

molecular quenching. But, we see no reasons to suspect drastically different triplet lifetimes between the two systems.

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on the electron density at C-8.

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Kinetics and Mechanisms of the Reactions of Organic Cation Radicals and Dications. III.¹ Arylation of Aromatic Hydrocarbon Cation Radicals

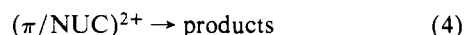
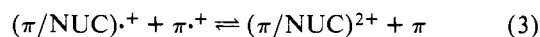
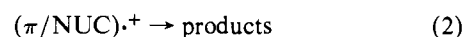
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Abstract: Aromatic hydrocarbon cation radicals undergo electrophilic attack on aromatic compounds such as anisole, toluene, benzene, and chlorobenzene to give the corresponding arylated compounds. The reactions were studied in media containing trifluoroacetic acid, and in some cases trifluoroacetoxylation of the cation radicals were significant competing processes. The radical ions studied most thoroughly were those from 9-phenylanthracene (PA) and anthracene (A). The reaction of PA with anisole (AN) obeys the rate law $-d[PA^{\cdot+}]/dt = k_{app}[PA^{\cdot+}]^2[AN]/(2.36 \times 10^{-3} + [PA])$. The data are consistent with a mechanism involving initial complex formation between the cation radical and AN followed by electron transfer to a second $PA^{\cdot+}$. The value of the constant in the denominator of the rate law is of such magnitude that the linear anisole dependence was used to conclusively rule out an alternate reaction mechanism involving the disproportionation of $PA^{\cdot+}$. As expected, the corresponding dications of the aromatic hydrocarbons were found to react at much greater rates with the aromatic compounds. The latter reactions are most likely simple bimolecular processes. Convincing support of the proposed reaction mechanism was obtained from experiments in which equal concentrations of $PA^{\cdot+}$ and dibenzodioxin (DBO) cation radical were allowed to react with AN and a large rate enhancement was observed as predicted by the mechanism considering the higher oxidation potential of DBO.

Electrophilic reactions of aromatic cation radicals have been studied in numerous cases.¹⁻⁹ The most common reactions result in the formation of carbon-heteroatom bonds although one case, the cyclization of the tetraphenylethylene cation radical which proceeds via disproportionation to the dication, involves carbon-carbon bond formation and has been studied in detail.^{1a} Cation radicals have been implicated in other electrophilic reactions of anodically generated intermediates, for example, the trimerization of anthracene¹⁰ and in the anodic arylation of naphthalene with alkyl benzenes.^{11,12} The latter studies involved only product determinations and little is known regarding the mechanisms of the reactions.

We have recently observed that several cation radicals of aromatic compounds react with simple aromatic compounds such as benzene, toluene, chlorobenzene, and anisole. Some of the reactions take place at rates convenient for kinetic studies. Previous papers in this series¹ describe the kinetics and mechanisms of various cation radical reactions and suggest a general mechanism for such reactions which involves an initial complexation of the radical ion with the other reactant (eq 1). Depending upon the reactivity of the initial complex, a first-order reaction leading to products (eq 2) or a bimolecular electron transfer reaction with a second radical ion leading to a dication complex (eq 3) which dissociates leading to products (eq 4) may occur. In some cases it has been possible to control the proportion of reaction following the first- and the second-order pathways by suitable adjustment of the cation radical concentration. In this paper we further demonstrate the generality of the complexation mechanism and report the new reactions: arylation of aromatic hydrocarbon cation radicals.



