Redox Equilibria of Aromatic Cation Radicals and Aromatic Compounds

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Equilibrium constants involving aromatic cation radicals with aromatic compounds were determined spectrometrically in a solvent mixture consisting of trifluoroacetic acid–dichloromethane (1 : 4). The observed equilibrium constants were compared to values calculated from voltammetric data using the Nernst equation. Deviations between calculated and observed equilibrium constants were small for compounds of similar structural type and considerably greater when more drastic structural changes were involved. It was concluded that the deviations were not due to errors associated with relating electrode potentials to $E°$ values but rather to changes in activity coefficients from one structural type as compared to another. The maximum deviation observed in log K was 0·8 and it was concluded that equilibrium constants can safely be estimated from voltammetric data with an order of magnitude reliability. Furthermore, it was concluded that disproportionation equilibrium constants for aromatic cation radicals can be estimated with a high degree of reliability from voltammetric data.

In an authoritive monograph,[1] Adams states, ' Only in rare instances can $E_{\frac{1}{2}}$ values measured at solid electrodes be identified justifiably with thermodynamic E^0's '. This conclusion was based on a number of factors including non-reproducibility of solid electrode surfaces and the existence of concentration overpotential. In spite of this, it is commonplace to find in the literature the use of potentials measured at solid electrodes as thermodynamic quantities without reservation when discussing mechanisms of electrode reactions. As an example, we can take the widely discussed electrode mechanism, disproportionation of a monocation to a dication and an uncharged species [equation (1)]. This mechanism is of current interest to electrochemists and organic chemists and differing viewpoints have been presented.[2-8]

$$2R^+ \rightleftharpoons R^{2+} + R \qquad (1)$$

$$R^{2+} \longrightarrow \text{products} \qquad (2)$$

To treat this mechanism theoretically, one must be able to calculate the equilibrium constant K_{disp} for equation (1). The latter can be accomplished by measurement of the potentials for the two charge transfers [equations (3) and (4)] at an electrode and

$$R \rightleftharpoons R^+ + e \qquad (3)$$

$$R^+ \rightleftharpoons R^{2+} + e \qquad (4)$$

application of the Nernst equation. The Nernst equation can be used once again to calculate the surface concentrations of electroactive species and concentration profiles can be constructed for all species. Using the method of digital simulation,[9,10] working curves can be calculated taking into account the kinetic complication of equation (2).

In the particular example chosen here, the disproportionation mechanism, the accuracy with which one can assign values to K_{disp} is of the utmost importance since the values are so small that in most cases it is possible to challenge the mechanism on the basis that reactions of the dications must be very near or even over the diffusion-controlled rate limit to account for the observed reaction rates.[7,8] Thus, it is of primary importance to be able to estimate the precision with which one can estimate equilibrium constants in organic systems in nonaqueous solvents using electrode potentials measured at solid electrodes. Of course another source of concern is that activity coefficients are never known in the organic systems under question and the potentials measured are at best formal rather than standard potentials and it is conceivable that activity coefficients could vary in such a way as to greatly reinforce errors in the calculations.

In this paper we have taken a completely empirical approach and have compared the equilibrium constants for the reaction between a number of aromatic cation radicals and aromatic compounds determined from electronic absorption spectra with values calculated from E^0 differences estimated by conventional voltammetric measurements. This study was made possible by the recent findings that aromatic cation radicals are unusually stable in media containing trifluoroacetic acid (TFA).[11,12]

RESULTS

The aromatic compounds and corresponding cation radicals which were included in this study are listed in Table 1. The solvent system used for all voltammetric and equilibrium constant measurements was CH_2Cl_2–TFA (4 : 1) containing $Bu^n{}_4NBF_4$ (0·2M). The potentials used in the equilibrium constant calculations were $E_a - \Delta E/2$. In order to evaluate the reversibility of the redox processes, voltammetric measurements were made as a function of voltage sweep rate for compounds (I)—(VII). The data are tabulated in Table 1.

