA-CN	0.093	7.0	16	17	0.17	17

[a] Measured in acetonitrile at 25 °C by monitoring the decay of the radical cation. Errors in the rate constants are ca. 10−15%. [b] From growth of the absorption of $Br_2^{\bullet-}$. The overlapping growth of the absorption of $Br_2^{\bullet-}$ at long wavelengths made measuring the decay kinetics of the radical cation difficult over a broad concentration range.

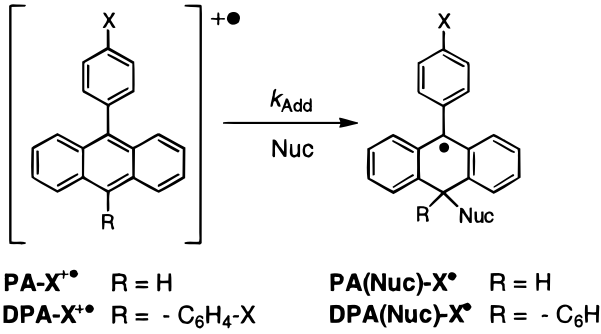
the anions and the amines used in this study reacted readily in a thermal reaction with the chloranil used as a photoinduced electron transfer (PET) sensitizer. Rate constant ratios (k_{PA}/k_{DPA}), comparing the reaction of PA-X$^{\bullet+}$ and DPA-X$^{\bullet+}$ with a particular reactant are given in Table 3.

$$k_{obs} = k_0 + k_R[\mathrm{Nuc}] \tag{4}$$

Reaction with Amines. In the presence of DABCO, the kinetics of decay of both the long and short wavelength absorptions of PA-X$^{\bullet+}$ and DPA-X$^{\bullet+}$ are equivalent. Furthermore, the bleach of the absorption of PA-X and DPA-X between 360 and 400 nm, which occurs as a result of the loss of its absorption on photoionization and formation of the radical cation, recovers completely with kinetics identical to that measured for the decay of the radical cation. This indicates that the reaction of these radical cations with DABCO does not involve any net consumption of the aromatic precursor. These kinetic and absorption spectral features are similar to those described and illustrated in our previous study where the reactivity of PA-H and DPA-H with other amines were examined[6] and are indicative of an electron-transfer reaction from DABCO to the radical cation (eq 5). This was confirmed in all cases by the concurrent growth of a transient absorption, with a maximum at 480 nm, that can be assigned to DABCO$^{\bullet+}$.[6] The rate constants of the reactions of DABCO with PA-X$^{\bullet+}$ and DPA-X$^{\bullet+}$ are all diffusion controlled, consistent with the observation that electron transfer is calculated to be exergonic by at least 8 kcal mol^{-1} for all systems. Furthermore, the rate constant ratios (k_{PA}/k_{DPA}) are equal to 1, indicative of a process insensitive to steric effects. The lack of variation in rate constants can be used as a probe to differentiate between ET and addition in these systems (vide infra).

$$\text{PA-X}^{\bullet+}\ (\text{DPA-X}^{\bullet+}) + \text{DABCO} \xrightarrow{k_{ET}} \text{PA-X (DPA-X)} + \text{DABCO}^{\bullet+} \tag{5}$$

In contrast, the reactivity of PA-X$^{\bullet+}$ and DPA-X$^{\bullet+}$ with *n*-BuNH_2 results in permanent bleaching (on the laser flash time scale) of the absorptions due to PA-X and DPA-X. While the kinetics for decay of the long wavelength absorptions are first order in the presence of amine, the short wavelength absorptions appear more complex due to overlapping growth of a long-lived transient product that also absorbs in this region. Kinetic traces for PA-$OCH_3$$^{\bullet+}$, measured at 315, 385, and 655 nm in the presence of 0.02 M of *n*-BuNH_2 are shown in Figure 2. At this concentration and on this time scale, the radical cation (monitored at 655 nm) is almost completely quenched; the increase in absorption at 315 nm due to the long-lived transient is assigned to the corresponding dihydroanthracenyl radical product (PA(Nuc)-X$^{\bullet}$ or DPA(Nuc)-X$^{\bullet}$) that results from addition of the amine (Nuc = $CH_3(CH_2)_3NH_2$) to the 10-position of the radical cation (eq 6). These species are characterized by an absorption spectrum with a maximum near 330 nm (this absorption maximum varies by ±5 nm as a function of the remote substituent). A transient absorption spectrum measured on the same solution at a time after the signal due to the radical cation is completely decayed in also shown in Figure 2. The position of the absorption maximum and its reactive insensitivity to oxygen is consistent with the known spectra and reactivity of other triphenylmethyl type radicals.[25] Similar spectral features are observed for the reaction of DPA-X$^{\bullet+}$ with *n*-BuNH_2, although the rate constants are found to be 20−110 times slower depending on the substituent (see Table 2). We have previously assigned this rate constant difference between PA-X$^{\bullet+}$ and DPA-X$^{\bullet+}$ to the increased steric interaction in DPA due to the extra substituent at the 10-position where addition is expected to occur.



[6]

A plot of log *k* versus F*E*° for the reactions of DPA-X$^{\bullet+}$ and PA-X$^{\bullet+}$ with *n*-BuNH_2 and DABCO is shown in Figure 3. Examination of this figure and Table 2 show that the reaction of *n*-BuNH_2 with PA-X$^{\bullet+}$ is only slightly sensitive to the electronic nature of the remote substituent; electron donating substituents having slightly lower rate constants for reaction. This limited electronic effect can be rationalized by the apparent leveling off of the rate constants at approximately 2×10^9 M^{-1} s^{-1} as the substituent is made more electron withdrawing. Such a leveling of the rate constants a full order of magnitude below the diffusion-limited rate constant in this solvent (2×10^{10} M^{-1} s^{-1}) has been previously observed for the reaction of amines of varying basicity with PA-H$^{\bullet+}$,[6] the reactions of substituted styrene radical cations with similar amines[4c,d] and for the reactions of diarylcarbocations with amines.[26] If one considers a reaction scheme in which the reactants form an intermediate complex prior to formation of product, then this leveling may result from the competition between dissociation of the complex and product formation (a preequilibrium). Alternatively, we

TABLE 3: Ratio of the Bimolecular Rate Constants, k_{PA}/k_{DPA}, for the Reactions of PA-X$^{\bullet+}$ and DPA-X$^{\bullet+}$ with the Various Anions and Amines[a]

k_{PA}/k_{DPA}	*n*-butylamine	DABCO	$CH_3CO_2^-$	CN^-	Br^-	N_3^-
X = CH_3O	110	1.3	363	213	35	1.2
X = CH_3	77	1.1	11	7.5	14	1.1
X = H	62	1.1	7	7	7	1.1
X = CN	24	2.0	1.6	1.4	0.7	2.2

[a] Calculated from data taken from Table 2.

