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Radical Cation–Nucleophile Combination Reactions. Displacement of Halogen during Ipso Attack on Haloanthracene Radical Cations

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Second-order rate constants for the reactions of radical cations of a number of haloanthracenes with pyridine and 2-substituted pyridines were determined in acetonitrile and dichloromethane using electrochemical techniques. Attack at the ipso positions was observed to be less favorable than attack at positions bearing hydrogen. The halo-substituents were observed to exert opposing electronic and steric effects on the second-order rate constants. The 10-positions of 9-haloanthracene radical cations were observed to be nearly 2 orders of magnitude more susceptible to nucleophilic attack by pyridine than the 9,10-positions of the parent radical cation.

Introduction

Radical cation–nucleophile combinations which usually involve attack at a position bearing hydrogen on an arene radical cation are facile reactions.[2] Renewed interest has recently been shown in the mechanisms of these reactions in both the solution[3–9] and the gas phase.[10]

We have found that 9-phenylanthracene derivatives (ArH) are especially well suited as radical cation precursors for the study of these reactions.[3–7] In the absence of nucleophiles ArH$^{+\bullet}$ are long-lived and in the presence of nucleophiles in solvents such as acetonitrile or dichloromethane, combination reactions with second-order rate constants ranging from about 10^2 to 10^{10} M^{-1} s^{-1} have been observed. Substitution of the 10-hydrogen by 10-deuterium results in secondary α-deuterium kinetic isotope effects ranging from 0.7 to 0.9 for the combination reactions.[6] The reaction rates are attenuated by steric effects resulting from either substitution in the 10-position or the use of bulky nucleophiles.[11] For example, the relative reactivities of 9-phenylanthracene and 9,10-diphenylanthracene radical cations toward pyridine nucleophiles is of the order of 10^3 while the rate constants for the reactions of the former vary from about 10^7 for pyridine to 10^3 for 2,6-dimethylpyridine as nucleophile.[6]

The electronic effects of substituents have been studied either by changes in substituents at the 10-position of anthracene[6] or at the 4-position of the phenyl group of 9-phenylanthracene.[7] The Hammett ρ's for the former reaction series with various pyridine derivatives were observed to be 2.4 ± 0.3 while remote substitution in the latter reaction series resulted in $\rho = 0.47 \pm 0.05$.

Nucleophilic displacements of halogen from radical cations have been observed in a number of instances[12–15] and the reaction sometimes initiates a chain process. The chain mechanism is described as the $S_{ON}2$ reaction[13,14] in analogy to the more familiar $S_{RN}1$ reaction of haloarene radical anions.[16] Although ipso[17] attack at halobenzene radical cations has been observed to be "slow",[15] there are no data available to compare the reactivity of nucleophiles toward radical cation reaction sites bearing either hydrogen or halogen substituents.

We now report the results of a study of the reactions of 9-halo-10-phenylanthracene radical cations with pyridine nucleophiles and compare the reactivity of the ipso positions of haloarene radical cations to that at the corresponding unsubstituted positions. Our results show that the barriers for ipso attack at positions bearing halogen substituents (I, Br, and Cl) are greater than those at positions bearing hydrogen and are dependent upon both the electronic and steric effect of the halogen atom.

Experimental Section

Materials. Acetonitrile and dichloromethane solvents were distilled from P_2O_5 and calcium chloride, respectively, and stored over active neutral alumina. Lithium perchlorate (Aldrich), tetrabutylammonium iodide (Koch-Light Laboratories), 9-bromoanthracene (Aldrich), and 9,10-dichloroanthracene (Aldrich) were used as received. Tetrabutylammonium hexafluorophosphate (Aldrich) was recrystallized from dichloromethane–ether before use. Pyridine, 2-methylpyridine, and 2-phenylpyridine were obtained from Aldrich and passed through a column of active neutral alumina before use. 9-Bromo-10-phenylanthracene,[18] 9-chloro-10-phenylanthracene,[18] 9-fluoro-10-phenylanthracene,[19] and 9,10-dibromoanthracene[20] were prepared as

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described in the literature. 9-Chloroanthracene (Aldrich) was recrystallized from 2-propanol–acetone.

