Reversible Anion Radical–Dianion Redox Equilibria Involving Ions of Simple Aromatic Compounds

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Summary Anthracene, benzophenone, nitrobenzene, and several other simple aromatic compounds undergo two consecutive reversible one-electron transfers to give first the anion radical and then the dianion, both species being stable during the time scale of cyclic voltammetry in several electrophile-free solvents.

THE reversible reduction of aromatic molecules to anion radicals is well known. Anion radicals of aromatic hydrocarbons, ketones or nitro compounds are readily observed by cyclic voltammetry, but apart from special cases, usually involving difunctional molecules, observation of the corresponding dianions is beyond present analytical methods. This is thought to be due to spontaneous protonation of the strongly basic dianions.[1] We now report reversible reduction of the anion radicals of simple examples of all three classes of compound and some previous hypotheses on the spontaneous reactions of the dianions, namely, those with solvent and supporting electrolyte, are shown in most cases to be incorrect.

Cyclic voltammograms for the reduction of anthracene, benzophenone and nitrobenzene in DMF containing Me_4NBr (saturated) and suspended neutral alumina[2] show that both charge transfers for all three compounds are reversible at the low voltage sweep rate of 306 mV s^{-1} (Table). Even carefully purified solvents have electrophilic impurities which react with the dianions as they are formed, so the neutral alumina is added to remove all traces of proton donors and other electrophilic impurities from the solvent–electrolyte system. In addition to DMF, comparable results have been obtained using tetrahydrofuran, hexamethylphosphoramide, pyridine and with less success, acetonitrile. These results conclusively show that protonation of the dianions by the solvent is not the general reason for the failure to observe dianions.

TABLE

Voltammetric data for the reduction of aromatic compounds

Compound[a]	$E_1^{0\,b}$	$E_2^{0\,b}$	$(i_p^O/i_p^R)^1$	$(i_p^O/i_p^R)^2$
Anthracene	1·92	2·66	1·0	0·9
Benzophenone	1·72	2·49	1·0	0·9
Nitrobenzene	1·09	2·15	1·0	0·9

[a] Substrate (1·0 mM) in DMF [containing Me_4NBr (saturated)].
[b] Potential in V *vs.* SCE, sweep rate = 306 mV s^{-1}.

It has previously been believed that tetra-alkylammonium ions containing β-hydrogen atoms are very effective proton donors for aromatic dianions. We find that neither Et_4N^+ nor $Bu^n_4N^+$ ions are sufficiently acidic to act as proton donors for the dianions of polycyclic aromatic hydrocarbons such as perylene and benzanthracene. More reactive dianions such as those from anthracene are protonated by Et_4N^+ but not by $Bu^n_4N^+$ ions on the voltammetric time scale at room temperature in DMF. At −30° protonation of the anthracene dianion by Et_4N^+ is negligible at a voltage sweep rate of 306 mV s^{-1}. For molecules in which the two negative charges of the dianion are in close proximity, (on the carbonyl group of benzophenone or at the 9,10 positions of anthracene), the reversibility of the anion radical–dianion couples ($E_{red} - E_{ox}$) are profoundly affected by the bulk of the counter ion.

The effect of the size of the counter ion is very pronounced during voltammetry of 9,10-diphenylanthracene in DMF. In the presence of $Bu^n_4N^+$ ion (0·2M), the second charge transfer is irreversible (Figure a. No chemical reactions take place) while addition of Et_4N^+ ion (0·02M) to the same solution results in a reversible charge transfer (Figure b). On the other hand, the charges of the dianions of polycyclic hydrocarbons such as perylene are dispersed over the much larger molecular framework and the reversibility of the anion radical–dianion couples are unaffected by the size of the counter ions.

Much of the current interest in anion radical chemistry is centred around reactions believed to proceed by disproportionation of the anion radicals to give reactive dianions and substrate [equation (1)].[3] Knowledge of the equilibrium constant for the disproportionation reaction is important in evaluating these mechanisms. Reversible potentials and disproportionation equilibrium constants for a large number of aromatic hydrocarbon ions in several solvent electrolyte systems will be reported later.

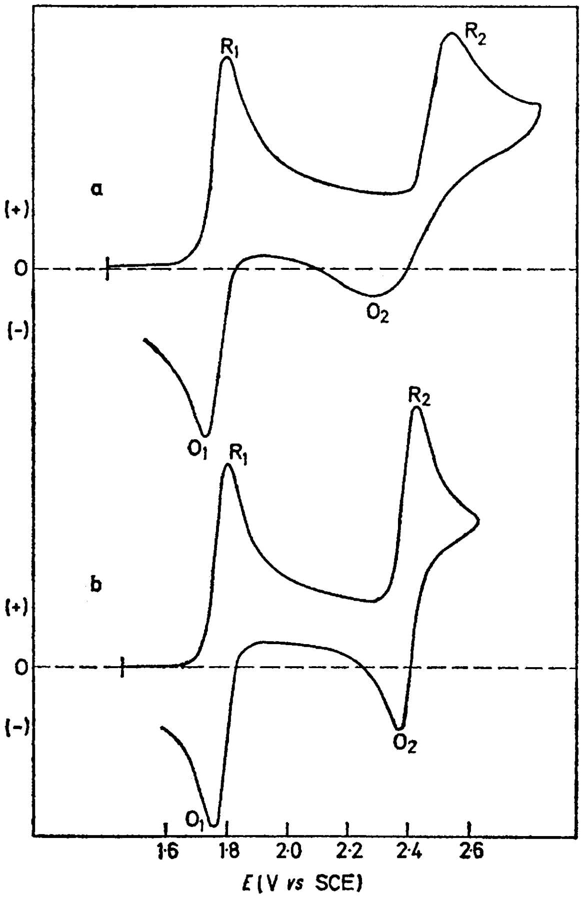

FIGURE. Cyclic voltammograms for the reduction of 9,10-diphenylanthracene at a platinum disc electrode in DMF at −36° in the presence of (a) $Bu^n_4NBF_4$ (0·2M) and (b) $Bu^n_4NBF_4$ (0·2M) $+ Et_4NClO_4$ (0·02M). Voltage sweep rate 153 mV s^{-1}.

$$2\pi^{\cdot -} \overset{k_{disp}}{\rightleftharpoons} \pi^{2-} + \pi \qquad (1)$$

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