

The Search for Remote Substituent Effects on Radical Cation–Nucleophile Combination Reactions

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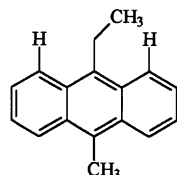
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The possibility that remote steric interactions between the *peri* hydrogen atoms at the 1,8-positions with 9-alkyl groups enhance the reactivities of 9-alkylanthracene radical cations toward nucleophiles has been examined by electrochemical kinetic techniques. Of a series of 9-alkylanthracene radical cation reactions with pyridine, the remote steric effect was only observed with the 9-*tert*-butyl derivative, and this resulted in a 10-fold rate enhancement. 9-*tert*-Butylanthracene radical cation was also observed to undergo a unimolecular decomposition reaction in 1,1,1,3,3,3-hexafluoropropan-2-ol to give anthracene and a butyl fragment. The latter reaction exhibits an Arrhenius activation energy of 8.2 kcal mol⁻¹.

Radical cation reactivity has been widely discussed in the past few years.^{1–12} The older work in this area¹ has been interpreted to indicate that radical cation–nucleophile combination and other ion radical reactions have high barriers and the phenomenon was explained on theoretical grounds.² This interpretation was challenged³ and later revised.⁶ The theoretical predictions^{2,6} are based on the magnitude of the vertical energy gap between reactant and product (in reactant geometry) valence bond configurations and thus refer only to the electronic contributions to the reaction barriers. It is evident from recent studies^{3c,12} that steric effects are often of more importance than the initial state energy gap.

The observation that radical cations of 9-ethyl-10-methylanthracene and 9,10-diethylanthracene undergo elimination of ethylene upon nucleophilic attack by water¹³ suggested the possibility of a remote steric effect, i.e., the interaction of the 9-ethyl group with the hydrogen atoms in the 1,8-positions (the ring positions shown in **1**).



We had previously observed that 9-*tert*-butylanthracene radical cation was short-lived in acetonitrile under conditions where other 9-alkylanthracene radical cations are

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persistent. These observations led us to study the effect of alkyl size on the reactions of 9-alkylanthracene radical cations with nucleophiles.

Results and discussion

Electrode reactions of 9-alkylanthracenes in 1,1,1,3,3,3-Hexafluoropropan-2-ol and in dry acetonitrile. A variety of radical cations have recently been observed to be persistent in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP).^{14–18} This work shows that HFP is the solvent of choice for measuring reversible electrode potentials for the formation of reactive radical cations. The remarkable persistence of radical cations in HFP has been attributed, at least in part, to a drastic deactivation of nucleophiles.^{16,17} The second column in Table 1 summarizes the peak potentials (vs. the ferrocenium/ferrocene couple) measured during cyclic voltammetry for the oxidation of

Table 1. Reversible oxidation potentials in HFP and v ($R'_1 = 0.5$) in acetonitrile.

Substituent	E^p/mV^a	v ($R'_1 = 0.5$) ^b
Methyl	714	11
Ethyl	707	4
Isopropyl	696	4
<i>tert</i> -Butyl	629	1100
Neopentyl	680	1

^aReversible oxidation potential relative to that of ferrocene measured in HFP–0.1 M Bu₄NPF₆ at 25 °C. ^bIn V s⁻¹ measured in acetonitrile–Bu₄NPF₆ (0.1 M) containing 1 mM substrate, defined as the sweep rate necessary to obtain a derivative current ratio of 0.5.

several 9-alkylanthracenes in HFP-Bu₄NPF₆ (0.1 M) at 298 K. The cyclic voltammograms for all of the 9-alkylanthracenes with the exception of 9-*tert*-butylanthracene appear reversible at a sweep rate (ν) of 100 mV s⁻¹ under these conditions. A sweep rate of about 1 V s⁻¹ was necessary for appreciable current to be observed on the return scan.

For the sake of comparison, the sweep rate necessary to observe a derivative current ratio equal to 0.5 (R_f) in acetonitrile-Bu₄NPF₆ (0.1 M) is shown in the third column. These data suggest that the lifetimes of the radical cations range from about 1 s (9-neopentylanthracene) to 1 ms (9-*tert*-butylanthracene). The differences in lifetimes of the radical cations in dry acetonitrile compared with HFP may be due to differences in reactivities toward either residual nucleophiles or to acetonitrile acting as a nucleophile.¹⁹

