J. Am. Chem. Soc. 1994, 116, 8279–8287

Reactivity of Aromatic Radical Cations. Rate Constants for Reactions of 9-Phenyl- and 9,10-Diphenylanthracene Radical Cations with Acyclic Amines[1]

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Received March 9, 1994[•]

Abstract: Rate constants were measured for the reactions of 9-phenylanthracene (PA) and 9,10-diphenylanthracene (DPA) radical cations with a number of primary, secondary, and tertiary amines in acetonitrile using nanosecond laser flash photolysis (NLFP). Generation of the radical cations of PA and DPA (PA$^{\bullet+}$ and DPA$^{\bullet+}$) was accomplished by 266- or 355-nm photoionization of the parent compound. Primary amines react with PA$^{\bullet+}$ with second-order rate constants in the range 8×10^6 to 2×10^9 M^{-1} s^{-1}, and rate constants for reaction of DPA$^{\bullet+}$ with the same amines are 60–250 times lower. For both radical cations, Brönsted-type plots of $\log(k_{\text{amine}}(\text{RNH}_2))$ versus $\text{p}K_\text{a}(\text{RNH}_3^+)$ serve to illustrate that the rates of reaction with primary amines increase with increasing amine basicity and decrease as the steric requirement of the amine increases. Transient absorption studies complement the kinetic data and demonstrate that primary amines react with both radical cation species by nucleophilic addition to generate the expected radical intermediates. The observed difference in reactivity between PA$^{\bullet+}$ and DPA$^{\bullet+}$ with these nucleophiles can be accounted for by the lack of steric hindrance toward nucleophilic attack at the 10 position in the former. In acetonitrile/water (9:1) solution, rates of reaction with the primary amines are retarded compared to those in acetonitrile and the extent to which the rates are slowed is largest for the more basic amines. It is suggested that the rate differences observed in the mixed solvent system are a result of the equilibrium between free and hydrated amine. Interestingly, the reactivity patterns for the addition of primary amines to these radical cations parallel those observed in carbocation chemistry. Tertiary amines and anilines were found to react with both radical cation species with *similar* rate constants, exclusively by electron transfer, regenerating PA or DPA concomitant with formation of the radical cation of the corresponding amine. Rate constants for reaction with tertiary amines range from 1.5×10^9 M^{-1} s^{-1} to rates approaching the diffusion-controlled limit in this solvent (2×10^{10} M^{-1} s^{-1}) and correlate with the oxidation potential of the amines. Secondary amines exhibit rate constants that do not reflect their basicity. For PA$^{\bullet+}$, electron transfer occurs competitively with nucleophilic addition and, thus, the rate constants measured reflect the relative contribution from each of these two processes. Nucleophilic addition to DPA$^{\bullet+}$ is in most cases slow enough that electron transfer dominates.

The importance of carbocation intermediates in organic chemistry has prompted a number of studies of their reactivities with nucleophiles in both aqueous and nonaqueous media.[2–6] On the other hand, considerably less is known about the dynamics of the reactions of nucleophiles with radical cations despite their importance in chemical processes.[7,8] The chemistry of radical cations is diverse, and only a few time-resolved studies of some of these processes, including fragmentation,[9] deprotonation reactions,[10,11] and their reactions with nucleophiles,[12–17] have been reported. The reaction of a radical cation with a nucleophile can, in principle, proceed either by addition or by electron transfer. For example, one of us recently reported rate constants for addition of anion and alcohol nucleophiles to the β-position of radical cations of substituted styrenes.[14] For anionic nucleophiles these

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[•] Abstract published in *Advance ACS Abstracts.* August 1, 1994.

(1) Issued as NRCC publication No. 37260.

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reactions proceeded with diffusion controlled rate constants with little selectivity in acetonitrile (MeCN) or 2,2,2-trifluoroethanol (TFE). However, in 4:1 aqueous MeCN the rate constants for reaction with the same nucleophiles varied over 4 orders of magnitude and the rate decreases were attributed to hydrogen bonding interactions of the nucleophiles with water. Steenken and co-workers observed similar selectivity for the reactions of the naphthalene radical cation in aqueous MeCN and attributed the rate differences to the relative nucleophilicity of the reactants.[15] By contrast, Koike and Thomas reported that the reactions of a variety of aromatic radical cations with nucleophilic quenchers in methanol and water were *exclusively* electron transfer processes with no evidence for nucleophilic addition.[16] In their analysis the variation in the observed rate constants was correlated with the driving force for electron transfer calculated by the energy-gap law. We have shown recently that the reactions of radical cations with anionic nucleophiles (in particular azide) can follow *either* a polar addition or an electron transfer pathway and that the partitioning between these two routes can be controlled by altering the oxidation potential of the nucleophile through solvent effects.[17]

The reaction of nitrogen-centered nucleophiles can also proceed by a variety of reaction pathways including polar addition, electron transfer, and deprotonation. To the best of our knowledge there have been no comprehensive time-resolved studies of the rates of reaction of radical cations with nitrogen-centered nucleophiles. Numerous product studies by Yasuda and co-workers have illustrated the potential synthetic application of the photoaddition of amines (and other nucleophiles) to arene radical cations produced via photoinduced electron transfer (PET) to dicyanobenzene as an electron acceptor.[18–20] They have shown that under PET conditions numerous arene radical cations can be efficiently substituted by primary amines as well as by other strong nucleophiles. Product formation from substitution of the same radical cation by secondary and tertiary amines was found to be extremely inefficient due presumably to a competition between electron transfer and addition.

One of us has been involved in studies aimed at understanding the mechanism of reaction of the radical cations of anthracene derivatives with nucleophiles using electrochemical techniques.[21–23] As part of these electrochemical studies the rates of reactions of 9-phenylanthracene derivatives with substituted pyridines and anionic nucleophiles in acetonitrile and dichloromethane were determined. Kinetics for the reaction were found to vary over a wide range (from 10^2 to 10^9 M^{-1} s^{-1}). These electrochemical studies have provided valuable information which has contributed to understanding the reactivity of radical cations. However, the general application of this approach for the determination of kinetic parameters is limited by the redox properties of the nucleophiles and by the requirement for prior knowledge of the electrochemical mechanisms. In particular, one must consider the involvement of other electroactive species (such as the more reactive dication) when investigating the reactivity of the radical cation.[24] The technique of nanosecond laser flash photolysis has the advantage that kinetic data can be measured directly and does not suffer the same limitations as the electrochemical methods. Nevertheless, the two methods are complementary and in combination can cover a kinetic range of 12 orders of magnitude.

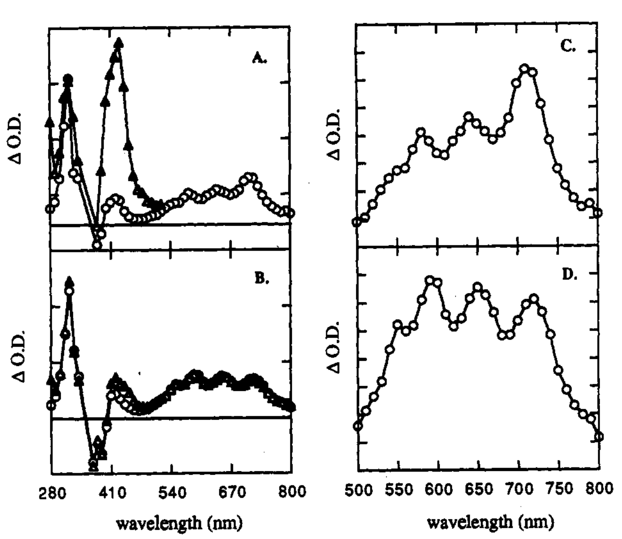
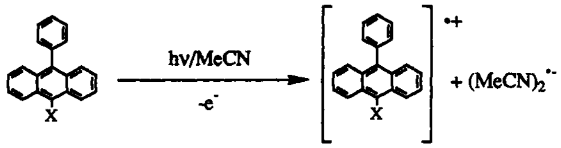


Figure 1. Transient absorption spectra recorded 160–320 ns after 355-nm excitation of 1 × 10^{-4} M solutions of (A) PA and (B) DPA in acetonitrile at 23 °C (○, oxygen saturated; ▲, nitrogen saturated). Spectra C and D are expansions of the 500–800-nm region of the oxygen-saturated spectra in Parts A and B.