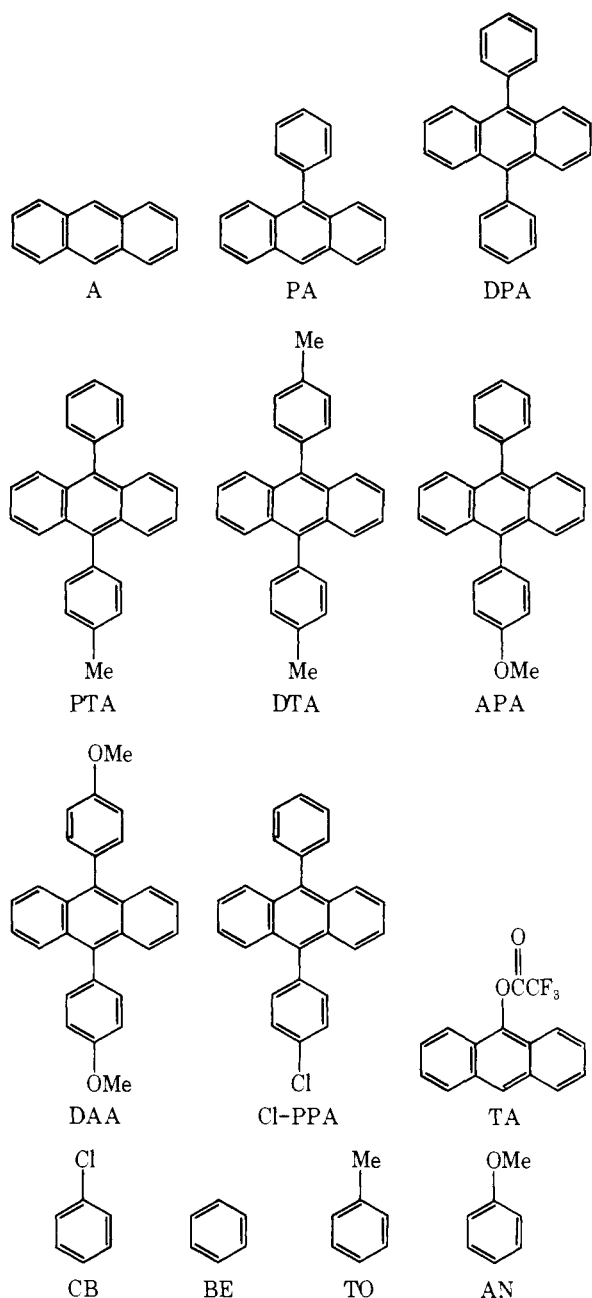
Results

Structures and identifying symbols of the aromatic compounds are summarized in Scheme I.

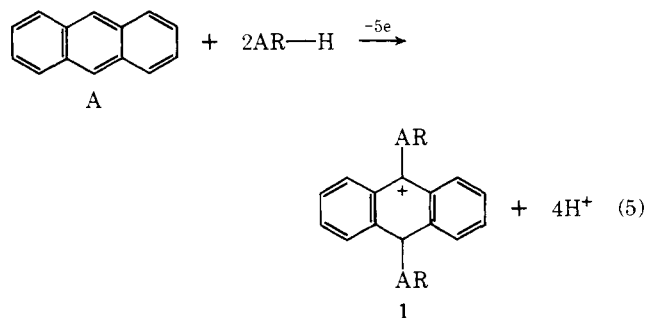
Reactions of Anthracene Cation Radical with Aromatic Compounds. The cation radical of anthracene (A) is readily observable by voltametric and spectrophotometric techniques during anodic oxidation of anthracene in dichloromethane containing trifluoroacetic acid anhydride (TFAn) and trifluoroacetic acid (TFA).¹³ Solutions of $A^{\cdot+}$ in the above medium prepared by anodic oxidation of A were found to react with anisole (AN), benzene (BE), toluene (TO), and chlorobenzene (CB). Since the lifetime of $A^{\cdot+}$ was limited by reaction with TFA, it was inconvenient to prepare reaction products by first oxidizing A and then admitting the aromatic compounds. The method of choice was to oxidize A in the presence of the aromatic compound. The products of the reactions, 9,10-diarlylanthracenes, were readily identified by their voltametric behavior and from the visible absorption spectra of the corresponding cation radicals.

