Reactions of Aromatic Anion Radicals and Dianions. V. Protonation and Solvation of Aromatic Dianions by Hydroxylic Compounds and the Consequences on Disproportionation Equilibria of Radical Anions

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The kinetics of the protonation of perylene dianion (PE^{2-}) and anthracene dianion (AN^{2-}) by MeOH in THF was studied by linear sweep voltammetry. Rate constants were calculated from the anodic shifts of the peak potentials for reduction of the anion radicals from the reversible values. At 10 °C, the second order rate constants were found to be equal to 7.5×10^4 and 1.5×10^7 M^{-1} s^{-1} for PE^{2-} and AN^{-2}, respectively. At [MeOH] greater than 0.1 M the calculated rate constants for the protonation of PE^{-2} became increasingly larger with increases in [MeOH] indicating a change in $\Delta E°$, the difference in standard potentials for the first and second charge transfers. The latter effect could not be investigated for AN since the more reactive AN$^{\cdot-}$ undergoes protonation at (MEOH] of about 0.1 M during cyclic voltammetric experiments. Benzophenone (BP) ions were found to be even more sensitive to the presence of low concentrations of MeOH with large shifts in $\Delta E°$ being observed at millimolar concentrations of MeOH. Shifts in $\Delta E°$ in the presence of MeOH were attributed to association of the dianions with the hydroxylic compound.

Our recent report of the reversible reduction of anion radicals of aromatic hydrocarbons to the corresponding dianions in aprotic solvents [1] opened the door to direct measurements of the kinetics of the protonation of the dianions. If the reversible potential for an electrode process is known, the rate constant for a reaction following electron transfer can readily be determined by the kinetic shift of the voltammetric peak potential.[2] Dispropor-

tionation mechanisms have recently been proposed to account for some of the protonation reactions of aromatic anion radicals.[3] In evaluating such mechanisms, K_{disp} (eqn. 1) determined in aprotic solvents in the absence of proton donors, is used to determine the second order rate constant for the dianion plus proton donor reaction. Implicit in this treatment is the assumption that low concentrations of the hydroxylic proton donors have no effect upon the difference in formal potentials for the first and second electron transfers ($\Delta E°$) to the aromatic compound and hence on the disproportionation equilibrium constants. Here we report the first direct measurement of dianion protonation kinetics and the observation of a profound effect of hydroxylic compounds upon the magnitude of disproportionation equilibrium constants of anion radicals of aromatic compounds.

$$2\pi^{\cdot-} \xrightleftharpoons{K_{disp}} \pi + \pi^{2-} \qquad (1)$$

In THF, $\Delta E°$ for the ions of perylene (PE) is equal to 520 mV at 11 °C, which corresponds to a value of 6×10^{-10} for K_{disp}. In order to measure the reversible potential for the second charge transfer, it was necessary to conduct the measurements in the presence of activated alumina.[1] Measurements of the peak potential differences (ΔE_p) for determination of the rate constant for the protonation of PE^{2-} with

Table 1. Pseudo first order and second order rate constants for the protonation of perylene dianion by methanol in THF.[a]

[MeOH]/M	ΔE_p/mV [b]	k_1/s^{-1} [c]	k_2/M^{-1} s^{-1} [d]
0.0	25	5.2×10^1	—
0.010	65	6.7×10^2	6.7×10^4
0.026	80	2.3×10^3	8.8×10^4
0.079	90	5.2×10^3	6.7×10^4
0.243	110	2.7×10^3	1.1×10^5
0.52	120	1.1×10^5	2.1×10^5
1.87	165	2.0×10^6	1.0×10^6

[a] 0.2 M Bu$_4$NBF$_4$, +10 °C, hanging mercury drop electrode. [b] Anodic shift from the reversible peak potential measured at a scan rate of 154 mV s^{-1}. [c] Pseudo first order rate constants calculated from three different scan rates. [d] Second order rate constants.