Reactions of 9-alkylanthracene radical cations with pyridine in acetonitrile and in dichloromethane. The kinetics of the reactions of the 9-alkylanthracene radical cations with pyridine in dichloromethane-Bu₄NPF₆ (0.2 M) were studied using the prepeak method (Table 2).²⁰ Under these conditions the second-order rate constant for the reaction of pyridine with the 9-phenylanthracene radical cation, probably the most frequently studied radical cation-nucleophile combination reaction, has been observed to be equal to 10⁷ M⁻¹ s⁻¹.^{3c} In both solvents, the rate constants for the reactions of all radical cations with the exception of that derived from 9-*tert*-butylanthracene differed very little, $\log k$ being equal to 7.0(0.1) in acetonitrile and 7.1(0.1) in dichloromethane. The corresponding values for the reactions of 9-*tert*-butylanthracene were observed to equal 7.9 (acetonitrile) and 8.2 (dichloromethane). Thus, the latter reacts about an order of magnitude faster with pyridine than the less hindered radical cations.

Temperature effects on radical cation-pyridine combination reactions. Negative or near-zero apparent Arrhenius activation energies are characteristically observed for the reactions of radical cations of anthracene derivatives

Table 2. Second-order rate constants for the reactions of 9-alkylanthracene radical cations with pyridine.

Substituent	$\Delta E_p/mV^a$	$\log(k_2)^b$	$\Delta E_p/mV^c$	$\log(k_2)^d$
Methyl	137	7.2	115	7.0
Ethyl	136	7.2	118	7.1
Isopropyl	134	7.1	112	6.9
<i>tert</i> -Butyl	174	8.2	148	7.9
Neopentyl	129	7.0	116	7.0

^aMain peak and prepeak potential difference in dichloromethane-Bu₄NPF₆ (0.2 M) containing substrate (1 mM) and pyridine (0.5 mM). ^bLogarithm of the second-order rate constants in dichloromethane. ^cMain peak and prepeak potential difference in acetonitrile-Bu₄NPF₆ (0.1 M) containing substrate (2 mM) and pyridine (1 mM). ^dLogarithm of the second-order rate constants in acetonitrile.

with nitrogen-centered nucleophiles.^{3c} The data in Table 3 serve as a comparison of rate constants for the reactions of either 9-*tert*-butyl- or 9-neopentylanthracene with pyridine in dichloromethane-Bu₄NPF₆ (0.2 M). A positive E_a equal to 3.9 kcal mol⁻¹ was observed for the *tert*-butyl derivative while the rate constant for the reaction of 9-neopentylanthracene radical cation with pyridine was observed to be independent of temperature in the range studied.

Decomposition reaction of 9-*tert*-butylanthracene radical cation in HFP. The cyclic voltammetry for the oxidation of 9-*tert*-butylanthracene in HFP-Bu₄NPF₆ (0.1 M) at $\nu=0.1$ V s⁻¹ at 298 K is illustrated in Fig. 1. Two oxidation peaks are observed in the forward scan (Fig. 1a). We suspected that the second peak was due a unimolecular decomposition of the radical cation producing anthracene and a butyl fragment which was confirmed by showing that the peak appears at the same potential as that during the oxidation of authentic anthracene (Fig. 1b) and by observing an increase in the height of

Table 3. Temperature effects and activation energies for the reactions of 9-*tert*-butyl- and 9-neopentylanthracene radical cations with pyridine.

$T/^\circ C$	<i>tert</i> -Butyl		Neopentyl	
	$\Delta E_p/mV^a$	$\log(k_2)^b$	$\Delta E_p/mV^a$	$\log(k_2)^b$
25	174	8.2	129	7.0
10	162	7.9	126	6.9
-5	160	7.9	129	7.0
-20	152	7.7	127	6.9
	$E_a = 3.9 \text{ kcal mol}^{-1}$ ($r^2 = 0.92$)		$E_a = 0$	

^aMain peak and prepeak potential difference in dichloromethane-Bu₄NPF₆ (0.2 M) containing substrate (1 mM) and pyridine (0.5 mM). ^bLogarithm of the second-order rate constants in dichloromethane.

