Relative Diffusion Coefficients of Aromatic Cations and Aromatic Compounds. Justification for Directly Equating Voltammetric Potentials to Formal Potentials

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Diffusion coefficient ratios for several aromatic compounds and the corresponding cation radicals as well as some cation radical–dication pairs were determined in acetonitrile and dichloromethane. The diffusion coefficients of the lower oxidation states were invariably found to be greater than that of the corresponding oxidized species. The ratios averaged *ca.* 1·3 in acetonitrile and *ca.* 1·5 in dichloromethane. The results were explained by an effective increase in molecular weight of the ions brought about by association with solvents and counter ions. It was concluded that the magnitudes of the diffusion coefficient ratios are not sufficiently great to bring about serious errors in the estimation of E^0 values from voltammetric data.

IN quiet solutions, the potential of a solid electrode is related to the half wave potential by (1) where i is the instantaneous current at potential E and i_L is the current limited by mass transport to the electrode.[1] The relationship between $E_{\frac{1}{2}}$ and the standard potential of the redox couple is given by (2) in which the ratio K_O/K_R may be identified with the diffusion coefficient ratio $(D_O/D_R)^{\frac{1}{2}}$ if activity coefficients are neglected. The ratio K_O/K_R is generally assumed to be equal to unity and $E_{\frac{1}{2}}$ can then be equated to E^0. In a previous paper [2] we demonstrated that equilibrium constants between aromatic compounds and aromatic cation radicals calculated from voltammetric data did not deviate seriously from those determined spectrophotometrically. In this paper we examine the ratio $(D_O/D)_R$ for a series of aromatic compounds and the corresponding cations in order to determine whether or not the assumption that the ratio is equal to unity is justifiable.

$$E = E_{\frac{1}{2}} + (0{\cdot}059/n)\log(i_L - i)/i \qquad (1)$$

$$E_{\frac{1}{2}} = E^0 - (0{\cdot}059/n)\log K_O/K_R \qquad (2)$$

Method for Determination of Diffusion Coefficient Ratios.—It has recently been demonstrated that aromatic cations are sufficiently stable in aprotic solvents containing small amounts of trifluoroacetic acid (TFA) or trifluoroacetic anhydride (TFAn) to allow for equilibrium measurements.[2-5] Thus, the relative diffusion coefficients of reduced and oxidized species can be determined

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[1] R. N. Adams, 'Electrochemistry at Solid Electrodes,' Dekker, New York, 1969, pp. 118—121.

[2] U. Svanholm and V. D. Parker, *J.C.S. Perkin II*, 1973, 1594.

[3] O. Hammerich and V. D. Parker, *J. Electroanalyt. Chem.*, 1973, **18**, 537.

[4] O. Hammerich and V. D. Parker, *J. Amer. Chem. Soc.*, 1974, **96**, 4289.

[5] O. Hammerich, N. S. Moe, and V. D. Parker, *J.C.S. Chem. Comm.*, 1972, 156.

in these media simply by measuring limiting currents before and after oxidation of the aromatic compounds. The limiting current at the rotating disc electrode is given by the Levich equation (3) [6] in which ω is the angular

$$i_L = 0{\cdot}62nFACD^{2/3}\gamma^{-1/6}\omega^{1/2} \qquad (3)$$

velocity of the disc, γ is the kinematic viscosity, and C is the concentration of electroactive species. It can readily be shown that the diffusion coefficient ratio for oxidized (O) and reduced (R) species is given by (4) in a particular solvent at the same electrode at constant angular velocity.

$$(i_L/C_R)_O/(i_L/C_O)_R = (D_R/D_O)^{2/3} \qquad (4)$$

In practice, several determinations of the ratio can be made in a single experiment in the following manner. The limiting oxidation current $(i_L^0)_O$ due to a solution of aromatic compound of known concentration is measured to give $(i_L/C_R)_O$. A partial conversion of the aromatic compound to the corresponding cation is then achieved by anodic oxidation. The concentration of oxidized species is then determined by $(i_L^0 - i_L)_O$, and $(i_L/C_O)_R$ can be determined from the limiting reduction current due to the cation. The diffusion coefficient ratio can then be calculated according to (4). The calculations can be carried out repeatedly after successive partial conversions of the reduced to the oxidized species. It is of the utmost importance that both the reduced and oxidized species can be stable during the time scale of the experiment. The latter can readily be checked by cathodic reduction of the oxidized species at the end of the experiment and comparing $(i_L/C_R)_O$ to that measured in the very beginning of the experiment.

