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 decamethyl-ferrocene. In the course of examining these ions as convenient photostimulated charge-transfer oxidants 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 CCl₄ 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 O₂N-C₆H₄-N₂⁺ 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 oxidation of perylene (1), 2,3,6,7-tetramethoxy-9,10-dimethanlanthracene (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 CCl₄–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 [CCl₄] for the oxidation of I in trifluoroacetic acid. The rate constant in trifluoroacetic acid extrapolated to [CCl₄] = 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.

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

<table>
<thead>
<tr>
<th>Aromatic compound</th>
<th>E°'</th>
<th>k₉</th>
<th>kobs</th>
<th>ΔH(act)</th>
<th>ΔS(act)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.770</td>
<td>10⁻¹⁵</td>
<td>2.17</td>
<td>22.4</td>
<td>18.0</td>
</tr>
<tr>
<td>2</td>
<td>0.386</td>
<td>10⁻⁸</td>
<td>36.6</td>
<td>17.8</td>
<td>8.3</td>
</tr>
<tr>
<td>3</td>
<td>0.525</td>
<td>10⁻¹¹</td>
<td>0.29</td>
<td>19.0</td>
<td>2.7</td>
</tr>
<tr>
<td>4</td>
<td>0.556</td>
<td>10⁻¹¹</td>
<td>13</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

*Measured by derivative cyclic voltammetry vs. Fc⁺/Fc²⁺ in acetonitrile/Bu₄PF₆ (0.1 M) at 298 K. *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. *Second-order rate constant (M⁻¹ s⁻¹) at 298 K in CCl₄/trifluoroacetic acid (3:2 v/v). The rate constant in acetonitrile for substrate 3 was about 40% higher than in this medium. *In kcal mol⁻¹. *In cal K⁻¹ mol⁻¹. This value is less precise than the order rate constants since ΔS* is not stable on the time scale of the kinetic experiments. *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 o-bonded complex (1).  

\[
\text{O}_2\text{N-C}_6\text{H}_4\text{N}_2^+ + \text{Ar-H} \rightarrow \text{O}_2\text{N-C}_6\text{H}_4\text{N}_2^-(\text{H})\text{Ar}^+ \\
\rightarrow \text{O}_2\text{N-C}_6\text{H}_4 \cdot + \text{N}_2 + \text{Ar-H}^+ 
\]  

(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 \(\Delta E^\circ\) 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-adsortion rather than to diffusion processes. The peak potential for reaction (2) in DMF at 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 diazynyl 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 diazynyl radical. If a correction is made for the probable kinetic shift, \(k_{\text{max}}\) (Table 1) becomes considerably smaller. For example, corrections of 180 and 300 mV gives rise to 10\(^5\) and 10\(^9\), respectively, decreases in \(k_{\text{max}}\).

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-

\[
\Delta G^\circ = \\
A^+ + e^- \rightleftharpoons A^- \\
B \rightleftharpoons B^+ + e^- \\
A^+ + B \rightleftharpoons A^- + B^+ 
\]  

(3, 4, 5)

\[
\Delta G^\circ = -R \ln K(A^+/B) \\
\Delta G^\circ = -F \Delta E^\circ(A/B) \\
\Delta G^\circ = -F \Delta E^\circ(A-B) 
\]  

(6, 7, 8, 9)

Scheme 2.

During the oxidation of aromatic compounds by \(\text{O}_2\text{N-C}_6\text{H}_4\text{N}_2^+/\text{Ar-H}^+\) the irreversible reaction corresponding to (10) is the unimolecular expulsion of dinitrogen from the diazynyl radical [eqn. (11)]. Diazynyl radicals are known to have very short lifetimes\(^10\) and reaction (11) is clearly irreversible.

Another interesting aspect of the kinetic results is the strength that a linear relationship is observed between log \(k\) and \(F \Delta E^\circ\) 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 inner-sphere 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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References

1. On leave from the Department of Chemistry, University of Kashmir, India.
6. A bonded mechanism was considered and rejected for the oxidation of hydroquinone by arenediazonium ions.\textsuperscript{2b}
9. The reduction potentials of the arenediazonium ions were not reported in acetonitrile but the data reported in Table V of Ref. 7 are indicative that the potentials are more negative in that solvent.
11. The rate constant for substrate 3 falls below the correlation line, presumably because of steric effects not present in the other substrates.

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