Letter

Oxidation of Aromatic Compounds by Diazonium Ions. Unexpectedly Facile Electron Transfer Reactions

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Arenediazonium ions undergo facile reduction by electron transfer reagents, potassium ferrocyanide and decamethylferrocene.[2,3] In the course of examining these ions as convenient photostimulated charge-transfer oxidants[4] of aromatic compounds to generate cation radicals, we discovered that anomalously rapid oxidations occurred under dark conditions. The reactions were carried out in the presence of CCl_4 to trap aryl radicals and trifluoroacetic acid to stabilize the resultant aromatic cation radicals. Although we have observed the oxidation of a variety of aromatic compounds by $O_2N-C_6H_4-N_2^+$ in the dark we have limited our kinetics and mechanism studies to substrates giving rise to cation radicals stable under the reaction conditions.
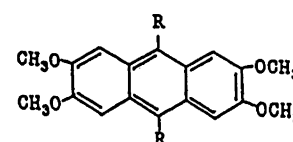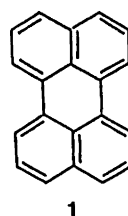
The kinetic data in Table 1 summarize our results for the

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2: R = CH_3
3: R = Ph
4: R = H

oxidation of perylene (**1**), 2,3,6,7-tetramethoxy-9,10-dimethylanthracene (**2**), 2,3,6,7-tetramethoxy-9,10-diphenylanthracene (**3**) and 2,3,6,7-tetramethoxyanthracene (**4**). The second-order rate constants were evaluated for the appearance of the cation radicals by monitoring absorptions in the visible using a Hewlett-Packard diode array spectrometer. The data in Table 1 refer to reactions carried out in CCl_4-trifluoroacetic acid (3:2 v/v) because of the high stabilities of the cation radicals in this medium but which take place at comparable rates in acetonitrile. For example, the second-order rate constant for the oxidation of **3** in acetonitrile at 298 K was observed to be 0.41 M^{-1} s^{-1}, 40 % greater than that in Table 1. A linear relationship was observed between log K and log $[CCl_4]$ for the oxidation of **1** in trifluoroacetic acid. The rate constant in trifluoroacetic acid extrapolated to $[CCl_4]$ = 1 M was observed to be 85 M^{-1} s^{-1}, 40 times greater than the value in Table 1. Reactions were carried out in an argon atmosphere.

Substrates **3** and **4** provide a probe for steric effects on the rates of reactions with $O_2N-C_6H_4-N_2^+$. Nucleophilic attack at the unhindered 10-position of 9-phenylanthracene cation radical takes place about 6 000 times faster than at the 9,10-positions of 9,10-diphenylanthracene cation radical.[5] The latter reaction should serve as a model for the expected steric effect for electrophilic attack on **3** and **4** at the reactive 9,10-positions. The fact that the relative rate constant for the reactions with the diazonium ion is higher by only a factor of 45 as compared with 6 000 for the model

Table 1. Electrode potential and kinetic data for the oxidation of aromatic compounds by p-nitrophenyldiazonium tetrafluoroborate.

Aromatic compound	E^{rev} [a]	k_{max} [b]	k_{obs} [c]	$\Delta H(act)$ [d]	$\Delta S(act)$ [e]
1	0.770	10^{-15}	2.17	22.4	18.0
2	0.386	10^{-8}	36.6	17.8	8.3
3	0.525	10^{-11}	0.29	19.0	2.7
4	0.556	10^{-11}	13[f]	–	–

[a] Measured by derivative cyclic voltammetry vs. Fc^+/Fc^g in acetonitrile/Bu_4PF_6 (0.1 M: at 298 K. [b] Maximum possible rate constant for outer-sphere electron transfer estimated from the equilibrium constant obtained from the electrode potentials. Comparable values are obtained by application of the Marcus equation. [c] Second-order rate constant (M^{-1} s^{-1}) at 298 K in CCl_4/trifluoroacetic acid (3:2 v/v). The rate constant in acetonitrile for substrate **3** was about 40 % higher than in this medium. [d] In kcal mol^{-1}. [e] In cal K^{-1} mol^{-1}. [f] This value is less precise than the order rate constants since 4^+ is not stable on the time scale of the kinetic experiments. [g] The potential of Fc^+/Fc (ferrocenium/ferrocene) is +0.29 V vs. SCE.
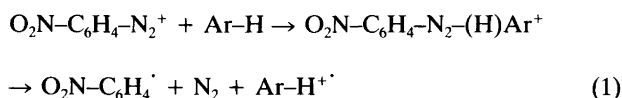
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reaction suggests that the oxidation does not involve a mechanism initiated by electrophilic attack on the aromatic compound by diazonium ion to form the σ-bonded complex (1).[6]

$$O_2N-C_6H_4-N_2^+ + Ar-H \rightarrow O_2N-C_6H_4-N_2-(H)Ar^+$$

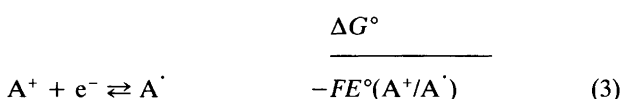$$\rightarrow O_2N-C_6H_4^{\cdot} + N_2 + Ar-H^{+\cdot} \quad (1)$$

The kinetics of the reactions are characterized by enthalpies of activation of about 20 kcal mol^{-1} and entropies of activation as high as 18 cal K^{-1} mol^{-1} depending strongly upon the structure of the aromatic compound. The observed second-order rate constants are as much as 10^{15} times greater than maximum values predicted for the outer-sphere electron exchange reactions. The electrode potential differences ($\Delta E°$) recorded refer to half-reactions involving the oxidation of the aromatic compounds and the reduction of the diazonium ion.