TABLE 1

Determination of diffusion coefficient ratios from rotating disc electrode measurements

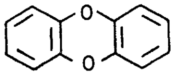
Compound	ΔI_O [a,b]	I_R [a]	(D_R/D_O)
DBT	2·65	2·00	1·33
	5·45	4·10	1·33
	8·00	6·00	1·33
	10·50	7·90	1·33
	12·00	9·05	1·33
	10·75	8·05	1·34
	7·95	5·95	1·34
	5·45	4·05	1·35
	2·85	2·05	1·39
	Average		1·34
DMB	2·60	2·20	1·18
	5·00	4·40	1·14
	7·40	6·30	1·17
	9·60	8·00	1·20
	7·10	6·00	1·18
	4·70	4·00	1·18
	Average		1·18

Solvent composition: CH_2Cl_2–TFA–TFAn (97 : 2 : 1), $[Bu_4NBF_4]$ = 0·1M.

[a] Values in arbitrary units at constant $\omega^{\frac{1}{2}}$. [b] $\Delta I_O = I_O^{\circ} - I_O$.

RESULTS AND DISCUSSION

The structures of the aromatic compounds studied are given along with identifying symbols. All the compounds are reversibly oxidized to either the cation radical or to the dication in the solvents containing TFAn.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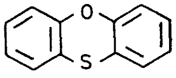
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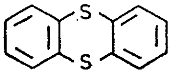
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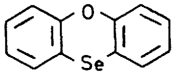
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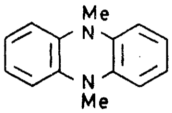
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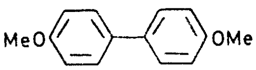
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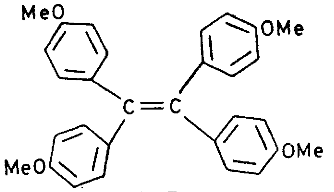
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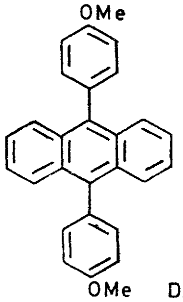
DAA

TABLE 2

Diffusion coefficient ratios for aromatic compounds and cations

Compound	D_R/D_O in A	D_R/D_O in B
DBO	1·66	1·32
DBT	1·55	1·36
TH	1·42	1·38
DMP [a]		1·23 and 1·25
DMB	1·28	1·21
TAE [a]	1·0 and 1·15	1·15 and 1·15
DAA	1·0	
DBS [b]	2·0	2·06

A = CH_2Cl_2–TFA–TFAn (97 : 2 : 1), $[Bu_4NBF_4]$ = 0·1M; B = MeCN–TFAn (99 : 1), $[NaClO_4]$ = 0·1M.

[a] First and second oxidation state change, respectively. [b] D_R/D_{dim}.

Examples of the rotating disc electrode measurements are given in Table 1. The decrease in oxidation current $(I_O^0 - I_O)$ for a given partial conversion divided by the corresponding reduction current (I_R) gives the ratio $(D_R/D_O)^{2/3}$. The average values are converted to D_R/D_O and are summarized in Table 2. In solvent B (MeCN), D_R/D_O values for the heterocyclic compounds, DBO, DBT, and TH are very nearly the same at *ca.* **1·35**. However, significant differences were observed between the compounds in solvent A (CH_2Cl_2) with D_R/D_O decreasing from 1·66 to 1·55 to 1·42 as the oxygens of DBO are replaced by sulphurs. The ratio for DMB was found to be substantially lower in both solvents but once again greater in A than in B. In solvent B, D_R/D_O for DMP and the cation radical was found to be 1·23 and the ratio for the cation radical–dication was almost identical at

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[6] V. G. Levich, 'Physicochemical Hydrodynamics,' Prentice Hall, Englewood Cliffs, 1962, pp. 60—70.

