

be dissected into 30% noncage and 70% cage reaction of the arylmethyl radicals (unpublished results of B. Matuszewski and D. Leung).
 (10) On leave from A. Mickiewicz University, Poznan, Poland.

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Cation and Electrolyte Concentration Effects on Equilibria and Kinetics of Processes Involving Disproportionation of Radical Ions

Sir:

Our recent measurements of reversible electrode potentials¹ for both the first and second charge transfers to aromatic hydrocarbons in tetrahydrofuran (THF) in the presence of various tetraalkylammonium salts gave results in sharp contrast to those reported by Rainis and Szwarc for potentiometric titrations using sodium biphenylide.² Our inability to make reversible potential measurements in the presence of sodium ion at that time made it impossible to determine whether the discrepancies were due to experimental error or if a large cation effect on disproportionation equilibria was operative. The experimental difficulties have since been resolved and we now report substantial differences between potentials measured in the presence of sodium ions and tetraalkylammonium ions as well as a significant effect of cation concentration. The latter is especially important since it may be used as a powerful tool in evaluating possible disproportionation mechanisms of radical ions.

The measurement of reversible potentials for the reduction of most aromatic hydrocarbon radical anions in the presence of sodium ion at a mercury electrode is precluded by the reversible reduction of sodium ion at a potential less negative than necessary to reduce the radical ions. Difficulties were also encountered¹ during attempts to use micro platinum electrodes for the measurements. We have now found that both platinum and glassy carbon electrodes are suitable for the measurements when freshly polished and when oxygen is completely removed from the electrolytic solutions. In order to obtain reversible potentials the measurements were conducted in solutions which were in contact with active alumina, a procedure which removed trace impurities that react with the highly reactive dianions.^{1,3} The voltammetric measurements were made in the manner previously described.^{1,4}

Data for the reversible reductions of perylene (PE) and anthracene (AN) in THF, 1,2-dimethoxyethane (DME), and dimethylformamide (DMF) are summarized in Table I. The disproportionation equilibrium constants (K_{disp}) at 11°C are calculated according to eq 1.

$$0.057 \log K_{\text{disp}} = E_2 - E_1 = \Delta E^0 \quad (1)$$

The reversibility of the two consecutive charge transfers to PE in the presence of sodium ions is demonstrated by the cyclic voltammogram in THF (Figure 1) where E_1 and E_2 refer to the peak potentials for the first and second charge transfers, respectively. The difference in peak potential, $E_2 - E_1$, for reversible charge transfers may be equated to the difference in formal potentials, ΔE^0 . The effect of Na^+ concentration on ΔE^0 for the two reduction stages of PE in THF is demonstrated by the data in Figure 2. Over the concentration range of NaBPh_4 investigated ΔE^0 increased lin-

Table I. Solvent, Cation, and Cation Concentration Effects on Disproportionation Equilibria

Compound	Solvent	Cation	[Cation], <i>M</i>	ΔE^0 , mV ^a	K_{disp}
Perylene	THF	Na^+	0.07	380	1.7×10^{-7}
		Bu_4N^+	0.22	550	1.6×10^{-10}
	DME	Na^+	0.04	540	4.1×10^{-10}
		Bu_4N^+	0.20	555	7.6×10^{-10}
	DMF	Na^+	0.20	605	5.9×10^{-11}
		Bu_4N^+	0.20	595	3.9×10^{-11}
Anthracene	THF	Na^+	0.07	300	2.2×10^{-6}
		Bu_4N^+	0.22	685	1.6×10^{-13}
	DME	Na^+	0.04	470	2.3×10^{-9}
		Bu_4N^+	0.50	700	2.9×10^{-13}
	DMF	Na^+	Not reversible		
		Bu_4N^+	0.20	750	2.2×10^{-14}

^aDifference in reversible peak potentials for first and second charge transfer, temperature 11°C.

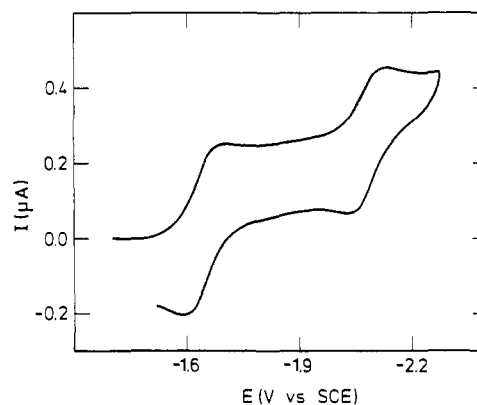


Figure 1. Cyclic voltammogram for the reduction of perylene in THF ($\text{NaBPh}_4 = 0.07 M$). Voltage sweep rate = 150 mV/sec. Temperature = 11°C.