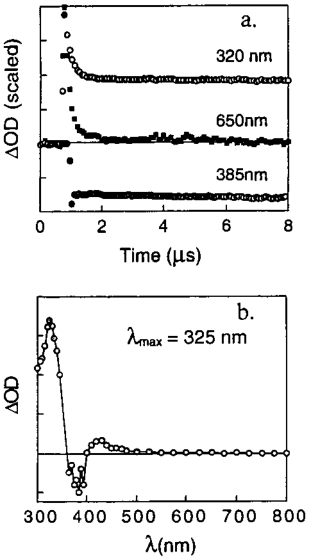


Figure 2. (a) Kinetic traces for PA-OCH$_3$ + 0.02 M *n*-butylamine measured at 320, 385, and 650 nm. (b) Transient absorption spectrum measured on the same sample 2 μs after the laser pulse.

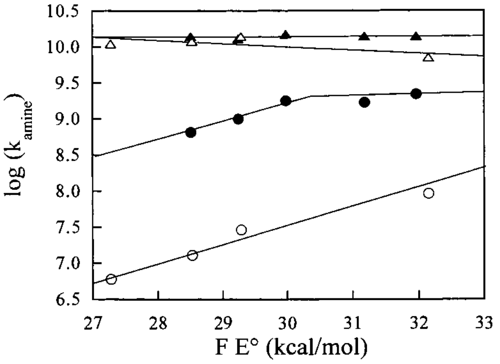


Figure 3. Plot of log(k) versus F$E°$ for the reactions of PA-X$^{•+}$ (solid symbols) and DPA-X$^{•+}$ (hollow symbols) with *n*-butylamine (circles) and DABCO (triangles). Data from Table 2. Lines drawn through data for DABCO are at the diffusion limit. The lines drawn for PA-X with *n*-butylamine are arbitrary, but meant to show the leveling of the rate constants observed at 2 × 10^9 M^{-1} s^{-1}.

previously suggested that in these reactions of hindered radical cations with an amine that the reaction may be entropically controlled and not every diffusional encounter would result in reaction.[6] Because both mechanistic possibilities would exhibit similar activation parameters to those determined for these reactions (small apparent activation energies and low preexponential factors) and because there has been no direct spectral evidence for the formation of an intermediate complex, we are unable to differentiate between these two possibilities. The reaction of DPA-X$^{•+}$ is more sensitive to the electronic effects of the remote substituent as expected for the lower overall reactivity observed in these systems with *n*-BuNH$_2$ due to increased steric interaction at the 10-position. If we account for leveling of the rate constants with *n*-BuNH$_2$ with PA-X$^{•+}$ then, for a given $E°$ value, DPA-X$^{•+}$ reacts approximately 2 orders of magnitude more slowly than PA-X$^{•+}$.

In principle, main features of the reactions of the radical cations with *n*-BuNH$_2$ and DABCO can be used to differentiate between addition and ET in the initial interaction of the same radical cations with anionic species. Criteria used to identify ET include: (i) *complete* recovery of the initial bleach of the radical cation precursors with rate constants identical to the rate constant for decay of the radical cation, (ii) no observation of the growth of a product transient with spectral features characteristic of the addition product dihydroanthracenyl radical, (iii) k_{PA}/k_{DPA} values close to 1, and (iv) the spectral observation of the oxidized form of the amine. Criteria used as an indicator for a nucleophilic addition process include: (i) complete and *permanent* bleaching of the radical cation precursor, (ii) formation of a new long-lived transient dihydroanthracenyl radical with maximum near 330 nm, (iii) k_{PA}/k_{DPA} values significantly greater than 1, and (iv) reaction rate constants significantly faster than those expected for ET based on Marcus theory.

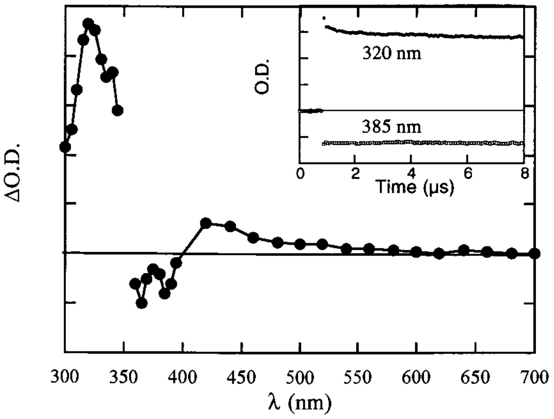


Figure 4. Transient absorption spectrum recorded measured 2 μs after the laser pulse of a sample containing DPA-CN + 1 mM AcO$^-$. Inset shows kinetic traces measured on the same sample at 320 and 385 nm.

Reaction with Anionic Species. *Acetate (AcO$^-$) and Cyanide (CN$^-$).* The kinetic and spectral characteristics of the reaction of acetate with PA-X$^{•+}$ and DPA-X$^{•+}$ are similar to those observed for the reaction with *n*-BuNH$_2$. Addition of acetate results in a product whose absorption spectrum (Figure 4) is consistent with addition (i.e., triarylmethyl-type radicals corresponding to PA(OC(O)CH$_3$)-X$^•$ or DPA(OC(O)CH$_3$)-X$^•$). Furthermore, there is complete and permanent bleaching of the absorption of the radical cation precursors (inset in Figure 4). The rate constants for PA-X$^{•+}$ with acetate are insensitive to electronic factors (all within a factor of less than 2 of each other) and all near the diffusion limit, >10^{10} M^{-1} s^{-1}. The reduction in rate constants expected for DPA-X$^{•+}$ due to steric factors is observed, except for the most reactive DPA-CN$^{•+}$, which reacts close to the diffusion controlled rate. In all cases, the rate constants are several orders of magnitude faster than those expected for outer sphere ET. For easy comparison, a plot of log k vs F$E°$ for the reactions of DPA$^{•+}$ with all anions is shown in Figure 5.