9-Iodo-10-phenylanthracene: Since the preparation of this compound from the corresponding Mg derivative, reported elsewhere,[21] afforded low yield it was synthesized through dediazo iodination of 9-phenyl-10-anthracene diazonium tetrafluoroborate. A well-stirred solution of 9-phenyl-10-anthracene diazonium tetrafluoroborate (1.83 g, 5 mmol), prepared according to a literature procedure,[19] and iodine (0.63 g, 5 mmol) in CH_2I_2 (20 mL) was treated with a solution of $Bu_4N^+I^-$ (3.69 g, 10 mmol) in CH_2I_2 (25 mL) dropwise under a nitrogen atmosphere at room temperature. The mixture was stirred for an additional 45 min and then treated with 10% $Na_2S_2O_3$ to destroy iodine. Conventional workup followed by recrystallization of the solid from 2-propanol afforded nonfluorescent greenish-yellow crystals of 9-iodo-10-phenylanthracene (1.24 g, 65%) melting at 132–133 °C (lit.[21] 132 °C).

Preparative Electrolyses. The experiments were performed using constant current coulometry between platinum mesh electrodes ($\simeq$10 cm^2) in an H cell charged with 20 mL of solution [$CH_3CN/LiClO_4$ (0.1 M)] in each compartment. Substrate (0.1 mmol) along with pyridine (0.2 mmol) was added to the anode compartment before a constant current (5.0 mA) corresponding to 2 faradays/mol was passed through the cell. Products were isolated by first evaporating to dryness. The resulting solid was rapidly rinsed with water followed by careful rinsing with dry benzene. Attempts to further purify the unstable solids by recrystallization or chromatography generally failed.

Instrumentation and Data Handling Procedures. Cyclic and linear sweep voltammetry were performed using JAS Instrument Systems, Model JDP-165A, potentiostat driven by a Hewlett-Packard 3314A function generator. The signals were filtered with a Stanford Research Systems, Inc., Model SR640 dual channel low pass filter before recording on a Nicolet Model 310 digital oscilloscope. An IBM AT compatible personal computer was used to control the oscilloscope and the function generator *via* an IEEE interface. The current-potential curves were collected and averaged at trigger intervals selected to reduce periodic noise.[22] The averaged signals were then treated with a digital frequency domain low pass filter before numerical differentiation.

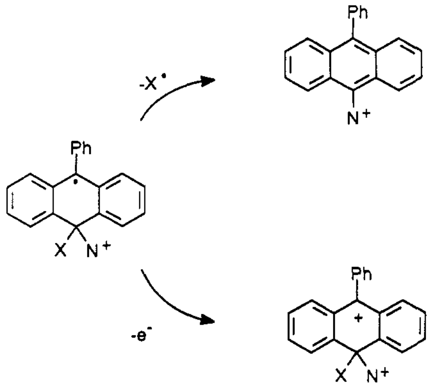
^1H NMR spectra were obtained on a Varian XL-300 (resolution 0.245 Hz) or a JEOL JNM-GSX270 (resolution 0.66 Hz) spectrometer, with residual protons in the solvent (CD_3CN, 1.93 ppm) as an internal reference. ^{19}F NMR spectra were obtained on the Varian XL-300 spectrometer, with external trifluoroacetic acid (−76.53 ppm) as a reference.

Derivative Cyclic and Derivative Linear Sweep Voltammetry Measurements. A one-compartment cell with three electrodes was used for all kinetic measurements. To minimize the effects of uncompensated solution resistance a positive feedback IR compensation circuit was used. Reference electrodes were $Ag/AgNO_3$ (0.01 M) in acetonitrile as described by Moe.[23] Working electrodes, 0.1–0.8 mm Pt, were prepared as described previously.[24] The electrochemical cell was immersed in a water bath controlled to 25 ± 0.3 °C. All measurements were performed under an argon atmosphere.

Kinetic Measurements. Rate constants were obtained by comparing experimental data to theoretical data obtained by digital simulation.[25] Derivative cyclic voltammetry[26] data were obtained for second-order rate conditions using solutions containing 1 mM substrate and 2 mM nucleophile. Derivative linear sweep voltammetry measurements were performed using the prepeak method[27] with solutions containing 1 mM substrate and 0.5 mM nucleophile.

