

sitating an additional procedure for detection of the *trans*-dichlorodimethylcyclopropane. This was accomplished by trapping the appropriate fraction from a gas chromatographic separation and examining the infrared spectrum of the sample, strong absorption

bands at 8.73 and 9.20  $\mu$  being used for identification and determination of yield.

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## Electron-Transfer Reactions of Aromatic Radical Ions

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*Studies have been made of one-electron oxidation-reduction reactions between normally stable molecules and resonance-stabilized radical ions. The combined techniques of electron paramagnetic resonance spectroscopy and electrochemistry rendered such reactions easy to follow. In all of the cases studied the reaction was predictable from a knowledge of the relative affinity for the extra electron by the two reactants involved. The reaction rates, although not specifically determined, were all quite rapid since all reactions were essentially complete within 1 min. from initial mixing. Steric and solvent effects were investigated and were found not to change the above results.*

Considerable interest has developed concerning electron-transfer reactions of aromatic systems following the extensive studies of Russell and co-workers on spontaneous formation of radical anions in basic media and electron transfer between various anions and unsaturated electron-acceptor systems.<sup>1-4</sup> Throughout these studies one-electron-transfer reactions predominated, but the products and rates of some of the reactions reflected a variety of effects due to the mode of formation of the anions, influence of the solvent, etc. We have examined the simplest of electron interchange reactions between radical ions and various unsaturated aromatic molecules using electron paramagnetic resonance (e.p.r.) methods. The radical ions were generated electrochemically so that at least one variable, the mode of formation of the ion radical, is essentially invariant. It might be claimed that such studies are trivial and that the order and extent of such interactions could be predicted *a priori* via the formal reduction potentials ( $E^{0'}$  values) of the compounds. This principle has never been satisfactory in inorganic oxidation-reduction reactions and there is no reason to presuppose it holds universally for organic processes. As examples of inorganic oxidation-reduction processes, which, in spite of having very favorable thermodynamic driving forces, do not proceed to any appreciable extent at room temperature without catalysts, are the oxida-

tion of Tl(I) by Ce(IV) and the oxidation of Sn(II) by Fe(III) in high acidities (without chloride present).<sup>5,6</sup> The present studies were carried out to investigate any such anomalies in one-electron interactions between aromatic species. Only a few studies with a limited variety of compounds have appeared in this area previously.<sup>7-10</sup>

### Experimental

The radical ions ( $R^-$  or  $R^+$ ) were generated *via* standard external electrochemical techniques.<sup>11</sup> The radical ions were then transferred to a mixing chamber where they were allowed to interact with the nonradical aromatic system. A portion of this reaction mixture was transferred to the e.p.r. cell. All transfers and mixing were done in a closed system with a stream of nitrogen excluding air contact. The nitrogen also provided for stirring in the mixing chamber. The

Table I. Reaction Potentials of Aromatic Systems in DMF

No.	Parent compd.		$E^{0'}$ <sup>a</sup>
	Name		
1	<i>trans</i> -Stilbene		-2.22
2	1,5-Naphthalene-disulfonate		-2.15
3	Pyrazine		-2.09
4	Anthracene		-1.95
5	<i>p</i> -Nitroaniline		-1.41
6	9-Fluorenone		-1.29
7	<i>p</i> -Nitrotoluene		-1.18
8	Nitrobenzene		-1.13
9	<i>p</i> -Chloronitrobenzene		-1.04
10	9,10-Anthraquinone		-0.87
11	<i>p</i> -Nitrobenzotrile		-0.83
12	<i>p</i> -Nitropyridine N-oxide		-0.78
13	<i>p</i> -Benzoquinone		-0.48

<sup>a</sup>  $E^{0'}$  in v. vs. s.c.e. according to reaction 3. The uncertainties in  $E^{0'}$  are  $\pm 0.05$  v. for pyrazine and  $\pm 0.02$  v. for all other systems.

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solvent, N,N-dimethylformamide (DMF), was dried over calcium hydride and vacuum distilled from phthalic acid. All solutions were 0.1 M in tetraethyl ammonium perchlorate (TEAP) as supporting electrolyte. The concentrations of  $R^-$  and  $R^+$  were ca.  $10^{-3}$  M and the concentration of nonradical aromatic compound in the mixing chamber was ca.  $10^{-3}$  M. The e.p.r. spectrometer was a Varian V-4500 with Fieldial attachment.