The spectral features observed for the reaction of the radical cations in the presence of cyanide also appear to be those expected for addition. For example, concomitant with the decay of the radical cation is the formation of a new long-lived transient whose absorption spectrum is similar to that observed with acetate or *n*-butylamine as the reactant (Figure 6) and the k_{PA}/k_{DPA} values show the same steric effect as is observed for the reactions with CH$_3$CO$_2^-$ (i.e., approaching a value of 1.0 for the most electron deficient aromatics where the reaction becomes diffusion controlled in both systems). Furthermore, the bleach does not recover with kinetics identical to the decay of the radical cation and all of the rate constants are, again, several orders of magnitude larger than those expected for a simple outer sphere ET.

Interestingly, for PA-X the absorption of the initial product, which we assign to the 10-cyano-9,10-dihydroanthracen-9-yl

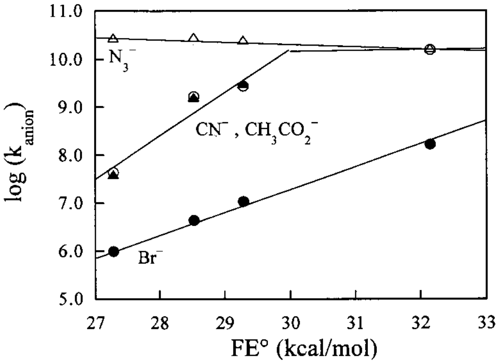


Figure 5. Plot of log(k) versus E° F for the reactions of DPA-X$^{\bullet+}$ with Br$^-$ (●), CN$^-$(▲), CH$_3$CO$_2$$^-$ (○), and N$_3$$^-$ (△). Data from Table 2.

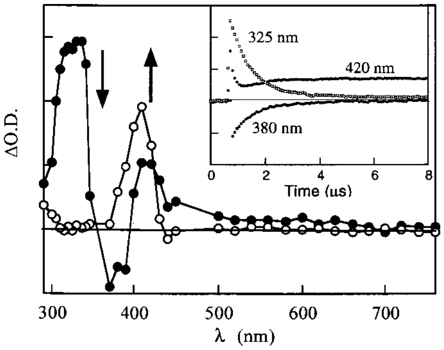


Figure 6. Transient absorption spectra measured for the reaction of PA-OCH$_3$$^{\bullet+}$ with 0.015 M CN$^-$: (●) 100 ns following laser pulse, showing spectrum assigned to PA-OCH$_3$(CN)$^\bullet$; (○) 4 μs after laser pulse, showing spectrum assigned to (CN)$_2$$^{\bullet-}$. Inset shows the kinetic traces measured on the same sample 1 μs after the laser pulse.

radical, is quenched by CN$^-$. This is most noticeable at high CN$^-$ concentrations (higher than is necessary for complete quenching of the radical cation). The bimolecular rate constant for quenching of PACN-X$^\bullet$ by CN$^-$ is 1×10^8 M^{-1} s^{-1} and is relatively insensitive to the substituent on PA-X. What is even more perplexing is that the decay of PACN-X$^\bullet$, monitored at 320 nm, is accompanied by the return of the initial bleach of the PA-X and growth of a new product with a relatively weak absorption and a maximum around 420 nm (Figure 6). This new absorption is similar to the reported spectrum of the pseudohalogen dimer, (CN)$_2$$^{\bullet-}$.[27] In contrast, even at high CN$^-$ concentrations, the initial addition adduct observed for the reaction with DPA(CN)-X$^{\bullet+}$ is *not* quenched by CN$^-$ under our reaction conditions. However, earlier studies by Evans and Blount[28] and Papouchado, Adams, and Feldberg[29] have shown that the product of the reaction of electrochemically generated DPA$^{\bullet+}$ with CN$^-$ is consistent with reduction of the radical cation (greater than 95% DPA recovered) and not cyanide addition. Thus, we expect that, on time scales longer than were investigated here, the recovery of DPA and overall reduction of CN$^-$ should be observed. Unfortunately, we are unable to observe the recovery with the techniques available in our laboratory.

This observation raises an important question regarding how electron-transfer products result from a *bimolecular* reaction with a putative σ-bonded radical intermediate (i.e., C−Nuc). In addition, the mechanism must account for the difference in apparent reactivity between PA(CN)-X$^\bullet$ and DPA(CN)-X$^\bullet$. There are at least three possibilities to rationalize the results. The first is a formal inner sphere ET in which the initially proposed σ-bonded radical product (PA(CN)-X$^\bullet$ or DPA(CN)-X$^\bullet$) is a weakly bound complex that is in equilibrium with PA-X (DPA-X) and CN$^\bullet$ (eqs 7 and 8, Nuc = CN); the latter then can combine with excess CN$^-$ in solution to form (CN)$_2$$^{\bullet-}$ (eq 9, Nuc = CN), presumably a diffusion controlled reaction.[30]

$$\text{PA-X}^{\bullet+} + \text{Nuc}^- \rightleftharpoons \text{PA(Nuc)-X}^\bullet \tag{7}$$

$$\text{PA(Nuc)-X}^\bullet \rightleftharpoons \text{PA-X} + \text{Nuc}^\bullet \tag{8}$$

$$\text{Nuc}^\bullet + \text{Nuc}^- \rightarrow (\text{Nuc})_2^{\bullet-} \tag{9}$$

The second alternative is a reaction in which the initial addition (k_7) is reversible (k_{-7}) and competes with a slow, endergonic outer sphere electron-transfer reaction (eq 10); the CN$^\bullet$ formed in this slow reaction then reacts with excess CN$^-$ at the diffusion controlled rate (eq 9).

$$\text{PA-X}^{\bullet+} + \text{Nuc}^- \rightarrow \text{PA-X} + \text{Nuc}^\bullet \tag{10}$$

Both of these alternatives require that the PA(CN)-X$^\bullet$ adduct radical be only weakly bound so that eqs 7 and 8 are reversible on the experiments time scale. The C−CN bond energy for PA(CN)-X$^\bullet$ can be roughly estimated as the difference between the C−CN bond energy in 10-cyano-9-phenyl-9,10-dihydroanthracene (ca. 103 kcal mol^{-1}, based on group additivities) and the triplet energy of 9-phenylanthracene (42 kcal mol^{-1}). The value of 61 kcal mol^{-1}, even given substantial error in the approximation, is too strong for the addition to be expected to be reversible (eq 7) or for homolysis (inner sphere ET, eq 8) to occur. This simple approximation gives the correct value for the C−H bond of the 9,10-dihydroanthracen-9-yl radical (ca. 40 kcal mol^{-1}) and what appears to be reasonable values for the PA(Y)-X$^\bullet$ radicals for Y = CH$_3$CO$_2$$^-$ (25 kcal mol^{-1}) and Y= Br (13 kcal mol^{-1}). The preceding thermochemical assessment was based on the assumption that the addition resulted in the formation of a C−CN bond. In principle, formation of a C−NC bond cannot be ruled out. In fact, the C−NC bond is significantly weaker than the C−CN bond (by ca. 23 kcal mol^{-1}). However, that would still leave a bond with a dissociation energy on the order of 40 kcal mol^{-1}.