Exhaustive constant current coulometry¹⁴ on 1 mM solutions of A in CH_2Cl_2 -TFA-TFAn (90:5:5) containing the aromatic compound (100 mM) resulted in the consumption of 5.0 faradays/mol and the formation of the cation radical of

Scheme I



the corresponding diarylanthracene according to eq 5. Under coulometric conditions, the yields of **1** were determined directly by visible absorption spectral measurements on the electrolytic solutions. The product of the competing reaction, 9-trifluoroacetoxyanthracene (TA), is about 300 mV more difficult to oxidize than the diarylanthracenes and thus does not form the corresponding cation radical under the reaction conditions. Data for the reaction of $A^{\bullet+}$ with the aromatic compounds are

Table I. Products from the Reactions of $A^{\bullet+}$ and $PA^{\bullet+}$ with Aromatic Compounds

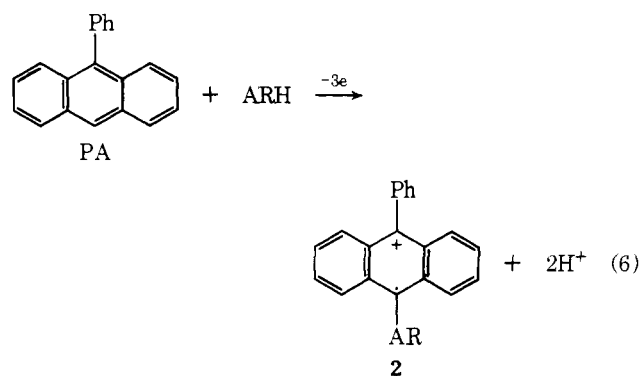
Cation radical	Aromatic compd	Product	% yield ^a
$A^{\bullet+}$	BE	DPA $^{\bullet+}$	50
$A^{\bullet+}$	TO	DTA $^{\bullet+}$	60
$A^{\bullet+}$	AN	DAA $^{\bullet+}$	70
$PA^{\bullet+}$	CB	Cl-PPA $^{\bullet+}$	70
$PA^{\bullet+}$	BE	DPA $^{\bullet+}$	95
$PA^{\bullet+}$	TO	PTA $^{\bullet+}$	~100
$PA^{\bullet+}$	AN	APA $^{\bullet+}$	~100

^a Yields were determined by a combination of visible spectral (Table II) and voltametric measurements. Trifluoroacetoxylation was always a significant competing process with $A^{\bullet+}$ and when $PA^{\bullet+}$ was allowed to react with CB.

summarized in Table I and the spectral characteristics of the product cation radicals are listed in Table II.

The reactions of $A^{\bullet+}$ with all the aromatic compounds except AN are sufficiently slow that even in the presence of the latter A is reversibly oxidized under cyclic voltametric conditions in the same solvent mixture as the other experiments. Reversible behavior is observed at higher sweep rates in the presence of AN. On the other hand, A^{2+} reacts rapidly with all the aromatic compounds. The latter is demonstrated in Figure 1 for the reaction with TO. When the direction of voltage sweep is reversed after the initial A oxidation peak (O_1), the corresponding reduction peak (R_1) of $A^{\bullet+}$ was observed (Figure 1a). When the initial sweep was extended (Figure 1b) to include the second charge transfer, an irreversible oxidation peak was observed (O_2). The second cycle revealed a new reversible couple (R_3 - O_3) due to the product, di-*p*-tolylantracene (DTA), the voltamogram of which is also shown (Figure 1c).

Reactions of 9-Phenylanthracene Cation Radical with Aromatic Compounds. The cation radical of 9-phenylanthracene (PA) is decidedly more stable in CH_2Cl_2 -TFA-TFAn (90:5:5) than is $A^{\bullet+}$. The reaction of $PA^{\bullet+}$ with aromatic compounds is a convenient method to prepare the unsymmetrically substituted diarylanthracenes (**2**). The reactions with AN, TO,



and BE are not complicated by competing trifluoroacetoxylation. However, in the case of the less reactive CB, the products consist of about two parts of arylation to one part trifluoroacetoxylation.