We now report rate constants for the reaction of a number of primary, secondary, and tertiary amines with the radical cations of 9-phenylanthracene (PA) and 9,10-diphenylanthracene (DPA) determined by nanosecond laser flash photolysis. The radical cations of these compounds can be generated readily by photoionization, allowing the kinetic studies to be performed in the absence of PET sensitizers. Since these two compounds have similar redox properties yet quite different steric requirements, the study of their reactivity with amines has provided important insights into the factors that control reactivity of aromatic radical cations with nitrogen-centered nucleophiles.

Results and Discussion

Formation of Radical Cations. Irradiation of 1 × 10^{-4} M oxygen-saturated solutions of 9-phenylanthracene (PA) and 9,10-diphenylanthracene (DPA) in acetonitrile (MeCN) by either 266- or 355-nm laser pulses of a nanosecond laser flash photolysis system (NLFP) produced transient absorption spectra with similar characteristics. Those obtained using 355-nm excitation are shown in Figure 1. Spectra obtained with both PA and DPA exhibit three distinct absorption bands: a relatively intense absorption centered at 320 nm, a weak absorption centered around 420 nm, and a structured, broad absorption band in the 530–760-nm region (see Figure 1C and D). The region between *ca.* 410 and 350 nm is not shown completely in either of the spectra in Figure 1, since the ground states absorb at these wavelengths and significant bleaching (measured as a negative absorption) is observed. The transient absorptions observed under the above conditions are assigned to the radical cations $PA^{\bullet+}$ and $DPA^{\bullet+}$ produced by photoionization of the corresponding phenylanthracene (eq 1). The assignment is based on the similarity of



(1)

PA : X=H
DPA: X = Ph

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these spectra with those generated by pulse radiolysis in low-temperature glasses and with those reported by Masnovi and Kochi, who generated the same radical cations by photolysis of charge-transfer electron donor–acceptor complexes of the substituted anthracenes with tetranitromethane in dichloromethane.[25] Other polycyclic aromatics, including anthracene and 9-styrylanthracenes have also been shown to photoionize to yield the corresponding radical cations under similar conditions to those described here.[26,27] In MeCN the solvated electron is known to exist as the dimer radical anion $(MeCN)_2^{\bullet -}$ [28] but absorbs too weakly to be observed in the accessible absorption region.[29] In aerated solvent the electron will presumably also be trapped by oxygen to form superoxide $O_2^{\bullet -}$. In nitrogen-saturated solutions the spectra are essentially identical except for an increase in the absorbance at 420 nm, as illustrated in Figure 1A and B. This increased absorption can be attributed to the triplet states of PA and DPA, which are known to absorb in this region.[30] A more significant increase is observed in the 420-nm absorption with PA, consistent with the fact that the quantum yield for intersystem crossing for the PA singlet is much higher ($\phi^{isc} = 0.51$) than that for DPA ($\phi^{isc} = 0.02$) in polar solvents.[31] Absorption spectra similar to those obtained in MeCN are also observed in TFE, a solvent that is known to stabilize cationic intermediates, further confirming our assignment of the absorptions due to the radical cations. In nonpolar solvents (such as cyclohexane) photoionization is inefficient and only the 420-nm absorption due to the triplets is observed.

Laser dose dependence studies, in which the initial yield of the radical cation (monitored at 650 nm for $DPA^{\bullet +}$ and 720 nm for $PA^{\bullet +}$) is measured as a function of the laser intensity, were carried out using both 266- and 355-nm excitation. The initial optical density of the radical cations was found to vary linearly with laser intensity in the absence and presence of electron scavengers (*vide infra*) at both excitation wavelengths, suggesting that photoionization of PA and DPA is a monophotonic process. Monophotonic photoionization is calculated to be endergonic by up to 1.2 eV (*ca.* 27 kcal/mol) using the Rehm–Weller expression for 355-nm excitation. However, this phenomenon has been observed for a number of polycyclic aromatic hydrocarbons (including anthracene) at low excitation energies (350–355 nm).[26,32,33] The apparent monophotonicity may result from photoionization of preassociated complexes of the aromatic with itself or with adventitious water. It is also possible to observe a linear laser dose dependence for a biphotonic process under certain conditions.[34]

Quantum yields for photoionization were estimated using the benzophenone triplet as an actinometer.[35] In this method the ΔOD values of the benzophenone triplet (monitored at 520 nm) and the radical cations (monitored at 720 nm for PA and 650 nm for DPA) immediately after excitation are measured as a function of laser intensity, which was adjusted using aqueous K_2CrO_4/Na_2CO_3 filter solutions. Solutions of benzophenone, PA, and DPA were prepared so that they were optically matched at the laser wavelength, and the measurements were performed on each sample consecutively in order to minimize errors due to changes in beam alignment or laser power. The plots of ΔOD for $PA^{\bullet +}$ and $DPA^{\bullet +}$ versus laser dose were linear (*vide supra*); however, the analogous plot for benzophenone showed marked negative curvature at high laser intensity. This has been shown previously to be the result of internal filter effects of triplet benzophenone and of repopulation of ground-state benzophenone by excitation of the triplet.[36] Analysis to determine the quantum yield therefore requires extrapolation of the ΔOD versus laser intensity plot to zero intensity. The quantum yield for photoionization ($\Phi^{\bullet +}$) is thus given by eq 2,[36] where $S^{\bullet +}$ and S^{Bz} are the slopes at the origin

$$\Phi^{\bullet +} = \frac{S^{\bullet +}\epsilon^{Bz}\Phi^{Bz}}{S^{Bz}\epsilon^{\bullet +}} \qquad (2)$$

of such plots for the radical cation and benzophenone, respectively, $\epsilon^{\bullet +}$ is the extinction coefficient for the radical cations, ϵ^{Bz} is the extinction coefficient of the benzophenone triplet (6500 M^{-1} cm^{-1} at 520 nm),[37] and Φ^{Bz} is the quantum yield for formation of triplet benzophenone ($\Phi^{Bz} = \Phi^{isc} = 1.0$).[38] The molar absorption coefficients ($\epsilon^{\bullet +}$) of the radical cations were obtained using the chloranil triplet (generated using 308-nm excitation) to sensitize formation of $PA^{\bullet +}$ (and $DPA^{\bullet +}$). By making the plausible assumption that the yield of $chloranil^{\bullet -}$ produced by electron transfer equals the yield of radical cation and by using a known value for the ε of $chloranil^{\bullet -}$ at 450 nm (9700 L mol^{-1} cm^{-1}),[39] the relative ΔOD of the two species gives an estimate for the ε of the radical cation. The ϵ_{max} values for $PA^{\bullet +}$ at 720 nm and for $DPA^{\bullet +}$ at 650 nm in air-saturated MeCN were found to be 8800 and 8400 L mol^{-1} cm^{-1}, respectively.[40] The quantum yield of photoionization using these estimates of ϵ_{max} was found to be 0.12 for PA and DPA. The efficiency of photoionization determined for PA and DPA is slightly higher than those estimated in a similar manner for anthracene (0.065)[26] and styryl derivatives of anthracene (0.03–0.09)[27] in the same solvent.