## Results and Discussion

Although the range of compounds investigated is limited, it appears, in fact, that there are no anomalies in the one-electron oxidation-reduction interactions of aromatic species. Table I lists the  $E^{0'}$  values (experimentally determined half-wave potentials). The anion radical of every compound (1-13) will interact with every compound below it in reduction potential to produce the anion radical of lesser  $E^{0'}$ . The radical ion species were verified in each case *via* the e.p.r. spectra. (The stoichiometry of these reactions was purposely arranged so that only the e.p.r. spectrum of the new radical ion species predominated. Reactions involving 1,5-naphthalenedisulfonate are somewhat difficult to observe since this compound is only very slightly soluble in DMF and the trianion is very reactive to solvent impurities and residual oxygen.) Since the  $E^{0'}$  values are a close measure of the reversible one-electron process ( $R + e \rightleftharpoons R^-$ ) they can be used to calculate the formal equilibrium constants of the reactions and there is no question but that the interaction sequence would be in the same order as the  $E^{0'}$  values.

While it was not clear that all of these reactions would be rapid, this is the case. The e.p.r. spectrum of the new radical ion formed was observed within 1 to 2 min. after the mixing. In no case did the e.p.r. signal intensity increase with time, showing that the reactions were essentially complete within this short interval. No more exacting rate measurements were attempted.

The addition of a hydroxylic solvent, while it naturally affects the physical and chemical properties of many of the radical ions,<sup>12</sup> does not noticeably affect the rates of the electron interchanges. In 10% water-DMF the reduction potentials of compounds 10-13 are shifted to the less cathodic values of -0.79, -0.75, -0.66, and -0.32 v. vs. s.c.e. respectively, and the order of their interactions is unchanged.

The possibility that a sterically hindered species might show differences in rate of reaction was investigated. The compound 2,6-dimethylnitrobenzene ( $E^{0'} = 1.47$  v.) was tested with anion radicals and acceptors close to it in reduction potential. Anthracene ( $E^{0'} = -1.95$  v.) and tetracene ( $E^{0'} = -1.56$  v.) anion radicals gave rapid rates of electron interchange. Similarly the anion radical of 2,6-dimethylnitrobenzene readily reduced *p*-nitroaniline ( $E^{0'} = -1.41$  v.) and 9-fluorenone ( $E^{0'} = -1.29$  v.). These interactions were in pure DMF-0.1 M TEAP.

Finally a few cation radicals of the diamine class were studied in 25% acetone-75% aqueous buffer (apparent pH 2.9). The diamine cations are quite stable in this medium and merely represent organic

oxidants of intermediate strength. In accord with the formal potentials, the cation radical of N,N,N',N'-tetramethylbenzidine oxidizes *p*-phenylenediamine and N,N,N',N'-tetramethyl-*p*-phenylenediamine (Wurster's Blue) to the corresponding radical cations.

Although the list of compounds studied is not exhaustive, it does represent a variety of parent and substituted aromatic hydrocarbons and heterocyclic systems. In all cases the simple one-electron oxidation-reduction reactions are predictable *via* the scale of electronegativities ( $E^{0'}$  values) and the rates of the reactions are rapid and relatively uninfluenced by small solvent variations or gross changes in molecular type and geometry. Large changes in solvent composition which could limit radical ion lifetimes or seriously alter their physical properties could cause changes in the present results. It is probably safe to conclude that some of the large differences in reaction rates in the more complex electron interchange systems studied by Russell and co-workers do not, in any event, belong to steps involving the simple one-electron interchanges studied here.

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## Appendix

*E.p.r. Coupling Constants and Their Assignments.* The hyperfine coupling constants of those radical ions which have not been reported previously in DMF and 10% water-DMF are stated in Tables II and III (except for *trans*-stilbene monoanion radical, the spectrum of which has not been completely interpreted). Those previously reported in DMF are *p*-chloronitrobenzene,<sup>13</sup> 9-fluorenone,<sup>14</sup> 2,6-dimethylnitrobenzene, nitrobenzene, and *p*-nitrobenzotrile.<sup>15</sup> The coupling constants of two of the diamine monocation radicals employed have been previously reported and are essentially the same as in the acetone-aqueous buffer solvent we used. Melchior and Maki have reported *p*-phenylenediamine in acetonitrile,<sup>16</sup> and Wurster's Blue was reported by Carrington and co-workers.<sup>17</sup> The interpretation of N,N,N',N'-tetramethylbenzidine monocation radical is complete and will be reported in the near future.

The errors given are the maximum values for twice the standard deviation. The notation is such that the number(s) in parentheses gives the position(s) of the atom(s) numbered on the sketch of the radical. When all positions for the given type of atom are equivalent, the number(s) is omitted.