Reaction Products of Radical Cation Nucleophile Combination. Products of the Reactions of the Radical Cations 1a–e with Pyridine. The reactions of the free radicals ($ArX^{\bullet}N^+$) generated upon attack of pyridine (N) on the radical cations of **1a** + **1c–e** result in the formation of monopyridinium salts (ArN^+) as the major reaction products. When X is H, ArN^+ is formed in nearly quantitative yield.[28] The yield of ArN^+ is readily assessed by the intensity of an oxidation peak about 500 mV more positive than that for the oxidation of the substrate (ArX) during cyclic voltammetry experiments.[12] When X is Cl, Br, or I; $ArX^{\bullet}N^+$ partitions between loss of $X^{\bullet}$ to give ArN^+ and further oxidation to give ArX^+N^+ (Scheme I). The latter then reacts with pyridine to generate the bis-pyridinium salt [$ArX(N^+)_2$]. Yields of ArN^+, determined by cyclic voltammetry, were observed to be 60% (X = Cl), 63% (X = Br), and 50% (X = I). The products were isolated as the ClO_4^- salts and the ^1H NMR spectra compared to that of authentic[28] ArN^+. Analyses of the crude reaction mixtures by ^1H NMR spectroscopy were indicative of the presence of $ArX(N^+)_2$ [X = Cl, Br, I] but attempts to isolate and purify the salts were not successful; there was evidence of extensive decomposition.

Scheme I



Cyclic voltammetry experiments on the oxidation of ArF in the presence of N failed to show a peak for the oxidation of ArN^+. Preparative experiments resulted in the isolation of $ArF(N^+)_2(ClO_4^-)_2$ as a tan powder in approximately 80% yield. The purity of $ArF(N^+)_2(ClO_4^-)_2$ was estimated to be >98% from the ^1H NMR spectrum obtained shortly after isolation. The salt was observed to be unstable, decomposing to unidentified mixtures of compounds. The ^1H and ^{19}F NMR spectral data are summarized below (An = anthracene ring; Pyr = pyridine ring; Ph = phenyl ring; numbers refer to positions, *i.e.*, H-4, Pyr-9 refers to the proton at the 4-position on the pyridine ring attached to the 9-position of anthracene).

9-Fluoro-10-phenyl-9,10-dipyridinioanthracene perchlorate: ^1H NMR δ 8.70 (t, 1H, J = 7.6 Hz, H-4, Pyr-9), 8.37 (d, 2H, J = 7.9 Hz, H-2, H-6, Pyr-9), 8.34 (d, 2H, J = 8.6 Hz, An), 8.25 (t, 1H, J = 7.6 Hz, H-4, Pyr-10), 8.16 (d, 2H, J = 5.9 Hz, H-2, H-6, Pyr-10), 8.05 (t, 2H, J = 7.3 Hz, H-3, H-5, Pyr-9), 7.92 (t, 2H, J = 7.6 Hz, An), 7.79 (t, 2H, J = 7.6 Hz, An), 7.51 (t, 2H, J = 7.6 Hz, H-3, H-5, Pyr-10), 7.28 (t, 1H, J = 7.3 Hz, H-4, Ph), 7.11 (t, 2H, J = 7.9 Hz, H-3, H-5, Ph), 6.95 (d, 2H, J = 7.9 Hz, An), 6.78 (d, 2H, J = 7.3 Hz, H-2, H-6, Ph). Signals in the spectrum were assigned by comparison with that of 9-fluoro-10-phenyl-9,10-dipyridinio-d_5-anthracene. ^{19}F NMR δ −113.23 ppm.

Products of the Reactions of 9-Halo- and 9,10-Dihaloanthracene Radical Cations with Pyridine. 9-Halo-9,10-pyridinioanthracene salts were the only products observed for the oxidations of 9-chloro-, 9-bromo-, 9,10-dichloro-, and 9,10-dibromoanthracene in the presence of pyridine in acetonitrile/Bu_4NPF_6 (0.1 M). In all cases, the yields judged by cyclic voltammetry as described in the previous section appear to be nearly quantitative.

The products were isolated in sufficiently pure form for ^1H NMR analysis as the unstable perchlorate salts by preparative electrolysis in acetonitrile/$LiClO_4$ (0.1 M). ^1H NMR spectral data are summarized below.

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Table I. Electrode Potentials for the Formation of and Second-Order Rate Constants for the Reactions of Radical Cations of 9-Phenylanthracene Derivatives with Pyridine in Acetonitrile

10–substituent	E_{ox}[a], V	k[b] M^{-1} s^{-1}	$k_{relative}$
H[c]	0.85	1.1×10^7	1.0
F	0.88	1.3×10^7	1.2
Cl	0.91	5.4×10^5	0.05
Br	0.94	7.6×10^5	0.07
I	0.93	4.2×10^5	0.04

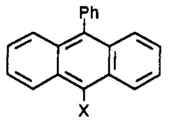
[a] Reversible electrode potential vs Fc/Fc$^{+\bullet}$ in acetonitrile. [b] Second-order rate constant for the reaction with pyridine at 298 K. [c] Data from ref 6.