methanol were conducted in THF which had been passed over active neutral alumina just prior to use. These data are summarized in Table 1. Peak potentials were determined at three different sweep rates for each value of [MeOH]. Pseudo first order rate constants (k_1) were then calculated from the shift in peak potential (ΔE_p) from the reversible value for the second charge transfer. Cyclic voltammetry showed that the first charge transfer remained reversible at all concentrations of MeOH used showing that protonation of PE$^{\cdot-}$ is slow during the time scale of the voltammetric measurements. The value of k_1 in the absence of methanol is that for the reaction of PE^{2-} with residual water in the solvent-electrolyte system.* At [MeOH] from 0.01 to 0.1 M the second order rate constant (k_2) for reaction (2) derived from

$$PE^{2-} + MeOH \xrightarrow{k_2} PEH^- + MeO^- \qquad (2)$$

k_1 values determined from peak potential data according to the method of Nicholson and Shain [2] were observed to be equal to 7.5×10^4 M^{-1} s^{-1} which is 150 times smaller than the estimate of Szwarc based on the apparent anion radical protonation rates.[4] At [MeOH]

* Second order rate constants are not listed due to the fact that the water concentration is not known.

greater than 0.1 M, the calculated k_2 values became increasingly larger with increases in the MeOH concentration.

The rate of protonation of anthracene (AN) dianions in THF by MeOH was investigated by means of the shift of the voltammetric peak potential from the reversible value. The observed second order rate constant was 1.5×10^7 M^{-1} s^{-1} at [MeOH] ranging from 0.01 to 0.07 M. The reaction of the dianion with residual proton donors made determination of the rate constant at lower [MeOH] impossible while protonation of the anion radical occurred at higher [MeOH]. The protonation of AN$^{\cdot-}$ was complete (no reverse current during cyclic voltammetry at 1 V s^{-1}) at [MeOH] of about 1.0 M whereas no reaction was observed for PE$^{\cdot-}$ under the same conditions.

Results obtained when the same procedure was applied to the protonation of benzophenone (BP) dianion in DMF were more dramatic. A large shift from the reversible potential was observed even before adding MeOH showing that BP^{2-} is rapidly protonated by residual water. The calculated values of k_2 were not constant and increased markedly with increasing [MeOH], in all cases being greater than the maximum possible value for a diffusion controlled reaction (Table 2).

The results presented above indicate that ΔE° for PE and AN are unaffected by the presence

Table 2. Apparent pseudo first order and second order rate constants for the protonation of benzophenone dianion by methanol in DMF.[a]

[MeOH]/M	ΔE_p/mV [b]	k_1/s^{-1} [c]	k_2/M^{-1} s^{-1} [d]
0	110	5×10^4	—
0.0037	275	1×10^{10}	3×10^{12}
0.015	355	5×10^{12}	4×10^{14}
0.041	410	5×10^{14}	2×10^{16}
0.109	450	2×10^{16}	2×10^{17}
0.271	470	1×10^{17}	4×10^{17}
0.850	505	1×10^{18}	2×10^{18}

[a] 0.02 M Me$_4$NBF$_4$+0.2 M Bu$_4$NBF$_4$, +10 °C, hanging mercury drop electrode. [b] Anodic shift from the reversible peak potential measured at a scan rate of 65 mV s^{-1} (Rate constants were calculated from three different scan rates and found to be independent of scan rate). [c] Apparent pseudo first order rate constants. [d] Apparent second order rate constants.
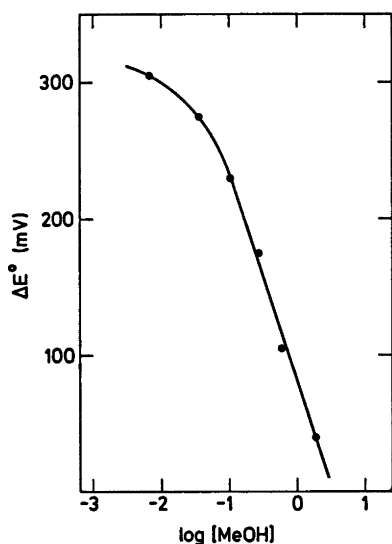
Fig. 1. The dependence of ΔE° for the two consecutive charge transfers to p-dinitrobenzene in THF on the concentration of added methanol.

of MeOH in THF up to concentrations of about 0.1 M and that at higher [MeOH], ΔE° decreases. In the case of BP, ΔE° appears to be even more sensitive to [MeOH], changing drastically even at the millimolar level.