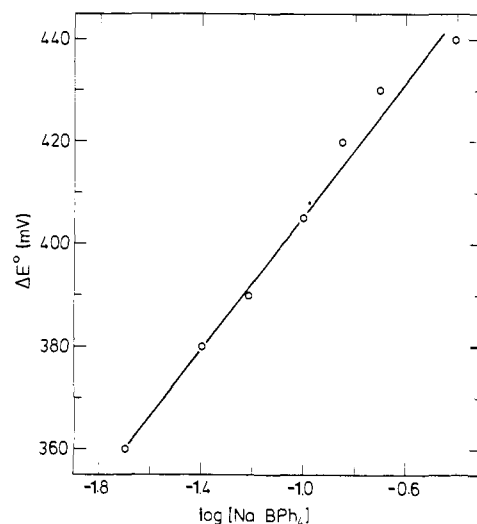


Figure 2. The effect of $[\text{NaBPh}_4]$ on ΔE^0 for the reduction of perylene in THF.

early with the logarithmic increase in the salt concentration according to eq 2.

$$(\Delta E^0) = (\log C_{\text{Na}^+})66 \text{ mV} \quad (2)$$

The data are extrapolated to a constant sodium ion concentration (0.02 *M*) in Table II and compared to that available from potentiometric titrations.² The slope of the ΔE^0 vs. $\log [\text{Bu}_4\text{NBF}_4]$ for the reduction of PE in DME was also found to be equal to 66 mV. The difference in formal potentials

Table II. Disproportionation Equilibrium Constants Standardized for Cation Concentration

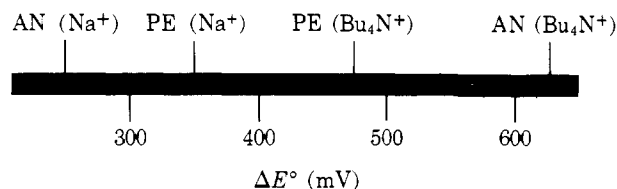
Compound	Solvent	Cation ^a	(C.V.) ^b	Pot. tit ^c
Perylene	THF	Na ⁺	7.2×10^{-7}	6.9×10^{-7}
		Bu ₄ N ⁺	2.8×10^{-9}	—
	DME	Na ⁺	5.5×10^{-10}	2.1×10^{-10}
		Bu ₄ N ⁺	1.9×10^{-9}	—
Anthracene	THF	Na ⁺	2.4×10^{-10}	—
		Bu ₄ N ⁺	3.7×10^{-10}	—
	DME	Na ⁺	1.9×10^{-5}	7.4×10^{-6}
		Bu ₄ N ⁺	1.1×10^{-11}	—
DMF	Na ⁺	9.8×10^{-9}	8.6×10^{-9}	
	Bu ₄ N ⁺	1.4×10^{-11}	—	
	DMF	Bu ₄ N ⁺	6.4×10^{-13}	—

^aCation concentration 0.02 M. ^b K_{disp} calculated from cyclic voltammetry, temperature 11°C. ^c K_{disp} from potentiometric titrations, temperature 25°C, data from ref 2.

was found to be almost independent of salt concentration in DMF.

In DMF, K_{disp} for both AN⁻ and PE⁻ is nearly the same when the cation is Na⁺ or Bu₄N⁺. In THF but not DME, K_{disp} for both PE⁻ and AN⁻ is greater in the presence of Na⁺ than in the presence of Bu₄N⁺. The latter is brought out dramatically by Scheme I. For PE in THF, ΔE^0

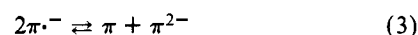
Scheme I



changed by only 135 mV in going from Bu₄N⁺ to Na⁺ while a change of 350 mV was observed in ΔE^0 for AN with the cation change. Changes have previously been observed in ΔE^0 for both PE and AN in the presence of Li⁺, Na⁺, and K⁺ and have been attributed to changes in the degree of solvation of the cations in the presence of the radical ions.² The previous discussion² assumed that both dianions, AN²⁻ and PE²⁻, bring about the desolvation of sodium ions which are solvated in THF in the presence of the corresponding anion radicals. If the increase in disproportionation equilibrium constants in THF and DME as compared to DMF is indeed due to the increased interaction between dianions and cations as compared to the anion radical-cation interaction in the less polar solvents, then the interaction must be greater for AN²⁻ and Na⁺ than for PE²⁻ and Na⁺. The latter is of course reasonable since the degree of interaction of dianions with cations is expected to increase as the dianion becomes smaller.⁵