The dication, PA^{2+} , as expected was observed to react much more rapidly with the aromatic compounds than the cation radical.

Product and spectral data are summarized in Tables I and II, respectively.

Kinetics of the Reaction of $PA^{\bullet+}$ with AN in CH_2Cl_2 -TFA-TFAn (97:2:1). As in other studies,^{1a-d} competing reactions of the cation radical in CH_2Cl_2 were minimized by the inclusion of small amounts of TFA and TFAn in the solvent. The reaction between $PA^{\bullet+}$ and AN in that solvent took place

Table II. Spectral Characteristics of A^{•+}, PA^{•+}, and the Product Cation Radicals

Cation radical	λ_{\max} , nm	$\epsilon \times 10^{-4}$	λ_{\max} , nm	$\epsilon \times 10^{-4}$	λ_{\max} , nm	$\epsilon \times 10^{-4}$
A ^{•+}			626		680	
PA ^{•+}	585	~0.8	645	~0.9	715	~1
Cl-PPA ^{•+}	594		656			
DPA ^{•+}	597	1.02	657	0.99	732	0.86
PTA ^{•+}	599	~1.40	657	~1.36		
DTA ^{•+}	606	1.08	666	1.19		
APA ^{•+}	608	1.25	670	1.38		
DAA ^{•+}	623	1.20	676	1.52		

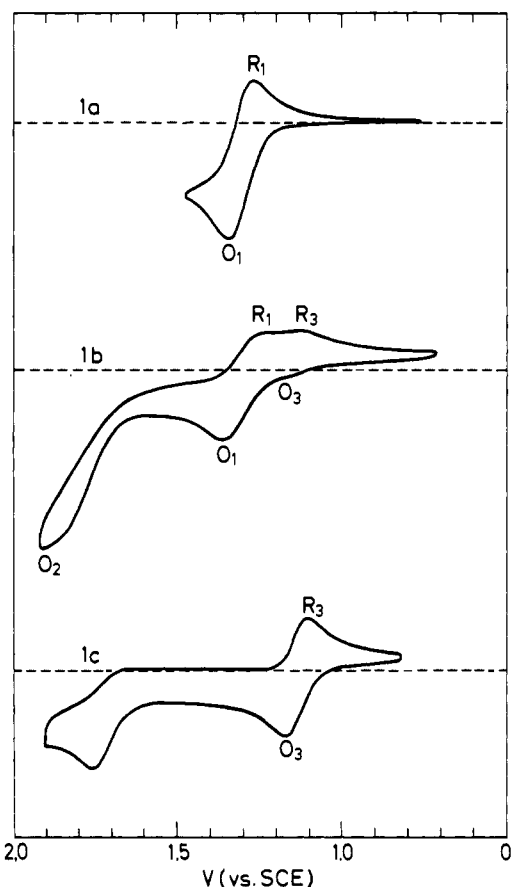


Figure 1. Cyclic voltammograms of A (1 mM) in CH₂Cl₂-TFA-TFAn (47:2:1) containing *n*-Bu₄NBF₄ (0.2 M) and TO (10 mM). Direction of voltage sweep (400 mV/sec) changed after (a) first charge transfer and (b) extended to include second charge transfer. (c) Cyclic voltammogram of authentic DTA (scan rate 100 mV/sec).