In order to firmly establish that low concentrations of MeOH in aprotic solvents can indeed cause substantial shifts in ΔE° for aromatic compounds in aprotic solvents, the reduction of p-dinitrobenzene (DNB) in THF containing MeOH was investigated. This compound was chosen because the dianion is very stable even in the presence of high concentrations of proton donors. In fact, it has recently been observed that addition of water to DMF causes a substantial shift in ΔE° for DNB.[5] The effect of added MeOH on ΔE° for DNB in THF is illustrated in Fig. 1. A large change in ΔE° was observed with changes in [MeOH].

The effect of the hydroxylic compound, methanol, on the voltammetry of p-dinitrobenzene in DMF is demonstrated by the cyclic voltammograms shown in Fig. 2. In the absence of methanol, ΔE° for the two charge transfers was found to be of the order of 650 mV (Fig. 2a) and decreased to about 400 mV at [MeOH] equal to 0.96 M (Fig. 2b). Further increases in [MeOH] were accompanied by the merging of

the two distinct peaks into a single quasi-reversible voltammetric peak (Fig. 2c).

The association of dianions of aromatic compounds with cations is a well-established phenomenon.[6] It has been pointed out that the association with small dianions such as those from benzoquinone is much stronger than with larger dianions such as those derived from polynuclear aromatic hydrocarbons.[7] The latter has been explained in terms of increasing delocalization of charge as the size of the dianion increases, thus lowering the requirements for strong pairing with counter ions.

The association of dianions of aromatic hydrocarbons with hydroxylic compounds has previously escaped detection, because until recently[1] it was not possible to obtain reversible potentials from cyclic voltammetry due to the great reactivity of the dianions to trace im-
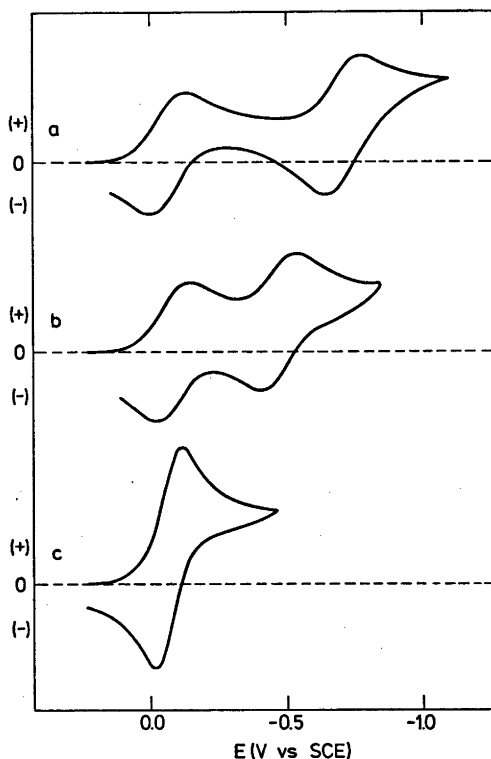

Fig. 2. Cyclic voltammograms of p-dinitrobenzene in DMF containing Bu_4NBF_4 (0.1 M) and Me_4NI (0.01 M) recorded at +10 °C at a voltage sweep rate of 65 mV/s. Solvent was DMF containig methanol: (a) 0, (b) 0.96 M and (c) 7.2 M in methanol.

purities in the aprotic solvents, and the other technique, potentiometric titration,[8] cannot be applied to systems containing water or alcohols.

The sensitivity of BP dianions to association with MeOH as compared to the PE dianions can readily be explained in terms of the lower degree of charge delocalization in BP^{2-}. A similar effect has been observed on ΔE° for BP in the presence of tetraalkylammonium ions of varying size.[9]

The results presented here are very pertinent to the study of protonation reactions of aromatic anion radicals, a topic of active current interest.[3,4,10] Studies on the kinetics of protonation of aromatic hydrocarbons dianions are continuing and will be presented in detail later.

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