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TABLE 1

Voltage sweep rate dependence of data [a]

Compound	Sweep rate mV s^{-1}	E_a [b]	E_c [c]	ΔE [d]	$E_a - \Delta E/2$	i_p/ V½ C
2,7-Dimethoxy-9,10-dihydrophenanthrene (I)	15·6	1·200	1·135	0·065	1·167	4·2
	30·9	1·200	1·130	0·070	1·165	4·1
	61·8	1·205	1·130	0·075	1·162	4·1
	124	1·210	1·125	0·085	1·167	4·0
	151	1·215	1·125	0·090	1·170	4·1
	236	1·215	1·125	0·090	1·170	4·2
9,10-Diphenylanthracene (II)	15·6	1·240	1·170	0·070	1·205	5·6
	30·9	1·240	1·165	0·075	1·202	5·6
	61·8	1·345	1·160	0·085	1·202	5·7
	124	1·255	1·160	0·095	1·207	5·8
	151	1·260	1·165	0·095	1·212	6·0
	236	1·265	1·145	0·120	1·205	5·9
9,10-Di-*p*-tolylanthracene (III)	15·6	1·190	1·125	0·065	1·157	5·8
	30·9	1·195	1·120	0·075	1·157	5·8
	61·8	1·200	1·115	0·085	1·157	5·8
	124	1·205	1·110	0·095	1·157	5·7
	151	1·210	1·105	0·105	1·157	5·7
	236	1·215	1·100	0·115	1·157	5·6
9,10-Bis-*p*-methoxyphenylanthracene (IV)	15·6	1·175	1·100	0·065	1·142	5·1
	30·9	1·175	1·100	0·065	1·142	5·0
	61·8	1·180	1·105	0·075	1·142	5·1
	124	1·180	1·105	0·075	1·142	5·0
	151	1·190	1·095	0·095	1·142	5·0
	236	1·200	1·090	0·110	1·145	5·0
Phenoxathiin (V)	15·6	1·290	1·225	0·065	1·257	5·2
	30·9	1·295	1·220	0·075	1·257	5·0
	61·8	1·300	1·215	0·085	1·257	5·0
	124	1·305	1·210	0·095	1·257	5·0
	151	1·310	1·205	0·105	1·257	4·9
	236	1·315	1·205	0·110	1·260	4·9
Thianthrene (VI)	15·6	1·315	1·240	0·075	1·277	7·8
	30·9	1·315	1·230	0·085	1·272	7·7
	61·8	1·325	1·230	0·095	1·277	7·6
	124	1·335	1·225	0·110	1·280	7·5
	151	1·340	1·225	0·115	1·282	7·5
	236	1·345	1·120	0·125	1·282	7·4
Dibenzo-*p*-dioxin (VII)	15·6	1·490	1·415	0·075	1·452	8·2
	30·9	1·495	1·410	0·085	1·452	8·3
	61·8	1·500	1·405	0·095	1·452	8·1
	124	1·510	1·400	0·110	1·455	7·9
	151	1·515	1·400	0·115	1·457	7·9
	236	1·525	1·395	0·130	1·460	7·8

[a] All potentials are expressed in V *vs.* SCE and were recorded at a platinum electrode. [b] Peak potential for oxidation of substrate. [c] Peak potential for reduction of cation radical. [d] $\Delta E = E_a - E_c$.

Electronic absorption spectral data for the cation radicals of compounds (I)—(VII) are summarized in Table 2.

Equilibrium constants for the reaction between cation radicals and aromatic compounds [equation (5)] were determined from the absorption spectra.* Since there was generally overlapping absorption bands at both wavelengths used for the calculations, the concentrations of

$$\mathrm{Ar_1}^{+\cdot} + \mathrm{Ar_2} \overset{K}{\rightleftharpoons} \mathrm{Ar_1} + \mathrm{Ar_2}^{+\cdot} \qquad (5)$$

$\mathrm{Ar_1}^{+\cdot}$ and $\mathrm{Ar_2}^{+\cdot}$ were determined by solving equations (6) and (7) where A_1 and A_2 are the absorbances at λ_1 and

$$A_1(\lambda_1) = \varepsilon_1 c_1 + \varepsilon_2 c_2 \qquad (6)$$

$$A_2(\lambda_2) = \varepsilon_3 c_1 + \varepsilon_4 c_2 \qquad (7)$$

λ_2, respectively, ε_1 and ε_3 are the extinction coefficients of $\mathrm{Ar_1}^{+\cdot}$ at λ_1 and λ_2, and ε_2 and ε_4 are the extinction coefficients of $\mathrm{Ar_2}^{+\cdot}$ at λ_1 and λ_2, respectively. When the magnitude of K allowed it, the concentrations of $\mathrm{Ar_1}$ and $\mathrm{Ar_2}$ were made sufficiently large so as not to change significicantly during equilibration.