The large bond energies appear to rule out an inner sphere (i.e., addition/homolysis) or reversible process. Thus the only remaining option is a bimolecular reaction between CN$^-$ and PA(CN)-X$^\bullet$. While the conclusion is inescapable, the reaction itself seems to be unprecedented. Two possibilities consistent with the apparent steric effect are direct reaction of CN$^-$ with the σ-bonded nitrile or isonitrile (PA(CN)-X$^\bullet$ or PA(NC)-X$^\bullet$). While the reaction with an isonitrile seems more plausible, we have no evidence that favors one intermediate over the other. This S$_N$2-like mechanism is consistent with the apparent lower reactivity of the DPA(CN)-X$^\bullet$ radical which would be entropically inhibited since substitution would be accompanied by flattening of an sp^3 carbon which requires rotation of the aryl ring. Furthermore, as pointed out above, these results also are consistent with the apparent DPA mediated electrochemical oxidation of CN$^-$.[28,29]

Why does the same reaction not occur after addition of CH$_3$CO$_2$$^-$? In the case of acetate the initially formed radical intermediate (PA(OC(O)CH$_3$)-X$^\bullet$) appears to be more weakly bonded than the nitrile analogue or isonitrile analogue (the C−O bond energy is estimated to be 28 kcal mol^{-1}, see above). Estimated bond dissociation energies of Et−OC(O)CH$_3$ (85 kcal mol^{-1}), Et−CN (120 kcal mol^{-1}), and Et−NC (98 kcal mol^{-1})[31] also are in agreement with this order. As was the case for CN$^-$, the addition is expected to be completely irreversible so the more simple inner sphere mechanisms (eqs 7−9, Nu =

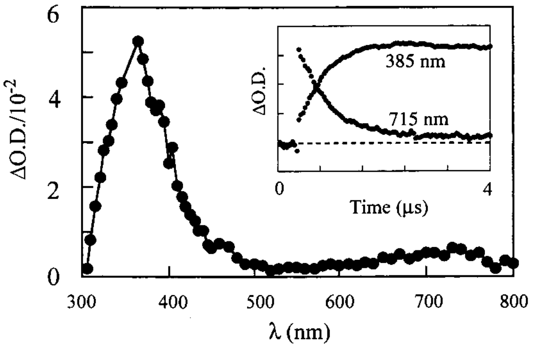


Figure 7. Transient absorption spectrum of $Br_2^{\bullet -}$ measured from photolysis of an air-saturated solution of 1×10^{-4} M PA-CN in the presence of 0.02 M Br^- and recorded 2 μs after the laser pulse. Inset shows kinetic traces showing decay of PA-$CN^{\bullet +}$ (measured at 715 nm) and the growth of $Br_2^{\bullet -}$ (measured at 385 nm) measured in the presence of 0.02M Br^-.

$CH_3CO_2^-$) can be ruled out. Acetate is more difficult to oxidize than CN^- so the overall energetics for the electron transfer, including a competing outer sphere mechanism (eq 10) are less favorable than for CN^-. Furthermore, the formal dimer ($X_2^{\bullet -}$), which stabilizes the halogens and pseudohalogens, lies on a completely dissociative surface in the case of acetate (i.e., the formal dissociative reduction product of acetyl peroxide). Thus, the dimerization that provides an additional driving force for cyanide is not available to acetate. In addition, the resulting carbonyloxyl radical is known to decarboxylate on the nanosecond time scale, so methylated products should be isolated preparatively if any of these processes should occur. Parker has shown that acetate reacts with PA-$H^{\bullet +}$ to yield formal acetate addition products.[18b]

Bromide. In the presence of Br^- the decay of the radical cations is accompanied by a complete return of the bleach and a growth of a new long-lived transient in the same region. In all cases, the growth kinetics measured at 385 nm matched the decay of the radical cations at all concentrations of Br^-. Representative kinetic traces and an absorption spectrum obtained in the presence of sufficient Br^- to quench the radical cation are shown in Figure 7. The spectrum, characterized by a λ_{max} at 365 nm, is identical to the spectrum observed by Scaiano et al on irradiation of vicinal dibromides in the presence of Br^- and is readily assigned to the well-known radical anion dimer, $Br_2^{\bullet -}$.[32] The latter is formed by the reaction of $Br^\bullet$ with excess Br^- in solution, which is known to occur with a rate constant of 1.6×10^{10} M^{-1} s^{-1} in MeCN with an equilibrium constant of 10^5 M^{-1}.[32]

Based on the relative redox potentials the reaction with bromide ion might be predicted to be by nucleophilic addition to yield the σ-bonded dihydroanthracenyl radical type product $[PA(Br)\text{-}X]^\bullet$ or $[DPA(Br)\text{-}X]^\bullet$. However, this reaction is isoelectronic with the reaction of $Br^\bullet$ with the neutral PA-X or DPA-X which is known to favor the formation of a π-complex.[33] Thus if the ET mechanism is to be an inner sphere process, as discussed for CN^- (eq 7−9, Nuc = Br) and discussed previously for addition of Br^- to 1,3-dioxole radical cations,[15a] it must proceed via the π-complex. Our spectroscopic evidence is consistent with an ET process with rate determining endothermic electron transfer followed by Br atom reaction with excess Br^- as shown in eqs 9 and 10 (Nuc = Br).