at rates convenient to be followed by measurement of the reduction current for PA^{•+} at the rotating disc electrode as a function of time.⁶ The variables investigated were cation radical concentration, unoxidized substrate (PA) concentration, as well as the nucleophile (AN) concentration. The data are summarized in Table III. Treatment of the data in the usual way^{1b-d} resulted in eq 7 for the relationship between the observed pseudo-second-order rate constant (k_{obsd}) and the apparent second-order rate constant (k_{app}) normalized for $[\text{PA}]_0$ and $[\text{AN}]_0$ which was derived from the plot of $1/k_{\text{obsd}}$ vs. $[\text{PA}]_0$ (Figure 2). The dependence of k_{obsd} on $[\text{AN}]_0$ (Figure 3) verified that the reaction is first order in $[\text{AN}]$. In all cases linear second order rate plots were obtained for at least one half-life. At higher conversions deviation from linearity was observed. The latter is to be expected since the stoichiometry of the reaction is given by eq 6 and 2 is reduced at about the same potential as PA^{•+}.

$$-d[\text{PA}^{\bullet+}]/dt = k_{\text{app}}[\text{PA}^{\bullet+}]^2[\text{AN}]/(2.36 \times 10^{-3} + [\text{PA}])$$

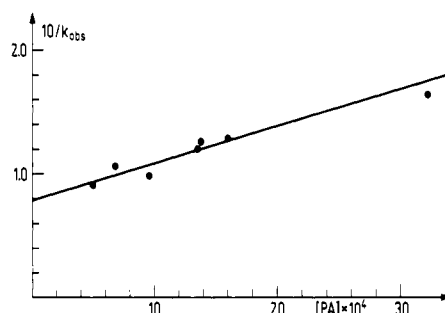


Figure 2. Plot of $1/k_{\text{obsd}}$ vs. $[\text{PA}]_0$ for the pseudo-second-order reaction between PA^{•+} and AN in CH₂Cl₂-TFA-TFAn (97:2:1) at 11°C ($[\text{AN}]_0 = 9.2 \times 10^{-2}$ M).

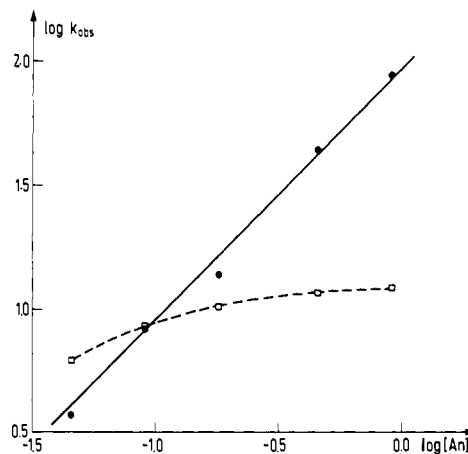


Figure 3. Dependence of k_{obsd} on $[\text{AN}]_0$ for the pseudo-second-order reaction between PA^{•+} and AN in CH₂Cl₂-TFA-TFAn (97:2:1) at 11°C: (●) experimental points, (□) calculation on the basis of the rate law for disproportionation.

or

$$k_{\text{obsd}} = k_{\text{app}}[\text{AN}]_0/(2.36 \times 10^{-3} + [\text{PA}]) \quad (7)$$

Kinetics of the Reaction of A^{•+} with AN in CH₂Cl₂-TFA-TFAn (95:4:1). In order to minimize competing reactions of A^{•+}, which is considerably more reactive than PA^{•+}, it was necessary to include higher concentrations of TFA. The latter was accompanied by the further complication of a new competing reaction, trifluoroacetoxylation of A^{•+}. The optimum conditions were found to be the above-mentioned solvent system and under the reaction conditions about two-thirds of the product was 9,10-dianisylanthracene and the balance was 9-trifluoroacetoxyanthracene. The reaction between A^{•+} and AN involves further electron transfer reactions after the rate determining step (eq 2), and some deviation from linearity of first-order rate plots was observed. However, the rate constants normalized for $[\text{AN}]$ were in close agreement. Attempts to plot the data for second-order kinetics revealed large deviations and