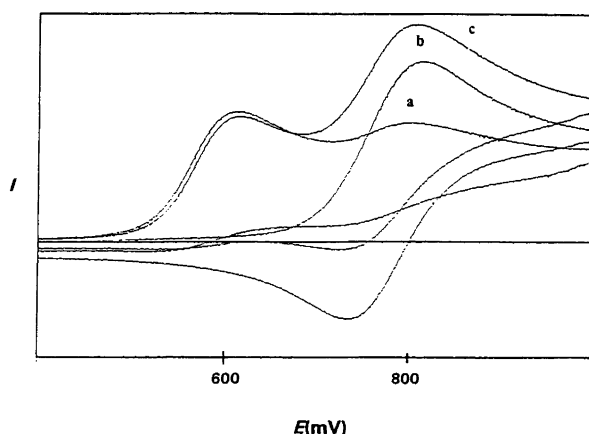


Fig 1. Cyclic voltammograms for the oxidation of 9-*tert*-butylanthracene in HFP-Bu₄NPF₆ (0.1 M) at 298 K ($\nu=0.1$ V s⁻¹): (a) 9-*tert*-butylanthracene (1 mM); (b) anthracene (2 mM) and (c) 9-*tert*-butylanthracene (1 mM)+anthracene (1 mM). Potential scale referred to ferrocenium/ferrocene.

the second peak upon adding anthracene to the solution (Fig. 1c). The relatively slow reaction of the radical cation could be 'out-run' by increasing v to 10 V s^{-1} . Under these conditions, the second peak due to the oxidation of product anthracene was not observed.

Rate constants for the unimolecular decomposition of 9-*tert*-butylanthracene radical cation in HFP were determined as a function of temperature (Table 4) by derivative cyclic voltammetry. The Arrhenius activation energy was observed to be equal to $8.2 \text{ kcal mol}^{-1}$ ($r^2 = 0.99$).

Conclusions. A remote steric effect involving the *peri* hydrogen atoms (1 and 8 positions) increases the rate of reaction between the 9-*tert*-butylanthracene radical cation and pyridine in acetonitrile and in dichloromethane. The effect cannot be detected with other 9-alkyl substituents including methyl, ethyl, isopropyl and neopentyl. In HFP, the *tert*-butyl substituted radical cation undergoes unimolecular decomposition producing anthracene and a butyl fragment. Although the remote steric effect is real for the latter radical cation, it is not general and is not a factor to consider in discussing the reactivities of other, less hindered radical cations derived from the anthracenes.

Experimental

Materials. Reagent-grade acetonitrile was distilled from P_2O_5 before being passed through a column of active neutral alumina to remove water and protic impurities. Dichloromethane, after passage through active neutral alumina, was used without further purification. 1,1,1,3,3,3-Hexafluoropropan-2-ol (Aldrich) was used as received. Tetrabutylammonium hexafluorophosphate (Aldrich) was recrystallized from dichloromethane-diethyl ether before use. 9-Alkylanthracenes were prepared using standard literature procedures.

Instrumentation and data handling procedures. Cyclic and linear sweep voltammetry were performed using a JAS Instrument Systems, J-1600-B potentiostat driven by a Hewlett Packard 3314A function generator. After being passed through a Stanford Research Systems, Inc. model SR640 dual channel low pass filter the data were recorded on a Nicolet model 310 digital oscilloscope with 12-bit

Table 4. The first-order rate constants for the unimolecular decomposition reaction of 9-*tert*-butylanthracene radical cation in HFP.

$T/^\circ\text{C}$	v ($R'_1 = 0.5$) ^a	k_1/s^{-1} ^b
5	0.34	1.05
15	0.50	1.54
25	0.87	2.69
35	1.42	4.39

^aSweep rates in V s^{-1} necessary for a derivative peak ratio of 0.5 measured in HFP-Bu₄NPF₆ (0.1 M) containing substrate (1 mM). ^bFirst-order rate constants.

resolution. The oscilloscope and function generator were controlled by an IBM AT compatible personal computer via an IEEE interface. The current-potential curves were collected at selected trigger intervals to reduce periodic noise²¹ and 20 curves were averaged before treatment with a frequency domain low pass digital filter and numerical differentiation.

Cyclic voltammetry measurements. A standard three-electrode one compartment cell was used for all kinetic measurements. Positive feedback IR compensation was used to minimize the effects of uncompensated solution resistance. Reference electrodes were Ag/AgNO₃ (0.01 M) in acetonitrile constructed in the manner described by Moe.²² The working electrodes, 0.2–0.8 mm Pt, were prepared by sealing wire in glass and polishing to a planar surface as described previously.²³ The working electrodes were cleaned before each series of measurements with a fine polishing powder (Struers, OP-Alumina Suspension) and wiped with a soft cloth. The cell was immersed in a water bath controlled to $25 \pm 0.2^\circ\text{C}$.

Kinetic measurements. Rate constants were obtained by comparing experimental derivative cyclic voltammetry²⁴ data with theoretical data obtained by digital simulation²⁵ using a commercially available program (Digisim 2.0, from Bioanalytical Systems Inc.).

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