Interestingly, the steric effects (suggested by the k_{PA}/k_{DPA} values) are usually indicative of an addition mechanism. However in this case the rate constants for outer sphere electron transfer to DPA-$X^{\bullet +}$ from Marcus theory are within a factor of 2 of the experimental values. Thus, for DPA-X, the variation in rate constant as a function of substituent simply reflects the change in the driving force. This distinguishes the reactions of bromide from the reactions of n-$BuNH_2$, cyanide, and acetate which react many orders of magnitude faster than the predicted outer sphere electron-transfer rate.

The variation in rate constant for reaction of bromide with PA-$X^{\bullet +}$ is smaller than predicted, based on a simple outer sphere mechanism. This decreased sensitivity to substituent and the source of the apparent steric effect may point to some inner sphere character in these reactions. In an attempt to observe the formation of the $Br^\bullet$/PA-X (DPA-X) π-complex, Br atoms were generated in the presence of PA-X and DPA-X by photolysis of α-bromoacetophenone (eq 11). No evidence for π-complex formation was obtained. What was observed was the growth of the absorption due to formation of the radical cation of the aromatics, formed by an exothermic ET (k_{-8}, eq 8, Nuc = Br). The rate constant k_{-8} was determined to be 3×10^{10} M^{-1} s^{-1} (i.e., diffusion controlled) by monitoring the growth of the radical cation as a function of [PA-X] or [DPA-X].

$$C_6H_5COCH_2Br \xrightarrow{h\nu} C_6H_5COCH_2^\bullet + Br^\bullet \qquad (11)$$

These experiments together with the ones summarized in Table 2 provide both the forward and reverse rate constants for reaction 10 allowing ΔG_{10} values to be calculated ($\Delta G_{10} = -RT \ln K_{10} = -F\Delta E°$). These values agree well with those calculated from $\Delta E°$ values ($E°(Br^-) - E°(PA\text{-}X) = \Delta G_{10}/23.06$) obtained from electrochemical measurements. For example, the ΔG_{10} value for PA-H obtained from the K_{10} value is 3.6 kcal mol^{-1} compared to the value of $\Delta E°$ from cyclic voltammetry of 4.1 kcal mol^{-1}. Similarly, for DPA-H the calculated and experimental values are 4.7 and 4.8 kcal mol^{-1}, respectively. Considering the close agreement between the experimental and estimated rate constants (within a factor of 2 for DPA-X and a factor of 10 for PA-X from Marcus theory) and the $\Delta E°$ values (within ±50 mV for all but one; PA-OCH_3 which is within 70 mV), there is no need to invoke the intermediacy of a π-complex in this reaction.

The results of electron-transfer reaction of these aromatic radical cations with Br^- is in sharp contrast to that of the nucleophilic substitution reported by Schepp and Johnston for the reaction of substituted styrene radical cations with Br^- in the same solvent, even though ET is thermodynamically more favorable in those systems than in the system described here (although still mainly slightly endothermic, depending on substituents).[4a] This difference is likely explained by the differences in the C−Br bond strength in the two different type of radical products; in their case, addition generates a β-bromophenethyl radical with an equilibrium constant (k_{add}/k_{-add}) of 5000 M in MeCN.[4a]

Azide. Reaction of N_3^- with our radical cations also exhibit the spectral and kinetic features expected for an electron-transfer reaction: complete recovery of bleach with identical kinetics to the decay of the radical cation (Figure 8) and no observation of a long-lived radical addition product at 320 nm. Azide had often been assumed to react with radical cations by nucleophilic addition by analogy to the reactivity of unstable carbonium ions. This assumption may have been due in part to some inconsistencies in the reported values for the oxidation potential of azide in solution. However, our recent work[5] and that of Wendt[34] has made it clear that in acetonitrile azide has a relatively low oxidation potential (0.775 V vs SCE) and will act as an efficient

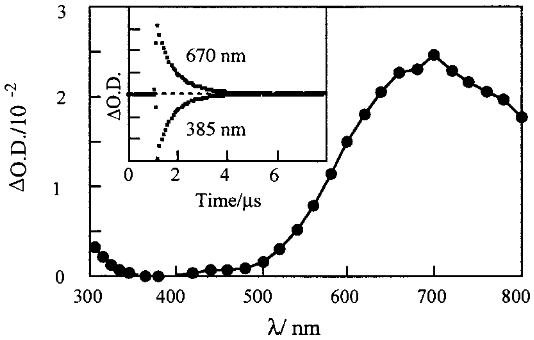


Figure 8. Transient absorption spectrum of $N_6^{\bullet-}$ measured from photolysis of an air-saturated solution of 1 × 10^{-4} M DPA-OCH$_3$ in the presence of 6 mM azide and recorded 1 μs after the laser pulse. Inset shows kinetic traces showing decay of DPA-OCH$_3^{\bullet+}$ (measured at 650 nm) and the complete recovery of the initial bleach of the absorption of DPA-OCH$_3$ (measured at 385 nm) measured in the presence of 0.5 mM azide.

reducing agent with all radical cations with an $E°$ greater than ca.0.8 V vs SCE.[5] In all cases presented here the driving force for electron transfer ($E°(N_3^-) - E°$ (PA-X$^{\bullet+}$ or DPA-X$^{\bullet+}$) is at least 9 kcal mol^{-1} exergonic. In addition to the kinetic evidence we also obtain spectroscopic evidence for the formation of $N_3^\bullet$. The absorption of the azidyl radicals produced by the ET is not observed directly, however $N_3^\bullet$ reacts with excess azide at the diffusion controlled rate to form the unusual pseudo-halogen radical anion dimer $N_6^{\bullet-}$ by a reaction strictly analogous to the case of bromide.[5,35,36] Unlike the formation of $Br_2^{\bullet-}$, the growth of $N_6^{\bullet-}$ is not observed because the equilibrium constant for its formation is about 3 orders of magnitude lower than that for $Br_2^{\bullet-}$ and is not a strong enough absorption to observe at room temperature at the low concentrations of N_3^- required for complete quenching of the radical cation.[35] However, at higher concentrations a strong absorption is observed at 700 nm and has unequivocally been assigned to $N_6^{\bullet-}$ (Figure 8).[35]