Table III. The Pseudo-Second-Order Reaction between PA^{•+} and AN^a

Run no.	[PA ^{•+}] × 10 ⁴	[PA] × 10 ⁴	[AN] × 10 ²	k _{obsd} , M ⁻¹ s ⁻¹ ^b	k _{app} , M ⁻¹ s ⁻¹
1	0.57	3.61	9.2	13.0	0.384
2	2.53	5.95	9.2	11.0	0.353
3	2.15	6.77	9.2	9.6	0.317
4	6.46	9.68	9.2	10.1	0.365
5	3.80	13.6	9.2	8.3	0.336
6	3.92	13.8	9.2	8.2	0.333
7	2.28	16.1	9.2	7.8	0.337
8	4.05	32.2	9.2	6.1	0.370
9	3.80	32.4	9.2	6.3	0.383
10	3.04	4.30	1.84	2.37	0.359
11	2.91	14.7	4.6	3.7	0.308
12	4.30	31.9	6.9	4.0	0.322
13	3.92	14.2	18.4	13.8	0.284
14	4.30	13.4	46	43.9	0.353
15	3.92	13.7	92	87.1	0.353
16 ^c			9.2	758	

^a Solvent: CH₂Cl₂-TFA-TFAn (97:2:1). Supporting electrolyte: *n*-Bu₄NBF₄ (0.1 M). Temp 11°. Concentrations in mol/l. ^b k_{obsd} = k_{app}[AN]/(2.36 × 10⁻³ + [PA]). ^c [PA^{•+}] + [DBO^{•+}] = 3.88 × 10⁻⁴, and [DBO] = 42 × 10⁻⁴.

Table IV. The Pseudo-First-Order Reaction between A^{•+} and AN^a

Run no.	[A ^{•+}] × 10 ⁴	[A] × 10 ⁴	[AN] × 10 ²	k _{obsd} (s ⁻¹) × 10 ² ^b	k _{app} , s ⁻¹
17	0.58	15.2	0.92	1.8	1.96
18	1.06	5.58	0.92	2.2	2.39
19	1.15	10.2	0.92	1.98	2.15
20	1.06	14.6	0.92	2.08	2.26
21	1.06	14.2	0.92	1.86	2.02
22	1.44	15.0	0.92	1.99	2.16
23	1.06	14.5	1.84	3.95	2.15
24	1.06	14.7	3.68	7.	1.90

^a Solvent: CH₂Cl₂-TFA-TFAn (95:4:1). Supporting electrolyte: *n*-Bu₄NBF₄ (0.1 M). Temp 11°. Concentration in mol/l. ^b k_{obsd} = k_{app}[AN].

the second-order constants decreased with increasing [A^{•+}]. The pseudo-first-order rate constants are summarized in Table IV.

Discussion

It is becoming increasingly clear that reactions of cation radicals with nucleophiles proceed via an initial complex (eq 1) which, depending upon the reactivity of the complex, may go directly to the products (eq 2) or require the transfer of an electron to another cation radical (eq 3), generating the more reactive dication complex which decomposes to the products (eq 4). The evidence which has emerged for this general mechanism is compelling. Several alternative possibilities for the anisylation of the thianthrene cation radical, such as disproportionation, were ruled out from both kinetic and thermodynamic data.^{1b} Electron transfer reactions between stable aromatic cation radicals and aromatic compounds were observed to conform to the correct rate law for mechanism 1-4, while alternative mechanisms could firmly be ruled out.^{1c} In accord with the complexation mechanism, the kinetics of the reaction between the thianthrene cation radical and phenol could be diverted from pseudo first order to pseudo second order by including TFA in the solvent system.^{1d} The latter was a consequence of slowing down the deprotonation of the initial complex which led to its decomposition, as in (2). The reactions involved in this study illuminate the situation still more. While the previous study^{1d} showed that the first-order pathway can be favored by using a nucleophile which imparts unusual reactivity to the initial complex, the present work shows that the same effect is brought about by increasing the reactivity of the cation radical.