9-Bromo-10-pyridinioanthracene perchlorate: ^{1}H NMR δ 8.98 (t, 1H, J = 7.9 Hz, H-4, Pyr), 8.95 (d, 2H, J = 6.9 Hz, H-2, H-6, Pyr), 8.76 (d, 2H, J = 8.9 Hz, An), 8.44 (t, 2H, J = 7.4 Hz, H-3, H-5, Pyr), 7.84 (t, 2H, J = 7.8 Hz, An), 7.71 (t, 2H, J = 7.7 Hz, An), 7.21 (d, 2H, J = 8.8 Hz, An).

9-Chloro-10-pyridinioanthracene perchlorate: ^{1}H NMR δ 8.99 (t, 1H, J = 8.0 Hz, H-4, Pyr), 8.95 (d, 2H, J = 6.9 Hz, H-2, H-6, Pyr), 8.71 (d, 2H, J = 8.9 Hz, An), 8.45 (t, 2H, J = 7.4 Hz, H-3, H-5, Pyr), 7.83 (t, 2H, J = 7.8 Hz, An), 7.72 (t, 2H, J = 7.7 Hz, An), 7.23 (d, 2H, J = 8.8 Hz, An).

Results and Discussion

Redox Potentials for the Oxidation of 9-Phenyl-10-haloanthracenes and Second-Order Rate Constants for the Radical Cation–Pyridine Combination Reactions. Derivative cyclic and linear sweep voltammetry[26] studies were carried out to determine the redox potentials of the substrates, 9-phenyl-10-haloanthracenes (**1b–e**), and second-order rate constants for the reactions of the radical cations with pyridines in acetonitrile solution.



1a X = H
1b X = F
1c X = Cl
1d X = Br
1e X = I

Radical cations of **1a–e** undergo rate-determining nucleophilic attack by pyridine in acetonitrile. The pyridine adducts partition between reaction pathways resulting in either mono- or bis-pyridinium salts as described earlier for the reactions of various anthracene radical cations.[28] Second-order rate constants for the reactions with pyridine at 298 K are summarized in Table I. The most pertinent feature of the data in Table I is that the rate constants are

$$\mathrm{ArX}^{+\bullet} + \text{pyridine} \rightleftarrows \pi\text{-complex} \qquad (1)$$

$$\pi\text{-complex} \rightarrow \sigma\text{-complex} \qquad (2)$$

dependent upon the halogen substituent diminishing with size. The reversible potential for the oxidation of **1a** is less positive than that for **1b–e**, implying that the latter are expected to be more reactive. We believe that the origin of the substituent effects is both electronic and steric in nature and that the steric effect dominates with the larger substituents. Since reaction 1 involves the reversible formation of a π-complex which is believed to occur rapidly, it is reasonable to expect reaction 2 to be rate limiting. The effect of the halogen substituents can be expressed by the rate constant relative to that where the substituent is H, k(X)/k(H). The relative rate constants are 1.2 (F), 0.05 (Cl), 0.07 (Br), and 0.04 (I). It is clear that ipso attacks when X is Cl, Br, and I are less favorable processes than attack at the 10-position bearing hydrogen.

Table II. Second-Order Rate Constants for the Reactions of 9-Halo-10-Phenylanthracene Radical Cations with Hindered Pyridines in Acetonitrile

	log k, M^{-1} s^{-1}[b]		
Substrate[a]	pyridine	2-methylpyridine	2-phenylpyridine
H[c]	7.04	6.04	4.49
F	7.11	4.94	2.74
Cl	5.73	3.90	2.02
Br	5.88	4.04	1.99
I	5.63	3.86	1.87

[a] 9-Substituent on 9-halo-10-phenylanthracene. [b] Measured at 298 K using derivative cyclic voltammetry. [c] Data from ref 6.

Table III. Second-Order Rate Constants for the Reactions of Radical Cations of Haloanthracenes with Pyridine in Acetonitrile and Dichloromethane

	log k, M^{-1} s^{-1} of 9,10-substituents			
solvent	Cl, Cl[a]	Br, Br[a]	Cl, H[b]	Br, H[b]
CH_3CN	6.65	6.70	8.96	8.73
CH_2Cl_2	6.10	6.29	8.97	8.59

[a] Measured at 298 K using derivative cyclic voltammetry. [b] Measured at 298 K using the prepeak method.