1·25. It was not possible to use solvent A for this compound due to the ease of protonation. In solvent A, D_R/D_O for the first oxidation state change of TAE was found to be 1·0 and for the second 1·15. In solvent B the two values were found to be equal at 1·15. Finally, a ratio of 1·00 was observed for the diffusion coefficients of DAA and the corresponding monocation in solvent A.

A factor which contributes to the magnitude of diffusion coefficients is the molecular weight or bulk of the species. Bacon and Adams determined diffusion coefficients of a series of aromatic hydrocarbons and found a nearly uniform variation with molecular weight with naphthalene having a D value of $2{\cdot}96 \times 10^{-5}$ s cm^{-2} and 9,10-diphenylanthracene showing a value of $2{\cdot}12 \times 10^{-5}$ s cm^{-2} in acetonitrile.[7] A logical explanation of the fact that the ions of the aromatic compounds have diffusion coefficients greater than the substrate is that the ions have greater effective molecular weight due to association with counter ions and the solvents. On this basis one can also explain why the diffusion coefficient ratios are greater in dichloromethane than in acetonitrile. The dielectric constant of dichloromethane is 9 and that of acetonitrile is 37.[8] In general, aromatic ions would be expected to associate with counter ions more strongly in solvents of low dielectric constant. Although there is little information available about the association of aromatic cations, the latter is well documented for the anions of aromatic compounds.[9] Thus, increased association brings about an effective molecular weight increase resulting in a lower diffusion coefficient. Solvation energies of doubly charged ions of aromatic compounds are predicted by the Born equation to be four times greater than that of the corresponding singly charged ions.[10] It is reasonable that the diffusion coefficients of the dications of DMP and TAE should be lower than those of the mono cations.

It is interesting to note that the heterocyclic compounds DBO, DBT, and TH exhibit significantly greater D ratios than the others studied. This could be due to the localization of charge on the more electronegative heteroatoms resulting in a greater association with counter ions. The order within the series in solvent A also supports the latter since oxygen is more electronegative than sulphur. The lowest ratios were observed for TAE and DAA whose ions should have very diffuse charge distributions over the large molecular frameworks.

The error in E^0, when taken to be equal to $E_{\frac{1}{2}}$, can be obtained from equation (2). From our data we find only one value of D_R/D_O greater than 1·56. Taking the square root of this value and substituting into equation (2), we find that $E_{\frac{1}{2}}$ differs from E^0 by only 6 mV. The latter is approximately the expected error in measurements of potentials at solid electrodes and thus cannot be considered significant. The error is considerably smaller than 6 mV in ΔE^0 when differences in potentials of aromatic compounds are used[2] since the ratios of diffusion coefficients for the various compounds were very similar. However, deviations in $(D_R/D_O)^{2/3}$ from unity are significant when the reduction current at the rotating disc electrode is used as a measure for the concentration of the oxidized species.

The effect of ionic size on the diffusion coefficient ratio is even more pronounced for cases where the cation radicals undergo reversible dimerization to diamagnetic dications. The dimerization of DBSe has been studied in acetonitrile and sulphuric acid[11] and in solvents A and B equilibrium (5) lies essentially all the way to the right at room temperature. Thus, the currents at the rotating

$$2\mathrm{DBSe}\cdot \xrightleftharpoons{K_5} (\mathrm{DBSe})_2^{\,2+} \qquad (5)$$

disc electrode, $(I_O^0 - I_O)$ and (I_R), give the diffusion coefficient ratio, D_R/D_{dim}. The average value for the ratio was found to be 2·0 in both solvent systems.

EXPERIMENTAL

Acetonitrile and dichloromethane were reagent grade and passed through a column of neutral alumina (Woelm W 200) immediately before use. Trifluoroacetic acid and trifluoroacetic anhydride were Fluka (purum grade) and used as obtained.

The apparatus used for voltammetric measurements has been described.[12] The cell used both for the preparation of the cation radical solutions and for the rotating disc electrode experiments was a cylindrical, round bottomed, jacketted container with openings for the auxiliary electrode compartment, reference electrode, inert gas supply, thermometer, and a Beckman rotating disc electrode. The temperature was controlled with tap water at 11°. The cation radical solutions were prepared by partial oxidation of solutions of the compounds in the solvent systems. Oxidations were carried out at constant current (12·5 mA) at a large area platinum gauze electrode.

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