9-Phenylanthracene cation radical is sufficiently stable in aprotic solvents, purified by conventional techniques, to show

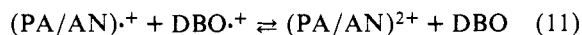
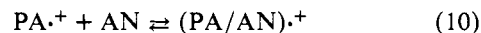
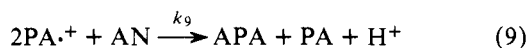
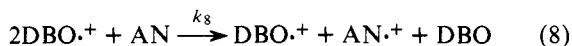
partially reversible voltametry.¹⁵ On the other hand, until recently it has been possible to observe A^{•+} during cyclic voltametry only if very rapid sweep rates are employed.¹⁶ The lifetimes of both PA^{•+} and A^{•+} are extended in aprotic solvents in the presence of neutral alumina so that reversible one-electron oxidations are observed during slow sweep cyclic voltametry.¹³ A more suitable way of stabilizing cation radicals for kinetic studies in organic solvents is to include small amounts of the nucleophile scavenger, trifluoroacetic acid anhydride.¹⁷ Under the latter conditions both PA^{•+} and A^{•+} solutions could be prepared by anodic oxidation of the hydrocarbons and were sufficiently stable to allow the other reactant, AN, to be added before kinetic measurements were commenced. The stability of cation radicals in aprotic solvents is profoundly affected by the presence of TFA.^{1d,18} Thus for the more reactive A^{•+} significantly higher TFA concentrations were necessary to allow kinetic measurements to be carried out.

Although it was not possible to study the reactions of PA^{•+} and A^{•+} under identical conditions, a reasonable estimate of the relative rates of product formation with anisole is that A^{•+} reacts about 10³ times more rapidly than does PA^{•+}. Only pseudo-first-order kinetics were observed with A^{•+} while only the second-order pathway was detected with PA^{•+}. Considering the complexation mechanism (eq 1-4), it seems reasonable to assume that the rate of the electron-transfer step (eq 3) should be nearly independent of π^{•+} since the relative oxidation potentials of π^{•+} and (π/NUC)^{•+} should be nearly the same for all π^{•+} even though the magnitude of the potentials change with changing π. Thus, the difference in rate between the reaction of A^{•+} and PA^{•+} lies in the increased rate of step 2 when the ion radical is A^{•+}. A possible explanation emerges by considering to what the structure of the initial complex most likely corresponds. Complexes between aromatic

cation radicals and aromatic compounds have been the subject of several investigations.¹⁹ It is generally concluded that both cation-radical dimers and complexes between cation radicals and uncharged aromatics have sandwich-like structures. If we look at the series of cation radicals, A^{•+}, PA^{•+}, and DPA^{•+}, one might predict that the complex from the cation radicals and AN increase in strength in going from A to PA to DPA due to the presence of the phenyl groups, the planes of which are not parallel to the anthracene nucleus. The bulky phenyl groups of PA^{•+} and DPA^{•+} would be expected to exert a steric repulsive force on the AN moiety of the complexes, thereby increasing the distance between the anthracene nucleus and the AN ring. Thus, the predicted order of reactivity on that basis is A^{•+} > PA^{•+} > DPA^{•+}. The latter is precisely the observed trend already discussed for the first two ions, and the previous study revealed that DPA^{•+} undergoes an electron-transfer reaction with AN via the complexation mechanism with a pseudo-second-order rate constant (k_{app}) of $3.5 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$; i.e., PA^{•+} is about 10^3 times as reactive toward AN as DPA^{•+}. Thus, substitution of phenyl groups at the 9 and 10 positions of the anthracene nucleus has the effect predicted by the complexation mechanism.