Summary

Our results indicate that the mechanism for the initial interaction for the radical cation/nucleophile combination can be described by the general mechanism illustrated in Scheme 2. The initial partitioning between addition and ET can often be predicted by the relative redox potentials of the radical cation and the anion or amine. When these values are known they provide an estimate for the driving force for ET. When the driving force for ET is exergonic, this pathway will dominate. This was illustrated by the reactions of PA-X$^{\bullet+}$ and DPA-X$^{\bullet+}$ with DABCO and N_3^-. The reverse is not true; in other words, if the driving force for ET is endergonic, addition is not necessarily the preferred reaction pathway. In this case other criteria including steric factors and the strength of the incipient bond become important. Thus, using PA-X and DPA-X as chemical probes, we have been able to establish simple criteria to delineate one mechanism from another. For electron-transfer one should observe (i) *complete* recovery of the initial bleach of the radical cation precursors with rate constants identical to the rate constant for decay of the radical cation, (ii) absence of the growth of a product transient with spectral features characteristic of the addition product dihydroanthracenyl radical, and (iii) the spectral observation of the oxidized form of the anion/amine (when a clear spectroscopic signature is available). For nucleophilic addition one should observe the following: (i) complete and *permanent* bleaching of the radical cation precursor, (ii) formation of a new long-lived transient dihydroanthracenyl radical with maximum near 330 nm, and (iii) reaction rate constants significantly faster than those expected for ET based on Marcus theory. In some cases the rate constant ratio (k_{PA}/k_{DPA}) can also be diagnostic. For example, (i) if k_{PA}/k_{DPA}= 1 and the rate constants are less than diffusion controlled then the reaction must be ET or (ii) if $k_{PA}/k_{DPA} \neq 1$ and one of the values is diffusion controlled, then the reaction must be an addition. Alternatively, if $k_{PA}/k_{DPA} = 1$ and both rate constants are diffusion controlled or if $k_{PA}/k_{DPA} > 1$ and neither rate constant is diffusion controlled, then other criteria must be used to decide the mechanism. Examples illustrating these criteria are found in Tables 2 and 3.

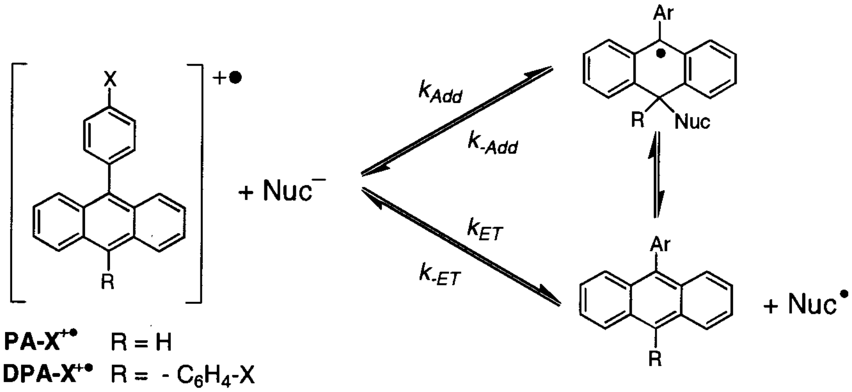
Only n-BuNH$_2$, acetate, and cyanide gave direct spectroscopic evidence for the initial formation of the addition to the radical cation at the 10 position forming the dihydroanthracenyl radical. In these cases, the trends in the rate constants for the addition exhibited the usual factors expected for addition reactions: steric effects illustrated by the k_{PA}/k_{DPA} and the effect of the remote substituent altering the electrophilicity of the cationic center of the radical cation, especially in DPA-X, where the rate constants were lower than the diffusional limit due to the steric effect. Remote substituents tend to modulate the electrophilicity and, thus, the nucleophilic reactivity of the radical cation (i.e., the reactivity increases as the electron demand of the substituent increases). This modulation of reactivity by the substituent is also apparent for the endergonic ET reactions with Br^- where the substituent acts to alter the redox property of the PA-X (DPA-X) and thus the driving force for ET. In no case was there direct spectroscopic evidence for the formation of a π-complex prior to the formation of the C−X bond. However, it is important to note that this does not exclude complex formation as the first step in the reaction.

For endergonic electron-transfer processes the stability of the dihydroanthracenyl radical adduct can be estimated from the difference between the triplet energy of PA-H (42 kcal mol^{-1}) and the C−Nuc bond energy in the 10-Nuc-9-phenyl-9,10-dihydroanthracene. This bond energy can often be estimated using group additivities. For example, in the case of acetate, the bond energy is estimated to be ≈25 kcal mol^{-1} (eq 8). Thus the adduct is stabilized by about 15 kcal mol^{-1} with respect to the ion pair (eq 7, $\Delta H_7 \approx \Delta H_8 - F\Delta E°$).

Photoinduced electron transfer and electrochemical methods have been used to successfully prepare substitution products from addition of CN^-,[37] acetate,[18b] amines,[38] and other electron rich species to aromatic radical cations.[39] The efficiency of the reaction to yield addition products varies dramatically as a function of the aromatic precursor and the reaction conditions. This is generally explained by the redox potentials of the reaction partners involved and by the relative nucleophilicities. However, the present results (especially those with CN^-) caution against these generalizations. Ultimately, the products observed in these radical cation/nucleophile reactions will not only depend on the mechanism of the initial interaction, but also on the fate of the initial formed intermediates, which can either be the radical adduct formed on addition or the aromatic radical cation precursor and the oxidized form of the anion/amine formed by ET.

The primary purpose of this study was to understand the factors that control the competition between addition and electron transfer in the initial interaction between an electron rich species with an aromatic radical cation. Our studies have shown that knowledge of these processes and their rate constants do not necessarily allow one to design appropriate conditions to maximize yields in preparative reactions. Clearly, any

SCHEME 2



synthetic strategy requires kinetic and mechanistic information for the reaction pathways of the intermediates formed in the initial reaction. Furthermore, the results illustrate the complexities of comparing of the reactivity of olefin radical cations to aromatic radical cations; the reactivity does not only depend on relative redox potentials. Mechanistic studies continue to provide insights into the reactivity of radical cations with electron rich species. It is clear from our studies much work needs to be done before generalizations, such as those used in carbocation chemistry, can be made with radical cations. This has important ramifications particularly in that the development of "clock" reactions in radical cation chemistry.