Values for the equilibrium constants calculated from the voltammetric data are compared to the values observed from spectral measurements in Table 3.

Sources and Magnitude of Experimental Error.—Owing to the fact that most of the spectral measurements were made in spectral regions where absorbance bands for both species of the cation radical pairs overlapped, errors in K of as high as 20% are estimated from this source. No attempt was made to refine these measurements since the error is small compared to the measurement of the electrode potentials. It is generally assumed that potentials at solid electrodes may be measured to within ±5 mV. Thus, in the equilibrium constant calculation involving two separate potentials the maximum error in log K becomes ±10/59 or ±0·17.

DISCUSSION

The equilibrium constant for the reaction of an aromatic cation radical with an aromatic compound [equation (5)] can be calculated from the difference in

$$\mathrm{Ar_1} \overset{E_1^0}{\rightleftharpoons} \mathrm{Ar_1}^{+\cdot} + \mathrm{e} \qquad (8)$$

$$\mathrm{Ar_2} \overset{E_2^0}{\rightleftharpoons} \mathrm{Ar_2}^{+\cdot} + \mathrm{e} \qquad (9)$$

E° values for the two redox couples [equations (8) and (9)], using the appropriate form of the Nernst equation (10). In order to calculate K_c from electrode potential data, it is necessary to make two approximations, (a) that the difference in peak or half wave

$$E_2^0 - E_1^0 = -\frac{RT}{nF} \ln \frac{a_{\mathrm{Ar_1}} a_{\mathrm{Ar_2}^{+\cdot}}}{a_{\mathrm{Ar_1}^{+\cdot}} a_{\mathrm{Ar_2}}};$$

$$K_a = \frac{a_{\mathrm{Ar_1}} a_{\mathrm{Ar_2}^{+\cdot}}}{a_{\mathrm{Ar_1}^{+\cdot}} a_{\mathrm{Ar_2}}};\ K_c = \frac{c_1 c_2^{+\cdot}}{c_1^{\cdot +} c_2} \qquad (10)$$

TABLE 2

Electronic absorption spectral data

λ/nm	429	551	589	597	605	623	657	665	676	682	732	750
						10^{-4}ε/l mol^{-1} cm^{-1} [a]						
(I)$^+$	3·71 [b]	0·01	0·02	0·03	0·36	0·50				1·14		1·62 [b]
(II)$^+$		0·64	0·97	1·02 [b]			0·99 [b]	0·97	0·85	0·79	0·86 [b]	0·75
(III)$^+$		0·56	0·87	1·02	1·08 [b]			1·19 [b]	1·10			0·79
(IV)$^+$		0·52	0·80			1·20 [b]			1·52 [b]		0·44	0·39
(V)$^+$		0·76	1·38 [b]				0·09	0·07	0·06	0·06		0·06
(VI)$^+$		1·02 [b]	0·25				0·02	0·02	0·02	0·02		0·02
(VII)$^+$		0·21	0·40	0·49						2·02 [b]		0·24

[a] At $\lambda_{\mathrm{max.}}$ and at the λ values used in the calculations. [b] At $\lambda_{\mathrm{max.}}$

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* The electron transfer reactions are very rapid with equilibrium being established instantaneously.

potentials is equal to the difference $E_2^0 - E_1^0$ and (b) that the activities of the equilibrium expression can be replaced by concentrations.* It is the purpose of this paper to examine the magnitude of error which will be encountered in estimating K_c from voltammograms of aromatic compounds in non-aqueous solvents using conventional measuring techniques. The purpose is not to refine the measurements to get better values of K_c but rather to use rather crude measurements such as are normally used in typical electro-organic studies and thus evaluate whether or not these measurements can justifiably be used to calculate K_c which in turn is needed for evaluation of mechanistic questions.