The absorptions of $PA^{\bullet +}$ and $DPA^{\bullet +}$ in the absence of any added quencher decay with mixed-order kinetics with half-lives ($\tau^{1/2}$) of a few microseconds, and as expected for radical cation species, the kinetics of their decay are not influenced by oxygen. In the presence of added electron scavengers, such as CCl_4, CH_2Cl_2, or CCl_3Br, the decays of the radical cations are much slower with half-lives of a few hundred microseconds. Figure 2a shows representative decay traces of $DPA^{\bullet +}$ recorded at 650 nm in the absence and presence of CCl_4 as an electron scavenger. The short- and long-wavelength absorptions of the radical cations exhibited identical kinetic behavior both in the absence and presence of electron scavengers. The scavenging of the electron by the alkyl halides occurs by the process illustrated for carbon tetrachloride in eq 3. The lengthening of the lifetime of the radical

$$e^- + Cl_3C\text{–}Cl \rightarrow Cl_3^{\bullet} + Cl^- \qquad (3)$$

cation therefore requires that the reaction of the halide anion with the radical cation be slow. This has been shown to be the

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[40] The ΔOD for chloranil at 450 nm was corrected for a slight absorption of the radical cations at this wavelength.

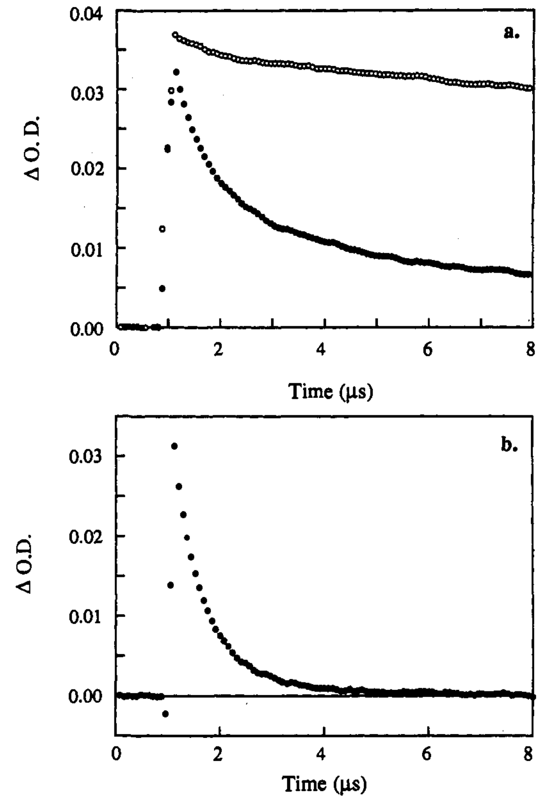


Figure 2. (a) Representative transient decay traces of $DPA^{\bullet+}$ recorded at 650 nm in the absence (●) and presence (○) of 20 mM CCl_4. (b) Decay trace of $PA^{\bullet+}$ recorded at 720 nm in an air-saturated acetonitrile solution containing 0.02 M *n*-butylamine.

case, as the addition of an extraneous source of halide anion at concentrations significantly higher than that expected from the process in eq 3 has no effect on the kinetics of decay of the radical cation. The effect of electron scavengers on the decay rate suggests that recapture of the solvated photoejected electron by the radical cation or reaction with $O_2^{\bullet-}$ are the major modes of decay in the absence of scavengers. The other possible mode of decay of the radical cations, bimolecular interaction with the ground state, does not contribute significantly to the fast component of the decay under our conditions. In TFE and 9:1 MeCN/water solution, in the absence of electron scavengers, the half-lives of the radical cations are also extended compared to those in MeCN, since these solvents are less nucleophilic.[41]

The kinetic measurements described below were carried out using 355-nm rather than 266-nm excitation in order to study a wide variety of quenchers without complications due to competing absorption of the excitation light by the quencher. In a few cases, where the problem of competing absorption was minimal, the rate constants for reaction were measured at both 266 and 355 nm and were independent of the excitation wavelength, as expected.

Rate Constants for Reaction with Primary Amines. In the presence of added amines the lifetimes of the long-wavelength absorptions of $PA^{\bullet+}$ and $DPA^{\bullet+}$ are shortened and the absorptions decay with first-order kinetics (see Figure 2b). The kinetics of the 320 nm band are slightly more complicated on addition of amine due to a concomitant growth of a new, long-lived transient species that overlaps with the decay of the radical cation in this spectral region (*vide infra*). Bimolecular rate constants for reaction of $PA^{\bullet+}$ and $DPA^{\bullet+}$ with a variety of primary amines $\{k_{amine}(RNH_2)\}$ were obtained from the slopes of the plots of the pseudo-first-order rate constants for decay (k_{obs}) of the appropriate radical cation (monitored at 650 nm for $DPA^{\bullet+}$ and 720 nm for $PA^{\bullet+}$) versus the concentration of added amine according to eq 4, where k_0 is the rate of decay of the radical cation in the absence

$$k_{obs} = k_0 + k_{amine}[\text{amine}] \qquad (4)$$

of amine. Plots of this type were linear for all amines examined, and representative examples for quenching of $PA^{\bullet+}$ with a number of amines are shown in Figure 3. Second-order rate constants obtained in this way for the reactions of $PA^{\bullet+}$ and $DPA^{\bullet+}$ with a number of primary amines are summarized in Table 1.

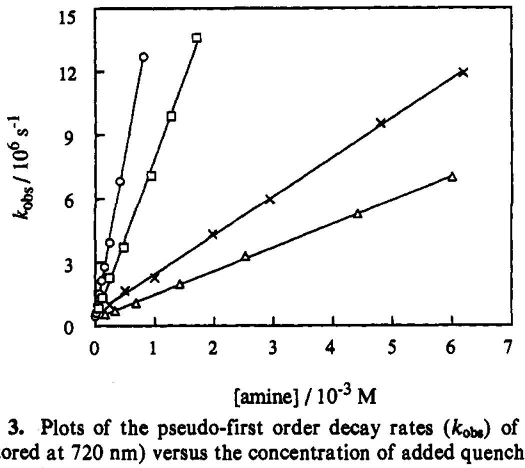
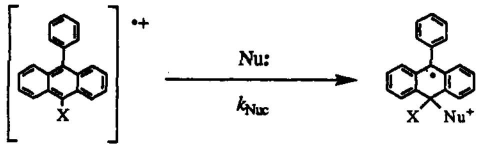


Figure 3. Plots of the pseudo-first order decay rates (k_{obs}) of $PA^{\bullet+}$ (monitored at 720 nm) versus the concentration of added quencher for reaction with several amines: ○, DABCO; □, quinuclidine; ×, *n*-butylamine; △ methoxyethylamine.

Transient absorption spectra recorded for samples containing sufficient quantities of amine to completely quench the radical cation exhibit a strong absorption at 320–330 nm that is independent of the amine nucleophile. Figure 4 shows a transient absorption spectrum recorded on an air-saturated solution containing DPA and 0.3 M *n*-butylamine, as a representative example. The portion of the spectrum between 350 and 400 nm was not measured due to considerable bleaching of the absorption of DPA (and PA) in this region. The spectral characteristics of this transient and its apparent lack of reactivity with oxygen under these conditions are consistent with those expected for the dihydroanthracenyl radicals $DPANu^{\bullet}$ and $PANu^{\bullet}$ on the basis of the known spectrum and reactivity of triphenylmethyl radicals.[42]

Such transients would be expected from nucleophilic addition of the amine to the 10 position of the radical cations. Numerous product studies have shown that anion and amine nucleophiles react with the radical cation of anthracene exclusively at the 9 (or 10) position.[18-20, 22,43] Thus, we interpret the rate constants in Table 1 as those for nucleophilic addition of the amine nitrogen to the 10 position of the radical cation to yield $DPANu^{\bullet}$ and $PANu^{\bullet}$ (eq 5). Furthermore, peak potentials (E_p) for the oxidation of the primary amines studied, determined by cyclic voltammetry, are all at least 250 mV more positive than the potentials for reduction of $PA^{\bullet+}$ ($E° = 0.832$ versus ferrocene) and $DPA^{\bullet+}$ ($E° = 0.812$ versus ferrocene). Since the peak potentials for the amines are shifted to less positive potentials than the thermodynamically significant $E°$ value by the follow-



$PANu^{\bullet}$: X = H
$DPANu^{\bullet}$: X = Ph

(5)

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[41] Masnovi, J. M.; Seddon, E. A.; Kochi, J. K. *Can. J. Chem.* **1984**, *62*, 2552.