Experimental Section

The compounds 9-phenyl- and 9,10-diphenylanthracene were commercially available from Aldrich. The remaining 9-aryl- and 9,10-diarylanthracenes were prepared by methods reported separately.[24] Each were purified by column chromatography and repeated recrystallizations and were verified to be of high purity using standard analytical methods. In addition, all compounds were of sufficient purity that time-resolved fluorescence measurements exhibit a single-exponential decay.[24]

The tetrabutylammonium salts of cyanide, acetate, bromide, (all from Aldrich), chloride and azide (TCI) were used as received. DABCO and *n*-butylamine (Aldrich) were purified prior to use. Acetonitrile (BDH, OmniSolv) and 2,2,2-trifluoroethanol were used as received for the NLFP experiments unless otherwise specified. For the electrochemical measurements MeCN was fractionally distilled over calcium hydride prior to use. Tetraethylammonium perchlorate was recrystallized 3 times from ethyl acetate:hexane (9:1) and dried prior to use.

Laser Flash Photolysis. Nanosecond laser flash photolysis experiments employed the pulses from a Lumonics HY750 Nd^{3+}: YAG laser (355 nm, 20 mJ/pulse, 20 ns pulse width) and a computer controlled detection system that has been described elsewhere.[40] Solutions of PA-X and DPA-X were prepared at concentrations such that the absorbance at the excitation wavelength was 0.4−0.5. Samples were contained in rectangular 7 × 7 mm^2 Suprasil quartz cells. Transient absorption spectra were measured employing a flow system which ensured a fresh volume of sample was irradiated by each laser pulse. Experiments using nitrogen or oxygen saturated solutions were prepared by bubbling a dry stream of the appropriate gas through the solution for at least 10 min. Quenching rate constants were measured on static samples, at ambient temperature (23−25 °C) on air saturated solutions unless specified otherwise. Quenchers were added directly to the sample by microliter syringe as aliquots of an appropriate solution of the quencher in MeCN or as the neat compound.

Cyclic Voltammetry. Electrochemical measurements were made using a standard three electrode single cell arrangement and an E. G. & G. model 173 Potentiostat interfaced to a Tektronix digital oscilloscope. In our arrangement the pseudo reference electrode was a Ag wire in electrolyte solution, the working electrode was a glassy carbon disk (0.5 mm), and a platinum wire was used as the counter electrode. Samples were purged with argon while stirring prior to data acquisition. Measurements were made on 1−2 mM samples in MeCN containing 0.1 M tetraethylammonium perchlorate as the supporting electrolyte. Peak potentials were referenced internally to the ferrocene (Fc^+/Fc) couple and converted to SCE ($E°(Fc^+/Fc) = 0.448$ V vs SCE).

Acknowledgment. V.D.P. thanks the National Science Foundation (Grant CHE-9708935) for financial support and M.S.W. thanks the Natural Sciences and Engineering Research Council of Canada for financial support. The authors also thank Dr. L. J. Johnston (NRC) for use of the LFP facility.

References and Notes

(1) Issued as NRCC publication #40881.

(2) (a) Schmittel, M.; Burghart, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2550−2589. (b) Fox, M. A., Chanon, M., Eds. *Photoinduced Electron Transfer*, Elsevier: Amsterdam, 1988; Parts A−D. (c) Roth, H. D. *Top. Curr. Chem.* **1992**, *163*, 133−245.

(3) (a) Yoon, U.-C.; Givens, R. S. In *Advances in Electron-Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press, Inc.: New York, 1994; Vol. 4. (b) Bauld, N. L. In *Advances in Electron-Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press Inc.: New York, 1992; Vol. 2. (c) Lewis, F. D. In *Advances in Electron-Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press, Inc.: New York, 1996; New York, 1996; Vol. 5. (d) Cossy, J.; Pete, J.-P. In *Advances in Electron-Transfer Chemistry*; Mariano, P. S. Ed.; JAI Press, Inc: New York, 1996; Vol. 5.

(4) (a) Johnston, L. J.; Schepp, N. P. *J. Am. Chem. Soc.* **1993**, *115*, 6564−6571. (b) Schepp, N. P.; Johnston, L. J. *J. Am. Chem. Soc.* **1994**, *116*, 6895−6903 (c) Johnston, L. J.; Schepp, N. P. *Pure Appl. Chem.* **1995**, *67*, 71−78. (d) Johnston, L. J.; Schepp, N. P. In *Advances in Electron-Transfer Chemistry;* Mariano, P. S., Ed.; JAI Press, Inc.: New York, 1996; Vol. 5, pp 41−102. (e) Schepp, N. P.; Johnston, L. J. *J. Am. Chem. Soc.* **1994**, *116*, 10330−10331. (f) Schepp, N. P.; Johnston, L. J. *J. Am. Chem. Soc.* **1996**, *118*, 2872−2881.

(5) Workentin, M. S.; Schepp, N. P.; Johnston, L. J.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1994**, *116*, 1141−1142.

(6) Workentin, M. S.; Johnston, L. J.; Wayner, D. D. M.; Parker, V. D. *J. Am. Chem. Soc.* **1994**, *116*, 8279−8287.

(7) (a) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P.; Mattes, S. L. *J. Am. Chem. Soc.* **1989**, *111*, 8973−8975. (b) Dinnocenzo, J. P.; Todd, W. P.; Simpson, T.; Gould, I. *J. Am. Chem. Soc.* **1990**, *112*, 2462−2464. (c) Todd, W. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R. *Tetrahedron Lett.* **1993**, *34*, 2863.

(8) (a) Maslak, P.; Vallombroso, T. M.; Chapman, W. H., Jr.; Narvaez, J. N. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 73−75. (b) Maslak, P. *Top. Curr. Chem.* **1993**, *168*, 1−46 and references therein.

(9) Sankararaman, S.; Perrier, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 6448−6449.

(10) (a) Masnovi, J. M.; Sankararaman, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 2263−2276. (b) Bobrowski, K.; Das, P. K. *J. Phys. Chem.* **1985**, *89*, 5079−5085.

(11) (a) Anne, A.; Hapiot, P.; Moiroux, J.; Neta, P.; Savéant, J.-M. *J. Phys. Chem.* **1991**, *95*, 2370−2377. (b) Anne, A.; Hapiot, P.; Moiroux, J.; Neta, P.; Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 4, 4694−4701.

(12) Baciocchi, E.; Del Giacco, T.; Elisei, F. *J. Am. Chem. Soc.* **1993**, *115*, 12290−12295.

(13) Neiminen, K.; Niiranen, J.; Lemmetyinen, H.; Sychtchikova, I. *J. Photochem. Photobiol. A* **1991**, *61*, 235−243.

(14) Brede, O.; David, F.; Steenken, S. *J. Chem. Soc., Perkin Trans. 2* **1995**, 23−32.