TABLE 3

Comparison of calculated and found equilibrium constants

Combination [a]	K Expression	log $K_{\text{electrode}}$	log K_{spectra} [b]	Δ log K [c]
$(I)^+ + (II)$	$c_I{}^+c_{II}/c_Ic_{II}{}^+$	0·64	−0·17	0·81
$(I)^+ + (III)$	$c_Ic_{III}{}^+/c_I{}^+c_{III}$	0·17	0·93	0·76
$(I)^+ + (IV)$	$c_Ic_{IV}{}^+/c_I{}^+c_{IV}$	0·42	0·83	0·41
$(I) + (V)^+$	$c_I{}^+c_V/c_Ic_V{}^+$	1·53	0·99	0·54
$(I) + (VI)^+$	$c_I{}^+c_{VI}/c_I/c_{VI}{}^+$	1·86	1·35	0·51
$(I)^+ + (VII)$	$c_I{}^+c_{VII}/c_Ic_{VII}{}^+$	4·83	4·33	0·50
$(II)^+ + (III)$	$c_{II}c_{III}{}^+/c_{II}{}^+c_{III}$	0·81	0·75	0·06
$(II)^+ + (IV)$	$c_{II}c_{IV}{}^+/c_{II}{}^+c_{IV}$	1·07	0·71	0·36
$(II)^+ + (V)$	$c_{II}{}^+c_V/c_{II}c_V{}^+$	0·88	1·23	0·35
$(II)^+ + (VI)$	$c_{II}{}^+c_{VI}/c_{II}c_{VI}{}^+$	1·27	1·54	0·27
$(II)^+ + (VII)$	$c_{II}{}^+c_{VII}/c_{II}c_{VII}{}^+$	4·18	4·50	0·32
$(III)^+ + (IV)$	$c_{III}c_{IV}{}^+/c_{III}{}^+c_{IV}$	0·26	−0·04	0·30
$(III)^+ + (V)$	$c_{III}{}^+c_V/c_{III}c_V{}^+$	1·70	2·07	0·37
$(III)^+ + (VI)$	$c_{III}{}^+c_{VI}/c_{III}c_{VI}{}^+$	2·04	2·53	0·49
$(IV)^+ + (V)$	$c_{IV}{}^+c_V/c_{IV}c_V{}^+$	1·95	2·08	0·13
$(IV)^+ + (VI)$	$c_{IV}{}^+c_{VI}/c_{IV}c_{VI}{}^+$	2·28	2·39	0·11
$(V)^+ + (VI)$	$c_V{}^+c_{VI}/c_Vc_{VI}{}^+$	0·34	0·34	0·00
$(V)^+ + (VII)$	$c_V{}^+c_{VII}/c_Vc_{VII}{}^+$	3·30	3·44	0·14
$(VI)^+ + (VII)$	$c_{VI}{}^+c_{VII}/c_{VI}c_{VII}{}^+$	2·96	3·17	0·21

[a] It was not possible to determine K for (III) + (VII) and (IV) + (VII) because of the magnitude of the equilibrium constants. [b] The mean values of three determinations. The agreement between separate determinations was within ±20% in all cases. [c] $\Delta \log K = |\log K_{\text{electrode}} - \log K_{\text{spectral}}|$.

The data in Table 1 show that all the compounds studied undergo quasi-reversible one electron oxidation. The peak separation $E_a - E_c$ for all compounds exceeded the theoretical value of 57 mV for a one electron transfer and was dependent on the voltage sweep rate. However, the mean value between the two potentials, $E_a - \Delta E/2$, was found to be a constant within the limits of experimental error (±5 mV) independent of the voltage sweep rate. Thus, the latter values can be expected to be the most reasonable estimates of $E°$ obtainable from the data.

Examination of the data (Table 3) shows that in all cases the agreement between separate determinations of K_c was within the expected range ±20% and more often ±10%. The deviations between log K_a estimated from the electrochemical data and log K_c from the spectrometric data are with the exception of equilibria involving compound (I) $<0{\cdot}50$. Deviations in cases involving (I) were uniformly high and in one case 0·79. The estimated deviation due to experimental error was less than 0·2. Thus, it is apparent that some error, greater than experimental, is encountered in estimating K_c from voltammetric data for the systems in question.