[42] Chatgilialoglu, C. In *Handbook of Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. II, Chapter 1.

[43] Reitstöen, B.; Parker, V. D. *Acta Chem. Scand.* **1992**, *46*, 464.

Table 1. Rate Constants for the Reaction of $PA^{\bullet+}$ and $DPA^{\bullet+}$ with RNH_2 in Acetonitrile at 23 °C[a]

R	pK_a(water)[b]	$k_{amine}(RNH_2)/10^9\ M^{-1}\ s^{-1}$		k_{PA}/k_{DPA}
		PA	DPA	
n-propyl	10.53	1.4 ± 0.2	0.024 ± 0.001	58
hydroxyethyl[c]	9.5	0.98 ± 0.20	0.0079 ± 0.0005	124
methoxyethyl	9.2	1.1 ± 0.1	0.0076 ± 0.0005	145
cyanoethyl	7.7	0.20 ± 0.01	0.000 88 ± 0.000 01	250
trifluoroethyl[c]	5.7	0.0081 ± 0.0004	*ca.* 0.000 03[d]	>250
n-butyl	10.59	1.8 ± 0.2	0.029 ± 0.001	62
isopropyl	10.63	0.83 ± 0.02	0.0041 ± 0.0004	202
isobutyl	10.43	1.4 ± 0.1	0.022 ± 0.002	67
sec-butyl	10.56	0.77 ± 0.01	0.0050 ± 0.0006	154
tert-butyl	10.55	0.33 ± 0.06	0.0053 ± 0.0003	63

[a] Errors quoted are ±2σ. [b] From ref 45. [c] Hydroxyethyl = ethanolamine; trifluoroethyl = 2,2,2-trifluoroethylamine. [d] Estimated on the basis of the absence of quenching at high [amine] and the ratio of the rate constants observed for reaction with cyanoethylamine.

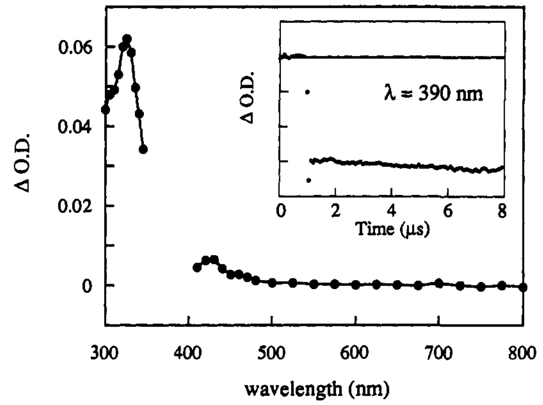

Figure 4. Transient absorption spectrum, recorded 80–160 ns after the laser pulse, of an air-saturated solution containing 1 × 10^{-4} M DPA in the presence of 0.3 M *n*-butylamine. Inset shows the kinetic trace for the bleaching of DPA measured at 390 nm.

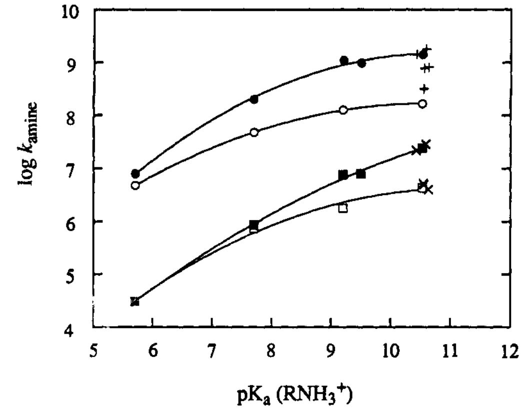

Figure 5. Brönsted-type plot showing the dependence of $\log(k_{amine}(RNH_2))$ on pK_a (RNH_3^+) for the reaction of *n*-propylamine, ethanolamine, methoxyethylamine, cyanoethylamine, and 2,2,2-trifluoroethylamine with $PA^{\bullet+}$ (●) and $DPA^{\bullet+}$ (■) in acetonitrile and with $PA^{\bullet+}$ (○) and $DPA^{\bullet+}$ (□) in 9:1 acetonitrile/water. The data for reaction of the other primary amines with $PA^{\bullet+}$ (+) and $DPA^{\bullet+}$ (×) in MeCN are also included. The curves are drawn through the points for *n*-propylamine, ethanolamine, methoxyethylamine, cyanoethylamine, and 2,2,2-trifluoroethylamine (solid points). Data for this plot are taken from Table 1.

up reactions,[24] the measured difference in oxidation potentials between the amines and the aromatics $\{E_p(\text{amine}) - E^\circ(\text{aromatic})\}$ represents a lower limit of the free energy change for electron transfer. Therefore, it is reasonable to conclude that electron-transfer processes do not contribute to the measured rate constants in these cases. In fact the bleaching observed is permanent (see inset, Figure 4), indicating that there is no detectable reaction that results in regeneration of starting material (*i.e.* electron transfer).

The primary amines included in Table 1 can be divided into two main categories: (i) amines of varying basicity but constant steric requirements (*n*-propylamine, ethanolamine, 2-methoxyethylamine, 2-cyanoethylamine, and 2,2,2-trifluoroethylamine) and (ii) amines of constant basicity with varying steric bulk (*n*-propylamine, *n*-butylamine, isopropylamine, isobutylamine, *sec*-butylamine, and *tert*-butylamine). For the amines listed in the above two categories rate constants for reaction of the primary amines with $PA^{\bullet+}$ in MeCN are in the range 8 × 10^6 to 2 × 10^9 $M^{-1}\ s^{-1}$ and are on the order of 60–250 times faster than those determined for the reaction of $DPA^{\bullet+}$ with the same nucleophiles. The slower rate of reaction of the amines with $DPA^{\bullet+}$ is the result of steric inhibition to nucleophilic attack, since both the 9 and 10 positions are substituted. This steric factor is not as important in $PA^{\bullet+}$, since the 10 position is unhindered. The rate variations between the two electrophiles with a particular amine cannot be rationalized from differences in the positive charge density at the C_9 (or C_{10}) positions of the radical cation. AM1 calculations[44] of the two radical cations indicate that the phenyl rings are twisted by *ca.* 60°, so there is little delocalization and the charge densities are not significantly altered by the addition of the second phenyl ring in $DPA^{\bullet+}$.

Differences in rates of addition to these two radical cations, illustrated by k_{PA}/k_{DPA} values, increase as the amine becomes less reactive. This trend has also been observed in previous electrochemical studies for the reaction of pyridine and substituted pyridines with these radical cations.[23] In these studies rates of addition of substituted pyridines to electrochemically generated $PA^{\bullet+}$ ranged from 10^5 to 10^7 $M^{-1}\ s^{-1}$, and k_{PA}/k_{DPA} values on the order of 10^3 were determined for these slower reactions. The combined laser flash and electrochemical data indicate that the selectivity for the reaction of $PA^{\bullet+}$ and $DPA^{\bullet+}$ with nitrogen-centered nucleophiles (illustrated by the k_{PA}/k_{DPA} values) adheres to reactivity–selectivity principles. Furthermore, as has been observed previously for the reactions of short-lived carbocations,[4,5] the reactivity of these radical cations do not follow Ritchie's N_+ relationship, which states that selectivity is independent of the electrophile.