The effect of electrolyte concentration on the degree of disproportionation of radical ions must be due to an effective increase in the dielectric constant of the medium as the salt concentration is increased. This is indicated by the following: (i) the magnitude of the effect decreases with increasing dielectric constant of the solvent, DME = THF \gg DMF; (ii) the magnitude of the effect is essentially independent of the radical anion, AN⁻ = PE⁻; and (iii) the effect is the same for Na⁺ as for Bu₄N⁺. Thus, it seems highly unlikely that the origin of the effect lies in any specific equilibria involving the organic anions and the cations. It follows from the above discussion that reactions involving a disproportionation (eq 3) of a radical ion to a reactive dianion (in DMF or THF) followed by product forming reactions of the dianion (eq 4) should decrease in rate as the salt

concentration is increased due to the decrease in K_3 accompanying the salt concentration change.



For example, a 100-fold increase in salt concentration brings about a change of 8×10^{-3} in disproportionation equilibrium constants of PE and AN radical anions. Thus, kinetic studies which involve measurements at various salt concentrations would be of great value in evaluating possible disproportionation mechanisms. The kinetics of protonation of aromatic hydrocarbon anion radicals have been the subject of several recent studies,⁶⁻¹¹ some of which have resulted in the conclusion that disproportionation is an important contribution to the overall mechanisms. In such cases, further work involving kinetic studies with variable salt concentrations should prove decisive in establishing mechanisms.

References and Notes

- (1) B. Svensmark Jensen and V. D. Parker, *J. Am. Chem. Soc.*, **97**, 5211 (1975).
- (2) A. Rainis and M. Szwarc, *J. Am. Chem. Soc.*, **96**, 3008 (1974).
- (3) B. Svensmark Jensen and V. D. Parker, *J. Chem. Soc., Chem. Commun.*, 367 (1974).
- (4) O. Hammerich and V. D. Parker, *Electrochim. Acta*, **18**, 537 (1973).
- (5) M. E. Peover, "Electroanalytical Chemistry", A. J. Bard, Ed., New York, 1967, Chapter 1.
- (6) S. Bank and B. Bockrath, *J. Am. Chem. Soc.*, **93**, 430 (1971).
- (7) S. Bank and B. Bockrath, *J. Am. Chem. Soc.*, **94**, 6076 (1972).
- (8) G. Levin, C. Sutphen, and M. Szwarc, *J. Am. Chem. Soc.*, **94**, 2652 (1972).
- (9) A. Rainis, R. Tung, and M. Szwarc, *J. Am. Chem. Soc.*, **95**, 659 (1973).
- (10) E. R. Minnich, L. D. Long, J. M. Cerasa, and J. L. Dye, *J. Am. Chem. Soc.*, **95**, 1061 (1973).
- (11) A. Rainis, R. Tung, and M. Szwarc, *Proc. R. Soc. London*, **339**, 417 (1974).

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The Electron Paramagnetic Resonance Spectra of α -Substituted Nitrotoluene Anion Radicals. The Influence of Electron-Withdrawing Substituents on the Coupling Constants for β -Hydrogen Atoms

Sir:

We have obtained new experimental and theoretical information which indicates that electron-withdrawing substituents importantly diminish the magnitude of spin delocalization to β -hydrogen atoms in radicals. These substituent effects are so large that the EPR coupling constants for β -hydrogen atoms, $a_{\beta\text{-H}}$, cannot be used without correction to estimate conformational preferences, to detect structural changes such as bridging (distortion), or to guide the experimental assessment of B_2 parameters for other β -atoms, such as fluorine.

Radicals with electronegative substituents often exhibit unusually low values of $a_{\beta\text{-H}}$.¹ Such results have often been interpreted as evidence for bridging (distortion at C_β) by X.^{1,2} However, according to the concept of hyperconjugation,³ electron-withdrawing substituents should diminish the donor properties of the β -carbon-hydrogen bonds. Thus, as pointed out by Symons and his associates,⁴ hyperconjugation alone may provide a satisfactory explanation for the influence of electronegative groups on $a_{\beta\text{-H}}$.