The radical cations of **1a–e** could conceivably undergo nucleophilic attack at the 9-position, *i.e.* ipso to the phenyl group. However, we have previously shown[3,4] that a phenyl substituent exerts a substantial steric effect on the reactivity toward nucleophilic attack. The rate constant ratio, k(Ph)/k(H), is expected to be of the order of 10^{-3} which is substantially lower than any of the k(X)/k(H) observed (Table I).

Combination Reactions between 10-Halo-9-phenylanthracene Radical Cations and Substituted Pyridines. Second-order constants for the reactions of the radical cations of a series of 10-halo-9-phenylanthracenes with hindered pyridines measured in acetonitrile are summarized in Table II. The data allow the steric effects exerted by halo-substituents and the 2-substituents on the pyridine ring to be evaluated. Data for the reactions with pyridine are included for comparison.

An interesting feature of the data is that combined electronic/steric effects of Cl, Br, and I are very similar for the reactions with all three nucleophiles. The relative rate constants for both of the hindered pyridines decreased in the order of 9-substituents: H > F > Br ≃ Cl ≃ I. It is of interest to note that the order for unsubstituted pyridine is F > H > Br ≃ Cl ≃ I. This change in the order of H- and F-substituted radical cations in going from pyridine to 2-substituted pyridines is indicative that F does not exert a significant steric effect unless the nucleophile is hindered. Furthermore, it appears that in going from left to right in Table II the electronic effects of the substituents diminish and the steric effects beging to dominate.

Combination Reactions between 9-Halo- and 9,10-Dihaloanthracene Radical Cations and Pyridine. Second-order rate constants for the reactions of the radical cations with pyridine in both acetonitrile and dichloromethane are tabulated in Table III. The data provide a basis to attempt to separate electronic and steric substituent effects. The ratio of the rate constants in the two solvents (CH_3CN/CH_2Cl_2) varies from 3.5 to 1.0 indicating the absence of a significant solvent effect on the reaction barriers.

The second-order rate constants for the reactions of haloanthracene radical cations are compared to those

Table IV. Effect of 9-Halo- and 9,10-Dihalo Substituents on Second-Order Rate Constants for Radical Cation Combination Reactions with Pyridine in Acetonitrile

		log k, $M^{-1}\ s^{-1}$[a]	
entry	substrate	bromo	chloro
1	anthracene	7.36 (H)[b]	7.36 (H)[b]
2	9-haloanthracene	8.73	8.96
3	9,10-dihaloanthracene	6.70	6.65
4	9-phenylanthracene	7.04 (H)[b]	7.04 (H)[b]
5	9-halo-10-phenylanthracene	5.88	5.73
6	9-halo enhancement (entry 2 − entry 1 + 0.30[c])	1.67	1.90
7	ipso-halo inhibition (entry 4 − entry 5)	1.16	1.31
	predicted effect (entry 6 + entry 7 − 0.30[c])	2.53	2.91
	observed effect (entry 2 − entry 3)	2.03	2.31

[a] The rate constants refer to attack at the ipso position unless otherwise noted. [b] Reference 6. Nucleophilic attachment at a position bearing H. [c] Statistical factor = log 2.

observed for the appropriate unsubstituted radical cations in Table IV. A relatively large electronic enhancement is observed for the reaction of pyridine at the 10-position of 9-haloanthracene radical cations when the substituent is Br ($\Delta\log k = 1.67$) and Cl ($\Delta\log k = 1.90$). The enhancements were derived by considering the relative rate constants for the 9-haloanthracene and anthracene radical cations taking into account a statistical factor of 2 for the reactions of the unsubstituted radical cation. 10-Halo-substituents inhibit the reactions, Br ($\Delta\log k = 1.16$) and Cl ($\Delta\log k = 1.31$), as shown by the relative rate constants for the reactions of 9-halo-10-phenylanthracene radical cations as compared to those of the parent compound.

The additivity of substituent effects, the enhancement by 9-halo and inhibition by 10-halo in the reactions of 9- and 9,10-dihaloanthracene radical cations with pyridine, was tested. The last two rows in Table IV give the predicted difference in log k for 9-halo and 9,10-dihalo substitution. The agreement between the experimental differences and those predicted assuming the effects should be additive is relatively good, with the observed differences being 0.5–0.6 log units.

Conclusions

Ipso substitution of haloanthracene radical cations by nucleophiles are facile reactions. The initial step in the reaction is rate-determining attack of the nucleophile at the ipso position. The halo-substituents exert both an electronic and a steric effect on the rate of attack of a nucleophile on the ipso position. The halo-substituents also exert an electronic effect on the rate of attack of the nucleophile at unsubstituted positions. The latter results in significant enhancements of second-order rate constants.

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