Brönsted-type plots of $\log(k_{amine})$ versus pK_a of the conjugate acids of the primary amines[45] (RNH_3^+) constructed from the data in Table 1 are shown in Figure 5. It should be noted that the reference pK_a's listed in Table 1 are those in water, since data was unavailable for the complete series of amines in MeCN. Coetzee and Padmanabhan have shown for several of the amines studied here that even though the pK_a values in MeCN are on average 7.6 units larger than that measured in water the relative magnitudes do not differ significantly.[46] Values of $\log(k_{amine})$ in MeCN of those amines in category one (*vide supra*) correlate with the basicity of the amine for both $PA^{\bullet+}$ and $DPA^{\bullet+}$ (*i.e.*

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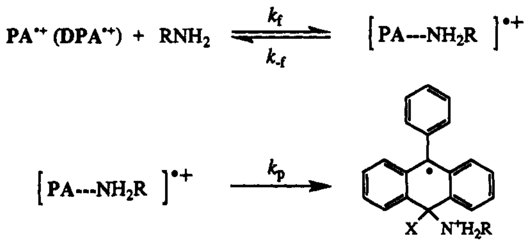
(44) Dewar Research Group; Stewart, J. P. *QCPE* **1986**, *24a.b.*

(45) Fasman, G. D., Ed. *Handbook of Biochemistry and Molecular Biology: Physical and Chemical Data*. 3rd ed.; CRC Press, Inc.: Cleveland, OH, 1976; Vol. 1.

(46) Coetzee, J. F.; Padmanabhan, G. R. *J. Am. Chem. Soc.* **1965**, *87*, 5005.

Scheme 1



decreasing rate constants with decreasing amine basicity). The plot for DPA$^{•+}$ is somewhat less well-defined than that for PA$^{•+}$, since the rate constant for reaction with $CF_3CH_2NH_2$ was too slow to measure by nanosecond laser flash photolysis (NLFP), and thus the point included is an estimate based on the rate constant for reaction of PA$^{•+}$ with the same amine and a k_{PA}/k_{DPA} value of 250. The Brönsted-type plots in Figure 5 also illustrate that for amines of constant basicity there is a moderate steric effect of the *nucleophile* on the rate constants for reaction of PA$^{•+}$ and DPA$^{•+}$. The rate constants decrease by a factor of 5 going from *n*-propylamine to *tert*-butylamine with either radical cation, indicating that the rate constants for reaction are sensitive to the steric requirements of both the electrophile and the nucleophile.

Slopes of linear fits of the Brönsted-type plots (β_{Nuc}) for the four amines with similar steric requirements are *ca.* 0.6. This β_{Nuc} value is consistent with the mechanism for reaction being nucleophilic in nature with considerable bond formation, and thus a substantial charge on nitrogen, in the transition state. On inspection, the Brönsted-type plot for PA$^{•+}$ is not linear but is curved, leveling off with a limiting rate constant of *ca.* 1–2 × 10^9 M^{-1} s^{-1}. The plot for DPA$^{•+}$ also appears to be curved, leveling off at a value 30 times lower than that for PA (*ca.* 5 × 10^7 M^{-1} s^{-1}) although the curvature is not as apparent as in the plot for PA$^{•+}$. The observation of nonlinear Brönsted plots of reactions of radical cations or carbocations has been considered previously in terms of a reaction scheme where the reactants form an intermediate complex which can then either separate or collapse to give addition products (Scheme 1, eq 6).[4,6,21–23] The curvature

$$k_{\text{amine}}(\text{RNH}_2) = \frac{k_f k_p}{k_{-f} + k_p} \tag{6}$$

$$k_{\text{amine}}(\text{RNH}_2) = \frac{k_f k_p}{k_{-f}} = K_{eq} k_p \tag{7}$$

$$k_{\text{amine}}(\text{RNH}_2) = k_f \tag{8}$$

may then be an indication of a change from rate-limiting product formation (k_p) to rate limiting complex formation (k_f) as the basicity of the amine increases. In the first limit, eq 6 reduces to eq 7 and in the second limit to eq 8. The observation of limiting rate constants below the diffusion-controlled limit ($k_d \approx 2 \times 10^{10}$ M^{-1} s^{-1} in MeCN) in reactions of carbocations[6] and radical cations[21–23] with amines has been rationalized as being a result of an unfavorable competition between k_p and k_{-f} (*i.e.* rate-limiting product formation or mixed kinetic control). We observe limiting rate constants well below the diffusion limit in the reactions of PA$^{•+}$ and DPA$^{•+}$. In these hindered aromatic radical cations one should consider the possibility that not every diffusional encounter will result in complex formation and thus the rate of its formation may be entropically disfavored. In these cases it is reasonable to expect that $k_{\text{amine}} = k_f$ and that k_f is considerably smaller than k_d. The extent to which k_f deviates from k_d as a result of these steric effects will be system dependent[11] and thus can explain the differences in the limiting values observed for PA and DPA. The alternative explanation is that $k_{\text{amine}} = K_{eq}k_p$. As the basicity of the amine increases, the K_{eq} increases, since equilibrium is a Lewis acid–base reaction (as opposed to pK_a). This means that at the plateau, as the pK_a(RNH_3^+) increases, there must be an accompanying decrease in k_p, thus increasing the steady-state concentration of the complex. However, we have found no spectral evidence for a π-complex in these systems.

For both mechanistic possibilities suggested above one expects small apparent activation energies and low preexponential factors from the temperature dependence of the rate constants. Parker *et al.* reported activation parameters for the reaction of aromatic radical cations (including PA$^{•+}$ and DPA$^{•+}$) with a variety of nucleophiles in MeCN using electrochemical techniques.[22a,23] The small and sometimes *negative* activation energies determined were interpreted to be indicative of a preequilibrium step involving the formation of the π-complex prior to bond formation. We have found that rate constants measured for the reaction of PA$^{•+}$ and DPA$^{•+}$ with *n*-butylamine and methoxyethylamine between −20 and 60 °C varied by less than a factor of 1.5 throughout this temperature region. Analysis of Arrhenius plots of the data gave negligible activation energies (0.7 ± 0.7 kcal mol^{-1}) and small preexponential factors (log(A) = 9.7 ± 0.5 and 7.8 ± 0.6 for PA$^{•+}$ and DPA$^{•+}$, respectively). On the basis of our data, we are unable to distinguish between the two possible mechanisms.

In a mixed MeCN/water (9:1) solution, the rates of reaction of the radical cations are lower than those measured in pure MeCN. The effect of water on the rates is found to be greatest for the more basic amines with rates changing by up to 1 order of magnitude for *n*-propylamine down to a factor of less than 2 for 2,2,2-trifluoroethylamine. This is illustrated graphically in Figure 5 for the reactions of $CF_3CH_2NH_2$, $CNCH_2CH_2NH_2$, $CH_3OCH_2CH_2NH_2$, and $CH_3CH_2CH_2NH_2$ with PA$^{•+}$ and DPA$^{•+}$. The effect of added water on the rates is consistent with hydrogen-bonding interactions with the lone pair on nitrogen rendering it unreactive as a nucleophile. The change in the rate constants thus reflects the relative equilibrium concentrations of the free amine. With the more basic (*i.e.* more reactive) amines, the hydrated form is favored more than with the less basic (*i.e.* less reactive) amines, with the result being a larger effect on the rate constant with the former. For the least reactive pairs the rates of addition are essentially the same in MeCN/water as they are in pure MeCN. Analogous rate retardation effects in aqueous MeCN solution have been observed for the reaction of anion and amine nucleophiles with a variety of aryl-substituted di- and triarylmethyl cations[5,6,47] and the retinyl cation.[48] McClelland *et al.* have provided a more quantitative analysis of the kinetic implications of hydration on the reactions of amines with carbocations.[6] Hydrogen-bonding interactions have also been used to explain the lower reactivity of styrene radical cations with anionic nucleophiles in MeCN/water solution.[14] On the basis of the effect of added water on the rate constants for addition, we considered the possibility that adventitious water in the MeCN could also explain the limiting of the rate constants which occurs for the more basic amines (*vide supra*). However this is not the case, since rate constants remeasured in MeCN which had been freshly distilled over CaH_2 and then passed through activated alumina, a process which is known to lower the water content to <2 ppm, were the same as those reported in Table 1.