A recent detailed study of the voltammetric reduction of arenediazonium ions in aprotic solvents using a battery of techniques[7] has clearly shown that the potentials reported earlier[8] refer to electro-adsorption rather than to diffusion processes. The peak potential for reaction (2) in DMF at
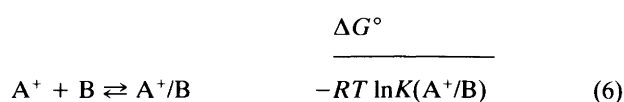
$$O_2N-C_6H_4-N_2^+ + e^- \rightleftarrows O_2N-C_6H_4-N_2^{\cdot} \quad (2)$$
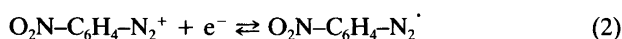
298 K was reported to be −0.405 at a voltage sweep rate of 500 mV s^{-1}.[7] The rapid decomposition of the resulting diazenyl radicals insures that the reversible potential for reaction (2) is at a more negative potential.[9] A kinetic shift of the peak potential for reduction of the diazonium ion as great as 200–300 mV can be expected for a rapid first-order reaction of the diazenyl radical. If a correction is made for the probable kinetic shift, k_{max} (Table 1) becomes considerably smaller. For example, corrections of 180 and 300 mV gives rise to 10^3 and 10^5, respectively, decreases in k_{max}.

The observation that reactions, the overall result of which is electron exchange between reactants, can occur much more readily than predicted by the thermodynamic electrode potential differences points out a more general problem. Electrode potential differences for electron transfer reactions can be broken down into the respective half-reactions as in Scheme 1. The equilibrium constant for reaction (5) is then calculated from the difference in poten-

	$\Delta G°$	
$A^+ + e^- \rightleftarrows A^{\cdot}$	$-FE°(A^+/A^{\cdot})$	(3)
$B \rightleftarrows B^{+\cdot} + e^-$	$FE°(B^{+\cdot}/B)$	(4)
$A^+ + B \rightleftarrows A^{\cdot} + B^{+\cdot}$	$-F\Delta E°(A-B)$	(5)

Scheme 1.

|	$\Delta G°$	
$A^+ + B \rightleftarrows A^+/B$	$-RT \ln K(A^+/B)$	(6)
$A^+/B \rightleftarrows A^{\cdot}/B^{+\cdot}$	$-FE°(A^+/B)$	(7)
$A^{\cdot}/B^{+\cdot} \rightleftarrows A^{\cdot} + B^{+\cdot}$	$RT \ln K(A/B^{+\cdot})$	(8)
$A^+ + B \rightleftarrows A^{\cdot} + B^{+\cdot}$	$-F\Delta E°(A-B)$	(9)

Scheme 2.

tials for reactions (3) and (4). The equilibrium constant obtained in this way neglects any mutual interactions between A$^+$ and B as well as those between A$^{\cdot}$ and B$^{+\cdot}$. The latter are taken into account in Scheme 2. Thus, the sum of the half-reactions (3) + (4) is equivalent to three distinct steps, (6)–(8). The thermodynamic barrier for eqn. (9) can be circumvented if reaction (7) is followed by a rapid and irreversible reaction (10).

$$A^{\cdot}/B^{+\cdot} \rightarrow C + B^{+\cdot} \quad (10)$$

During the oxidation of aromatic compounds by $O_2N-C_6H_4-N_2^+$ the irreversible reaction corresponding to (10) is the unimolecular expulsion of dinitrogen from the diazenyl radical [eqn. (11)]. Diazenyl radicals are known to have

$$O_2N-C_6H_4-N_2^{\cdot}/Ar-H^{+\cdot} \rightarrow O_2N-C_6H_4^{\cdot} + Ar-H^{+\cdot} \quad (11)$$
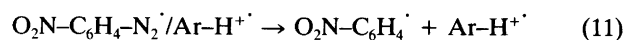
very short lifetimes[10] and reaction (11) is clearly irreversible.

Another interesting aspect of the kinetic results is that a linear relationship is observed between log k and $F\Delta E°$ when the data for 3 are not included.[11] The slope of the correlation line (r = 0.996), on the other hand, corresponds to about a fifth of that predicted by the Marcus equation ($1/2.3RT$) for endergonic electron transfer.[12] This could be a consequence of the fact that the electron transfer mechanism (6)–(8) is interrupted by the rapid irreversible reaction (11).

It has recently been concluded that inner-sphere electron transfer mechanisms involving radical ions should have an inherent preference over the corresponding outer-sphere mechanism unless intermolecular overlap is precluded for steric or other reasons.[13] Transition-state overlap energies for innersphere electron transfer between radical anions and neutral compounds were estimated to fall in the range 2.3–7 kcal mol^{-1}. It would appear to be reasonable to suggest that the diazonium ion – neutral molecule electron-transfer transition states have overlap energies in this range since weak charge transfer complexes can be detected.

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