In cases where the assignments of coupling constants to specific nuclei are at all questionable we have

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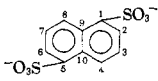

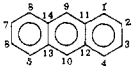
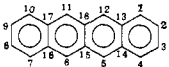
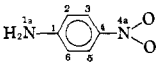
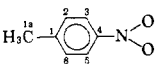
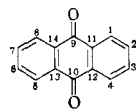
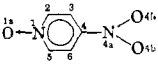
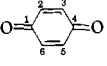
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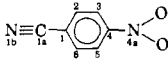
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**Table II.** E.p.r. Coupling Constants of Radical Anions in DMF

Radical	Coupling constants, gauss
1,5-Naphthalenedisulfonate <sup>3-</sup> 	$a_{N(4,8)} = 4.79 \pm 0.02$ $a_{H(3,7)} = 1.60 \pm 0.02$ $a_{H(2,6)} = 2.14 \pm 0.01$
Pyrazine <sup>-</sup> 	$a_N = 7.16 \pm 0.02$ $a_H = 2.61 \pm 0.01$
Anthracene <sup>-</sup> 	$a_{H(9,10)} = 5.31 \pm 0.02$ $a_{H(2,3,6,7)} = 1.47 \pm 0.01$ $a_{H(1,4,5,8)} = 2.68 \pm 0.01$
Tetracene <sup>-</sup> 	$a_{H(5,6,11,12)} = 4.20 \pm 0.02$ $a_{H(1,4,7,10)} = 1.48 \pm 0.01$ $a_{H(2,3,8,9)} = 1.21 \pm 0.01$
<i>p</i> -Nitroaniline <sup>-</sup> 	$a_{N(4a)} = 11.50 \pm 0.03$ $a_{H(3,5)} = 3.26 \pm 0.02$ $a_{H(2,6)} = 0.83 \pm 0.04$ $a_{N(1a)} = 1.08 \pm 0.01$ $a_{H(1a)} = 1.08 \pm 0.01$
<i>p</i> -Nitrotoluene <sup>-</sup> 	$a_N = 10.06 \pm 0.03$ $a_{H(2,6)} = 1.08 \pm 0.01$ $a_{H(3,5)} = 3.38 \pm 0.01$ $a_{H(1a)} = 4.05 \pm 0.01$
9,10-Anthraquinone <sup>-</sup> 	$a_{H(2,3,6,7)} = 0.94 \pm 0.02$ $a_{H(1,4,5,8)} = 0.27 \pm 0.02$
<i>p</i> -Nitropyridine N-oxide <sup>-</sup> 	$a_{N(4a)} = 6.15 \pm 0.02$ $a_{H(2,6)} = 1.28 \pm 0.01$ $a_{H(3,5)} = 3.38 \pm 0.01$ $a_{N(1)} = 4.73 \pm 0.02$
<i>p</i> -Benzoquinone <sup>-</sup> 	$a_H = 2.41 \pm 0.01$

**Table III.** E.p.r. Coupling Constants of Radical Anions in DMF-Water<sup>a</sup>

Radical	Coupling constants, gauss
9,10-Anthraquinone <sup>-</sup>	$a_{H(2,3,6,7)} = 0.95 \pm 0.02$ $a_{H(1,4,5,8)} = 0.40 \pm 0.02$
<i>p</i> -Nitrobenzotrile <sup>-</sup> 	$a_{N(4a)} = 8.17 \pm 0.03$ $a_{N(1b)} = 0.80 \pm 0.04$ $a_{H(3,5)} = 3.16 \pm 0.02$ $a_{H(2,6)} = 0.73 \pm 0.03$
<i>p</i> -Nitropyridine N-oxide <sup>-b</sup>	$a_{N(4a)} = 7.11 \pm 0.02$ $a_{H(3,5)} = 3.32 \pm 0.02$ $a_{N(1)} = 4.49 \pm 0.02$ $a_{H(2,6)} = 1.18 \pm 0.01$
<i>p</i> -Benzoquinone <sup>b</sup>	$a_H = 2.37 \pm 0.01$

<sup>a</sup> 10% water in DMF by volume. <sup>b</sup> For these radicals the position numbers refer to the diagrams in Table II.

followed the order found by McLachlan-modified Hückel LCAO molecular calculations<sup>18</sup> following the method as outlined by Fraenkel and Rieger.<sup>19</sup> Fraen-

kel's research group has demonstrated well the applicability of these calculations to a wide variety of radicals.<sup>14, 15, 19, 20</sup> Our results for these calculations and a list of parameters employed are available on request.

We have developed a computer program for these calculations which is rapid, efficient, very accurate, and easy to learn to use. The program is set up in Fortran IV for use on the IBM 7040 computer using the Jacobi method<sup>21</sup> for calculation of matrix eigenvalues and eigenvectors (molecular orbital energy values and coefficients for the atomic orbitals, respectively). The Jacobi method has been demonstrated to be superior to others for accuracy.<sup>22</sup>

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