The reactivity of these radical cations with primary amines in many ways parallels that observed for addition of the same nucleophiles to carbocation species of similar structure especially with respect to the effects of amine basicity, steric factors, and solvent effects. It is interesting to note that the upper rates for reaction of the primary amines with PA$^{•+}$ are similar to the rate constants measured by McClelland and co-workers for the reaction of the same amines with diarylmethyl carbocations in the same solvent. The maximum rate constant measured in their system

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(47) Alonso, E. O.; Johnston, L. J.; Scaiano, J. C.; Toscano, V. G. *Can. J. Chem.* **1992**, *70*, 1784.

(48) Pienta, N. J.; Kessler, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 2419.

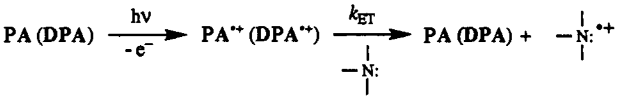
Table 2. Rate Constants for the Reaction of $PA^{\bullet+}$ and $DPA^{\bullet+}$ with Tertiary Amines and Anilines in Acetonitrile at 23 °C[a]

	$k_{amine}(R_3N)/10^9\ M^{-1}\ s^{-1}$		
amine	PA	DPA	k_{PA}/k_{DPA}
diethylmethylamine	3.0 ± 0.2	1.7 ± 0.1	1.7
triethylamine	4.8 ± 0.5	3.3 ± 0.1	1.5
diisopropylethylamine	8.8 ± 0.6	8.2 ± 0.9	1.1
DABCO[b]	15.3 ± 0.6[c]	13.9 ± 0.6[c]	1.1
quinuclidine[b]	7.6 ± 0.3	5.6 ± 0.3	1.4
tropane[b]	2.9 ± 0.2	1.6 ± 0.1	1.8
N,N'-dipiperidinoethylamine	5.1 ± 0.3	2.7 ± 0.3	1.9
N,N,N',N'-tetramethyl-1,4-butanediamine	6.5 ± 0.4	3.2 ± 0.3	2.0
N,N,N',N'-tetramethyl-ethylenediamine	5.6 ± 0.3	2.7 ± 0.1	2.0
aniline	11.2 ± 0.1[d]	9.8 ± 0.2[d]	1.1
N-methylaniline	13.0 ± 0.2[e]	11.0 ± 0.2[e]	1.2
N,N-dimethylaniline	9.5 ± 0.1[f]	9.2 ± 0.5[f]	1.0
N,N-diethylaniline	20.7 ± 1.4[g]	14.1 ± 0.1[g]	1.5

[a] Errors quoted are ±2σ. [b] DABCO = diazabicyclo[2.2.2]octane. Quinuclidine = azabicyclo[2.2.2]octane. Tropane = 8-methyl-8-azabicyclo[3.2.1]octane. [c] Spectrum of $DABCO^{\bullet+}$ observed with maximum centered at 480 nm. [d] Spectrum of $aniline^{\bullet+}$ observed with maxima at 412 and 435 nm. [e] Spectrum of N-$methylaniline^{\bullet+}$ observed with maximum at 440 nm. [f] Spectrum of N,N-$dimethylaniline^{\bullet+}$ observed with maximum at 455 nm. [g] Spectrum of N,N-$dimethylaniline^{\bullet+}$ observed with maximum at 460 nm.

was *ca.* 4.5 × $10^9\ M^{-1}\ s^{-1}$, only about twice as fast as the fastest rate measured in our system. However, in contrast to our results, they observed very little variation in the rates of addition of the amines to the diarylmethyl cation in MeCN with the rate constants all in the 2–4.5 × $10^9\ M^{-1}\ s^{-1}$ range. Comparisons of this type are typically discussed in terms of the curve-crossing model developed by Shaik and Pross,[49] which predicts that a carbocation will be more reactive toward nucleophilic addition than a radical cation of the same electron affinity. Comparisons of our data with the data of McClelland and co-workers do not give particular insights into this model, since there are obvious differences in electronic, thermodynamic, and structural properties of the species involved. However, it is clear that the rates of reaction of nucleophiles with radical cations can approach the same values as those for reactions of carbocations with the same nucleophiles.

Rate Constants for Reaction with Tertiary Amines and Anilines. Bimolecular rate constants for reaction of $PA^{\bullet+}$ and $DPA^{\bullet+}$ with a number of tertiary amines and N-substituted anilines $\{k_{amine}(R_3N)\}$ were determined in the same manner as that described for the primary amines. Table 2 contains a list of the amines and anilines used, along with the second order rate constants for reaction with the radical cations. The rate constants observed are all on the order of 10^9–$10^{10}\ M^{-1}\ s^{-1}$ and are *at least* as fast as the fastest rate constants measured for the primary amines. In addition, the rate constants for reaction with $PA^{\bullet+}$ and $DPA^{\bullet+}$ are relatively *invariant* with k_{PA}/k_{DPA} ratios on the order of 1–2, pointing to a process that is not particularly sensitive to steric effects. The results suggest that tertiary amines and anilines quench the radical cations by electron transfer to generate neutral PA or DPA and the radical cation of the corresponding amine (eq 9). The variation in the rate constants as a function of structure



$$PA\ (DPA) \xrightarrow[-e^-]{h\nu} PA^{\bullet+}\ (DPA^{\bullet+}) \xrightarrow[-\overset{|}{\underset{|}{N}}:]{k_{ET}} PA\ (DPA) + -\overset{|}{\underset{|}{N}}:^{\bullet+} \qquad (9)$$

is a reflection of the relative electron-donating ability of the amine. In general the rate constants follow the ease of oxidation of the amine, approximated from relative peak potentials determined by cyclic voltammetry, with the more easily oxidized amines reacting at faster rates. For the reaction with 1,4-diazabicyclo-[2.2.2]octane (DABCO) and the anilines, the rate constants are at the diffusion controlled limit (*ca.* 2 × $10^{10}\ M^{-1}\ s^{-1}$).

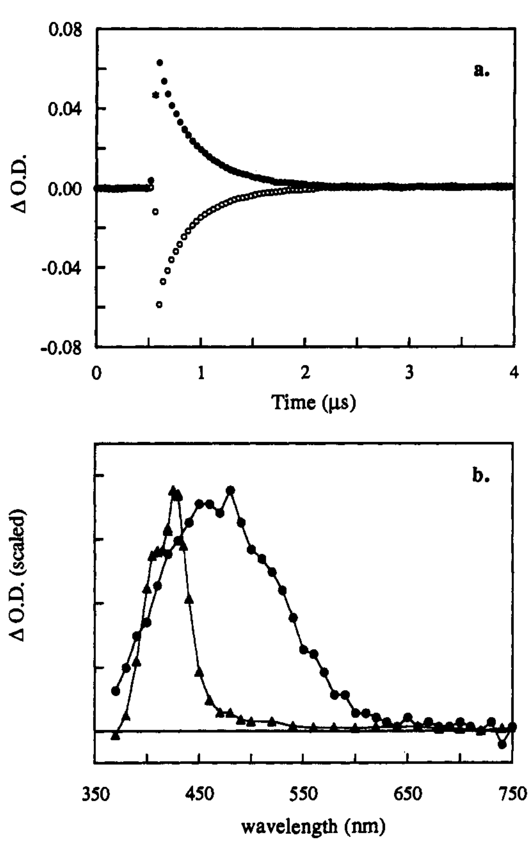


Figure 6. (a) Transient kinetic traces showing (●) the decay of $DPA^{\bullet+}$ measured at 650 nm and (○) the complete return of bleaching of DPA, measured at 390 nm, in an air-saturated acetonitrile solution containing 0.2 mM DABCO. (b) Transient absorption spectra of the DABCO radical cation (●) and aniline radical cation (▲) generated by electron transfer to $DPA^{\bullet+}$. The spectra were recorded on oxygen-saturated acetonitrile solutions containing 6 mM substrate and were measured 0.3–0.4 μs after the laser pulse. The spectra are normalized with respect to the absorption maxima.