(15) (a) Trampe, G.; Mattay, J.; Steenken, S. *J. Phys. Chem.* **1989**, *93*, 7157−7160. (b) Steenken, S.; Warren, C. J.; Gilbert, B. C. *J. Chem. Soc., Perkin Trans. 2*, **1990**, 335−342.

(16) Koike, K.; Thomas, J. K. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 195−200.

(17) (a) Parker, V. D. *Acc. Chem. Res.* **1984**, *17*, 243−250. (b) Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, 55−189.

(18) (a) Parker, V. D.; Tilset, M. *J. Am. Chem. Soc.* **1987**, *109*, 2521−2523. (b) Reitstöen, B.; Norrsell, F.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 1, 8463−8465. (c) Parker, V. D.; Reitstöen, B.; Tilset, M. *J. Phys. Org. Chem* **1989**, *2*, 580−584. (d) Wang, H.; Zheng. G.; Parker, V. D. *Acta Chem. Scand.* **1995**, *49*, 311−312.

(19) (a) Reitstöen, B.; Parker, V. D. *J. Am. Chem. Soc.* **1991**, *113*, 6954−6958. (b) Norrsell, F.; Handoo, K. L.; Parker, V. D. *J. Org. Chem.* **1993**, *58*, 4929−4932. (c) Reitstöen, B.; Parker, V. D. *Acta Chem. Scand.* **1992**, *46*, 464−468. (d) Parker, V. D.; Chao, Y.; Reitstöen, B. *J. Am. Chem. Soc.* **1991**, *113*, 2336−2338. (e) Reitstöen, B.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 4968−4969. (f) Parker, V. D.; Pedersen, M.; Reitstöen, B. *Acta Chem. Scand.* **1993**, *47*, 560−564. (g) Xue, J.; Parker, V. D. *J. Org. Chem.* **1994**, *59*, 6564−6566. (h) Parker, V. D.; Chao, Y. T.; Zheng, G *J. Am. Chem. Soc.* **1997**, *119*, 11390−11394.

(20) (a) Wayner, D. D. M. In *Handbook of Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, 1989; Vol. II, Chapter 18. (b) Savéant, J.-M. *J. Phys. Chem.* **1994**, *98*, 3716−3724.

(21) (a) Shaik, S.; Pross, A. *J. Am. Chem. Soc.* **1989**, *111*, 4306. (b) Shaik, S. *Prog. Phys. Org. Chem.* **1985**, *15*, 197.

(22) For examples, see: (a) Amyes, T. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 7888−7900. (b) Richard, J. P. *J. Am. Chem. Soc.* **1989**, *111*, 1455−1465 and references therein (c) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 8238−8248. (d) Fishbein, J. C.; McClelland, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 2824−2825. (e) McClelland, R. A.; Kanagasabapathy, V. M.; Banait, N. S.; Steenken, S. *J. Am. Chem. Soc.* **1991**, *113*, 1009−1104 and references cited.

(23) Carmichael, I.; Helman, W. P.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1987**, *6*, 239.

(24) Morkin. T. L.; Magri, D.; Workentin, M. S. Manuscript in preparation.

(25) Chatgilialogula, C. In *Handbook of Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. II, Chapter 1.

(26) McClelland, R. A.; Kanagasabapathy, V. M.; Banait, N. S.; Steenken, S. *J. Am. Chem. Soc.* **1992**, *114*, 1816−1823.

(27) (a) Draganic, I. G.; Draganic, Z. D.; Holroyd, R. A. *J. Phys. Chem.* **1971**, *75*, 608−612. (b) Martins, L. J. A. *J. Chem. Soc., Faraday Trans 1* **1982**, *78*, 533−543.

(28) Evans, J. F.; Blount, H. N. *J. Am. Chem. Soc.* **1978**, *100*, 4191−4196.

(29) Papouchado, L.; Adams, R. N.; Feldberg, S. W. *J. Electroanal. Chem.* **1969**, *21*, 408.

(30) Nagarajan, V.; Fessenden, R. W. *J. Phys. Chem.* **1985**, *89*, 2330−2335.

(31) Griller, D.; Kanabus-Kaminska, J. M.; Maccoll, A. *J. Mol. Struct. (THEOCHEM)* **1988**, *163*, 125.

(32) Scaiano, J. C.; Barra, M.; Krzywinski, M.; Sinta, R.; Calabrese, G. *J. Am. Chem. Soc.* **1993**, *115*, 8340−8344.

(33) Raner, K. D.; Lusztyk, J. Ingold, K. *J. Phys. Chem.* **1989**, *93*, 564−570.

(34) Plazk, V.; Wendt, H. *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 481−495.

(35) Workentin, M. S.; Wagner, B. D.; Negri, F.; Zgierski, M.; Lusztyk, J.; Siebrand, W.; Wayner, D. D. M. *J. Phys. Chem.* **1995**, *99*, 94−101.

(36) Workentin, M. S.; Wagner, B. D.; Lusztyk, J.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1995**, *117*, 119−126.

(37) (a) Yasuda, M.; Pac, C.; Sakurai, H. *J. Chem. Soc.*, *Perkin Trans. 1* **1981**, 746−750. (b) Andreades, S.; Zahnow, E. W. *J. Am. Chem. Soc.* **1969**, *91*, 4181−4190. (c) Cauquis, G.; Serve, D. *Bull. Soc. Chim. France* **1979**, *2*, 145.

(38) (a) Yasuda, M.; Matsuzaki, Y.; Shima, K.; Pac, C. *J. Chem. Soc., Perkin Trans. 2* **1988**, 745−750. (b) Yasuda, M.; Shiomori, K.; Hamasuna, S.; Shima, K.; Yamashita, T. *J. Chem. Soc., Perkin Trans. 2* **1992**, 305−310. (c) Yasuda, M.; Yamashita, T.; Matsumoto, T.; Shima, K.; Pac, C. *J. Org. Chem.* **1985**, *50*, 3667. (d) Yasuda, M.; Yamashita, T.; Shima, K.; Pac, C. *J. Org. Chem.* **1987**, *52*, 753. (e) Yamashita, T.; Shiomori, K.; Yasuda, M.; Shima, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 366−374.

(39) Yasuda, M.; Yamashita, T.; Shima, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 938−946.

(40) Kazanis, S.; Azarani, A.; Johnston, L. J. *J. Phys. Chem.* **1991**, *95*, 4430−4435.