The above discussion allows one to draw some general conclusions regarding the relative importance of the first- and second-order reaction pathways. In general, cation radicals of benzene derivatives and naphthalene are much more reactive than those of the condensed ring aromatics such as the anthracenes and larger molecules. The smaller, more reactive ions would be expected to form complexes with nucleophiles which are not very stable, and thus the first-order pathway should be rapid enough to preclude the second-order pathway, the rate of which is limited by the low concentrations of the complex and diffusion of the reacting entities. On the other hand, cation radicals which are in themselves stable, in the absence of effects such as steric inhibition of complexation as proposed for the phenyl anthracenes, should form relatively stable complexes which could undergo electron transfer with the cation radical to give the more reactive dication complex and second-order kinetics.

The synergistic effect of DBO^{•+} on the rate of the reaction between PA^{•+} and AN requires further comment. The pseudo-second-order rate constant (k_{app}) for reaction 8 is equal to $2 \text{ M}^{-1} \text{ s}^{-1}$ in CH₂Cl₂-TFA-TFAn (97:2:1) at 11 °C while k_{app} for reaction 9 is equal to $0.35 \text{ M}^{-1} \text{ s}^{-1}$ under comparable conditions. When equimolar amounts of PA^{•+} and DBO^{•+} react with AN, k_{app} was observed to be equal to 54.²¹ A similar effect has previously been observed during the anisylation of TH^{•+} in the presence of DBO^{•+} and was attributed to DBO^{•+} shifting equilibrium 3 to the right owing to its greater oxidizing power.¹ The results of this work can be interpreted similarly. If we assume that PA^{•+} participates in complex formation with AN to a greater extent (eq 10) than DBO^{•+}, the synergistic effect arises from the fact that equilibrium 11 is of the order of 5×10^2 further to the right when the oxidant is DBO^{•+} as compared with a comparable equilibrium involving PA^{•+}. In fact, the relative rate constants $k_8/k_9 = 154$ fits this interpretation very well.



The rate law for the disproportionation mechanism is given by eq 12,^{1b} which predicts that the reaction should not be first order in [AN]. Since the reaction is clearly first order in [AN] (Figure 3), the disproportionation mechanism can be ruled out.

$$-d[\text{PA}^{\bullet+}]/dt = k[\text{PA}^{\bullet+}]^2[\text{AN}]/(\text{constant}[\text{AN}] + [\text{PA}]) \quad (12)$$

Experimental Section

Dichloromethane was passed through a column of neutral alumina (Woelm W 200) immediately before use. Trifluoroacetic acid and trifluoroacetic acid anhydride were used as obtained (Fluka, purum grade).

The apparatus used for voltametric measurements²⁰ and the cell^{1b} used both for the kinetic study and for the preparation of the cation radical solutions have been described. The procedures used for preparations^{1b} of the cation radical solutions and for carrying out the kinetic runs⁶ were those previously described.

Preparation of DAA. Anthracene (10 mmol) in CH₂Cl₂-TFA-TFAn (47:2:1) containing *n*-Bu₄NBF₄ (0.2 M) and anisole (100 mmol) were subjected to anodic oxidation at a platinum gauze electrode at a constant current of 200 mA in a two-compartment cell cooled by tap water. After 5 faradays/mol had passed (402.5 min), the product cation radical was reduced by adding Zn to the anolyte. After stirring for 2 h, the solution was filtered and evaporated almost to dryness. A small amount of MeCN was added to the residue and the product precipitated upon cooling (80% yield). The product was washed with cold MeCN and was identical with authentic 9,10-dianisylanthracene.

Preparation of APA. 9-Phenylanthracene (10 mmol) in CH₂Cl₂-TFA-TFAn (97:2:1) containing *n*-Bu₄NBF₄ (0.2 M) and anisole (100 mmol) was subjected to anodic oxidation as described above. After 3 faradays/mol had passed, the product was isolated as described above in 70% yield. NMR, ir, and mass spectra are in accordance with those expected for 9-anisyl-10-phenylanthracene.

References and Notes

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- To arrive at this result it was necessary to assume that the relationship between k_{obsd} and k_{app} is the same when the cation radical mixture in the presence of excess DBO reacts as was determined for the PA^{•+} reaction with AN (eq 7).