Transient absorption and other kinetic evidence support the conclusion that tertiary amines react with these radical cations by electron transfer. In the case of the tertiary amines listed in Table 2, the rate of decay of the 320-nm absorption matches that observed from the longer wavelength absorptions at all concentrations of amine with no evidence for a concurrent growth due to the absorption of $PANu^\bullet$ or $DPANu^\bullet$ as is observed with the primary amines. Furthermore, the bleaching of the starting material, which can be conveniently monitored at 390 nm for DPA and 365 nm for PA, recovers at a rate identical to the rate of decay of the radical cation at all concentrations of tertiary amine, indicating that the starting material is not being consumed but is completely regenerated during reaction. This is shown for the reaction of $DPA^{\bullet+}$ with DABCO in Figure 6a.

In the case of DABCO and the four aniline compounds, new transients are observed that can be assigned to the radical cations of the respective quenchers formed on electron transfer to $PA^{\bullet+}$ or $DPA^{\bullet+}$. The transient absorption spectra of $DABCO^{\bullet+}$ and $aniline^{\bullet+}$, observed on addition of sufficient amine to quench all of the $DPA^{\bullet+}$, are shown in Figure 6b. The spectra of the methyl-substituted aniline radical cations are similar in shape and intensity to that observed for aniline itself except the absorption maxima are shifted to longer wavelengths (see footnotes in Table 2). The assignment of these absorptions is based on the similarity to

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

Table 3. Rate Constants for the Reaction of $PA^{\bullet+}$ and $DPA^{\bullet+}$ with Secondary Amines in Acetonitrile at 23 °C[a]

amine	$k_{amine}(R_2NH)/10^9\ M^{-1}\ s^{-1}$ PA	$k_{amine}(R_2NH)/10^9\ M^{-1}\ s^{-1}$ DPA	k_{PA}/k_{DPA}
diethylamine	2.5 ± 0.5	**0.38 ± 0.01**	6.6
diisopropylamine	2.2 ± 0.1	**0.061 ± 0.002**	36
N-methyl-*tert*-butylamine	2.2 ± 0.2	**0.32 ± 0.01**	6.9
di-*sec*-butylamine	**0.32 ± 0.1**	**0.11 ± 0.01**	2.9
N,*N'*-dimethylethylenediamine	5.2 ± 0.5	1.3 ± 0.1	4
dicyclohexylamine	**1.3 ± 0.1**	**0.53 ± 0.02**	2.5

[a] Errors quoted are ±2σ. Cases where the rate constant is that for electron transfer only, estimated from complete return of bleaching, are in boldface. Other rate constants are those where $k_{amine} = k_{ET} + k_{Nuc}$.

absorption spectra of the same species reported elsewhere.[25a,50] The transient absorptions grow in at rates proportional to the concentration of added quencher although accurate analysis of the growth kinetics is difficult due to overlapping absorption of $PA^{\bullet+}$ or $DPA^{\bullet+}$ in the same regions. Direct spectral evidence (with the exception of the return of bleaching of starting material) for electron transfer to the other tertiary amines could not be obtained, since their respective radical cations do not have appreciable absorptions above 320 nm.

Rate Constants for Reaction with Secondary Amines. Rate constants measured for the reaction of several secondary amines $\{k_{amine}(R_2NH)\}$ are collected in Table 3. The rate constants and rate constant ratios (k_{PA}/k_{DPA}) vary in a less predictable manner than those for the reaction of primary and tertiary amines. This is the result of a number of factors that are unique to secondary amines in these systems. We have shown that the reaction of a primary amine with $PA^{\bullet+}$ and $DPA^{\bullet+}$ proceeds by nucleophilic addition while tertiary amines react by electron transfer. Secondary amines on the other hand are particularly interesting, since the E_p values for the oxidations of these compounds are all less than 100 mV less positive than the reduction potential of $PA^{\bullet+}$ and $DPA^{\bullet+}$ (*i.e.* they appear easier to oxidize). Depending on the magnitude of the expected kinetic shift of the E_p from the true $E°$ value (as a result of fast chemical follow-up reactions of the radical cations),[24] electron transfer may or may not be energetically favorable. In addition, the higher basicity of the secondary amines compared to the primary amines makes them potentially better nucleophiles.[51] Therefore, the observed rate constant $k_{amine}(R_2NH)$ for a particular secondary amine will be the sum of the rate constants for the two competing reactions ($k_{Nuc} + k_{ET}$) represented by eqs 5 and 9, respectively. For reaction pairs where electron transfer is close to thermoneutral or endergonic, the competition between electron transfer and nucleophilic addition is difficult to predict.

We were able to determine the extent to which $k_{amine}(R_2NH)$ contains a contribution from k_{Nuc} by measuring the recovery of bleaching of PA and DPA in the reaction of their radical cations with secondary amines. For an electron transfer reaction (*i.e.* $k(R_2NH) = k_{ET}$), complete return of the initially bleached absorption for PA and DPA is expected (as was observed for tertiary amines, Figure 6a). Those cases for which complete recovery of bleaching (*i.e.* electron transfer) is observed are indicated by boldface type in Table 3. The rate constants for electron transfer to the secondary amines are all considerably smaller than those measured for the tertiary amines and are a reflection of the much smaller driving force $\{E°(\text{amine}) - E°(\text{aromatic})\}$ for electron transfer in these cases. For the sterically hindered di-*sec*-butylamine and di-cyclohexylamine, k_{Nuc} is sufficiently small that the reaction with both $PA^{\bullet+}$ and $DPA^{\bullet+}$ occurs by electron transfer (see for example Figure 7a and b). For all of the other secondary amines there is at least some contribution of addition to the observed rate constant for the reaction with $PA^{\bullet+}$, since some permanent bleaching of the aromatic is observed (see Figure 7d and f). In cases where the rates of addition and electron transfer are similar, there is also evidence for formation of the radical addition products from their absorption at 320–330 nm, which overlaps with the decay of the radical cation. On the basis of the reactivities of primary and tertiary amines with $PA^{\bullet+}$ and $DPA^{\bullet+}$, we conclude that, in cases where the rates of electron transfer and addition are of similar magnitude for reaction with $PA^{\bullet+}$, the electron transfer must dominate for the reaction with $DPA^{\bullet+}$ due to its inherent lower reactivity to addition. This is observed for all cases with the exception of *N*,*N'*-dimethylethylenediamine, where addition can compete with electron transfer for both radical cations. In principle, it should be possible to estimate the relative proportion of the two competing reactions from the relative amount of recovery of the initial bleach. However, this approach is not straightforward, since overlapping absorptions of the radical cation and the addition product as well as incomplete fluorescence correction lead to some uncertainty in the magnitude of the optical density change in the initially bleached PA or DPA spectrum. In some cases these problems are evident in the kinetics of the recovery of bleaching. Figure 7f shows kinetic traces where the recovery of the bleached PA occurs at a rate which is apparently faster than the decay of the radical cation—a situation which is not kinetically feasible. In the reactions of $DPA^{\bullet+}$ where $k(R_2NH) = k_{ET}$ (see boldface entries in Table 3), it is reasonable to assume, on the basis of our results with the tertiary amines, that k_{ET} for the reaction of the same amine with $PA^{\bullet+}$ will be within a factor of 2. We can thus estimate k_{Nuc} for the reaction of $PA^{\bullet+}$ with these secondary amines from $k_{Nuc} \approx k_{amine}(PA^{\bullet+}) - \{2k_{amine}(DPA^{\bullet+})\}$. Interestingly $k_{Nuc}(PA^{\bullet+})$ values estimated in this way are on the order of $2 \times 10^9\ M^{-1}\ s^{-1}$, the upper limit for k_{amine} measured for the primary amines.

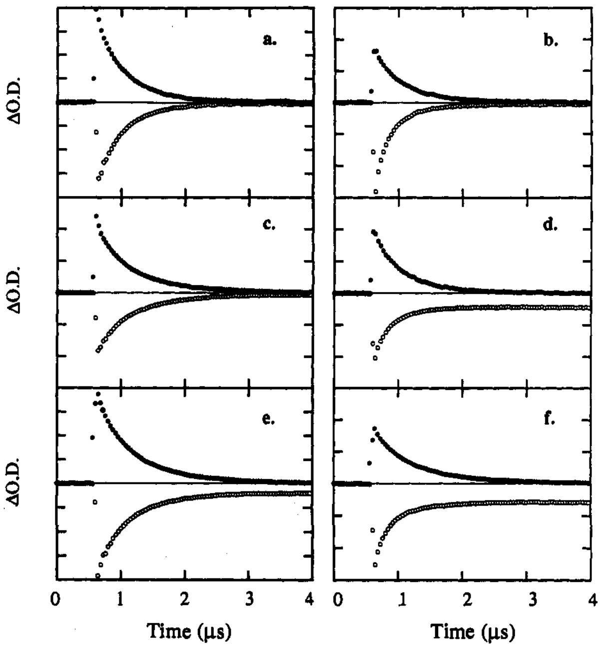

Figure 7. Transient kinetic decay traces showing the decay (●) and the bleaching (○) of $DPA^{\bullet+}$ (a, c, e) and $PA^{\bullet+}$ (b, d, f) in the presence of (a and b) di-*sec*-butylamine, (c and d) diethylamine, and (e and f) *N*,*N'*-dimethylethylenediamine in MeCN.

Our data are consistent with results of Yasuda *et al.*, who have shown that amination of aromatic radical cations with excess dimethyl- and diethylamine in MeCN/water solution is inefficient compared to reaction with primary amines.[20] The same trend is observed here, since in many cases electron transfer dominates the reactivity. They suggest that under their conditions efficient addition can only occur when the amine is more difficult to oxidize

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(50) (a) Gebicki, J.; Marcinek, A.; Stradowski, C. *J. Phys. Org. Chem.* **1990**, *3*, 606. (b) Devadoss, C.; Fessenden, R. W. *J. Phys. Chem.* **1990**, *94*, 4540.

(51) Ritchie, C. D.; Virtanen, P. O. *J. Am. Chem. Soc.* **1973**, *95*, 1882.

than the aromatic by more than 400 mV. However, in neat MeCN, where nucleophilic rate constants are larger, addition will compete more effectively with electron transfer over a wider range of potentials. For a given radical cation the partitioning between the two competing reaction pathways will then be a function of the relative oxidation potentials of the two interacting species (which govern the rate of electron transfer) as well as the factors that govern the rate of nucleophilic addition. For these reasons, the development of a simple model that will allow one to predict and control the selectivities of the reactions of secondary amines with radical cations is doubtful.

Conclusions

The radical cations of PA and DPA are readily generated by photoionization in MeCN, TFE, and aqueous MeCN. This method has permitted the kinetic and spectroscopic studies of the reactivity of $PA^{•+}$ and $DPA^{•+}$ with a variety of amines without any added complications that would arise if it were necessary to employ a photosensitizer. Primary amines react with $PA^{•+}$ and $DPA^{•+}$ by nucleophilic addition at the 10 position, forming the corresponding dihydroanthracenyl radicals with rates that depend on both electronic (basicity) and steric factors. The latter include contributions from both the nucleophile and the electrophile. Further, the rate of nucleophilic addition can be adjusted for the more reactive amines by altering the solvent composition from pure MeCN to MeCN/water mixtures. The rate constants for the reaction of these amines with the radical cations level off at values below that for diffusion. This has been attributed either to the involvement of a preequilibrium prior to bond formation or to high entropic barriers in the interaction between the hindered radical cations and the amines. Tertiary amines react with $PA^{•+}$ and $DPA^{•+}$ by electron transfer, suggesting that amination of the radical cations is not feasible. The essentially 1:1 ratio of rate constants for the reaction of $PA^{•+}$ versus $DPA^{•+}$ can be used as a mechanistic probe for electron transfer in these systems. In addition, the extent of the recovery of bleaching of PA and DPA provides a useful diagnostic indicator for electron transfer. Secondary amines react by both nucleophilic addition and electron-exchange processes. The relative contribution of the two pathways to the observed rate constant is determined by the relative oxidation potentials of the amines and anthracenes and by the various factors that affect the rates of nucleophilic addition. In cases where the reaction of the radical cation with the amine involves nucleophilic addition, reactivity patterns parallel those observed in carbocation chemistry.

Amines can react with arene radical cations by a number of processes. Therefore, it is important to emphasize that an understanding of the redox properties of the particular system is essential in order to predict which path(s) the reaction is likely to follow. By simply adjusting the redox properties of the substrate either through chemical modifications or by solvent effects, it should be possible to direct the reaction of the corresponding radical cation with a single nucleophile from a case of pure nucleophilic addition to one of electron transfer. Substituents at the 10 position of 9-phenylanthracene or on the phenyl rings of PA or DPA provide a convenient method to alter the redox properties of the two aromatic radical cations described here. Systematic studies of substituent effects on the rates and mechanism of reaction of phenylanthracene radical cations with various nucleophiles are currently in progress.

Experimental Section

Materials and General Methods. The compounds 9-phenylanthracene and 9,10-diphenylanthracene were obtained from Aldrich and used as received. Acetonitrile (BDH, OmniSolv), 2,2,2-trifluoroethanol (Aldrich), and water (Caledon, HPLC grade) were used as received for the NLFP experiments unless otherwise specified. The amines used as quenchers and the chlorinated hydrocarbons were all commercially available and were purified by the appropriate method immediately prior to use. For the electrochemical measurements MeCN was distilled from calcium hydride under argon prior to use. Chloranil and benzophenone were recrystallized before use. Tetrabutylammonium perchlorate was recrystallized three times from ethylacetate/hexane (9:1) and dried prior to use. UV-visible absorption spectra were recorded on a Varian CARY 3 spectrophotometer.

Laser Flash Photolysis. Nanosecond laser flash photolysis experiments employed the pulses from a Lumonics HY750 Nd^{3+}:YAG laser (266 nm; 80 mJ/pulse; 10-ns pulse width or 355 nm; 20 mJ/ pulse; 20-ns pulse width) or a Lumonics excimer laser (308 nm; ≤45 mJ/pulse; 8-ns pulse width) and a computer-controlled detection system that has been described elsewhere.[52] Solutions of PA and DPA were prepared at concentrations such that the absorbance at the excitation wavelength was 0.3–0.6. 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. Samples used in the kinetic measurements were contained in rectangular 7×7 mm^2 Suprasil quartz cells. Quenching rate constants were measured on static samples, at ambient temperature 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 TDS620 digital oscilloscope. In our arrangement the reference electrode was 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 tetrabutylammonium perchlorate as the supporting electrolyte. Peak potentials were referenced to the ferrocene/ferrocinium couple.

Acknowledgment. The authors wish to thank Ms. Maryam Amoli for technical assistance. V.D.P. thanks the National Science Foundation for financial support.

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