If we consider equilibria involving compounds of the same structural type, for example the hydrocarbons (II) and (III), the observed deviation is 0·06. However, for equilibria involving the methoxy-substituted anthracene (IV) with (II) and (III) the deviation becomes greater than that expected from experimental error. Equilibria involving the closely related heterocyclic compounds (V)—(VII) all gave very small deviations between log K_a and log K_c, well within the expected experimental error. Combinations of the hydrocarbons (II) and (III) with the heterocyclic compounds gave deviations considerably greater than experimental error while combinations involving the diarylanthracene (IV) with the heterocycles (V) and (VI) gave very small deviations. As mentioned earlier, equilibria involving (I) gave uniformly large deviations. If we consider the structure of (I) relative to the other compounds we see that it lacks the common feature of the other compounds, that is, the three ring, anthracene-like nucleus. Thus, in view of the observation of small deviations for the structurally most similar compounds, it perhaps is not surprising that the structurally most different of all compounds (I) gives the largest deviations.

The argument relating deviations between log K_a and log K_c to differences in structural type suggests that the main source in deviations above that due to the experimental error is due to activity coefficient differences. If activity coefficients of the structurally similar compounds are similar, a seemingly reasonable assumption, a cancellation would be achieved and K_a and K_c would be expected to be similar. The quantity of data is too limited to assign the deviations to structural differences; however the trends are definitely present. Thus, it would appear that relating of the voltammetric data to $E°$ values is not a serious source of error in the estimation of equilibrium constants.

Since the largest deviation observed in log K was 0·8, a reasonably safe margin of error to place on estimated values of log K would appear to be ±1·0. Thus, reliable order of magnitude estimates of equilibrium constants for reactions between aromatic cation radicals and aromatic compounds should be possible from voltammetric data. However, it should be emphasized that only 19 equilibrium constants in one particular solvent system do not allow for general conclusions.

In the specific case of the disproportionation reaction of aromatic cation radicals, the experimental error in $E_2 - E_1$ [equations (3) and (4)] should be very small since the difference is measured on a single voltammogram. And since the structural change in going from the cation radical to the dication should be minimal, it would appear that highly reliable equilibrium constant estimations should be possible for such systems. Unfortunately, none of the systems in which disproportionation has been postulated [3,4,6] are amenable to experimental determination of K values.

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* K_c Refers to the equilibrium constant expressed in concentrations and K_a to that expressed in activities.

EXPERIMENTAL

Voltammetric apparatus and the procedure used for constant current coulometry has been described previously.[13,14] Trifluoroacetic acid was reagent grade and used without further purification. Spectral grade dichloromethane was passed through a column of neutral alumina before use.

Extinction Coefficients of Cation Radicals.—Constant current electrolysis was carried out at 12·5 mA on a solution of aromatic compound ($5{\cdot}0 \times 10^{-3}$M) in CH_2Cl_2–TFA (4 : 1) containing Bu_4NBF_4 (0·2M) for 3·22, 6·44, 9·66, and 12·88 min to give solutions of the corresponding cation radical of concentrations of $2{\cdot}5 \times 10^{-4}$, $5{\cdot}0 \times 10^{-4}$, $7{\cdot}5 \times 10^{-4}$, and $1{\cdot}0 \times 10^{-3}$M, respectively. After appropriate dilution with the solvent mixture, the extinction coefficient was calculated from the visible absorption spectra. Values for the four determinations were averaged. Individual values differed from the average by no more than 5%. That the generation of cation radicals was quantitative was demonstrated by coulometric reduction.

Typical K Determination.—Compound (III) (0·1 mmol) was dissolved in CH_2Cl_2–TFA (4 : 1) containing Bu_4NBF_4 (0·2M). Constant current oxidation was carried out for 3·22 min at 12·5 mA. An aliquot portion of the resulting solution (300 μl) was diluted to 5·0 ml with solvent mixture containing the calculated amount of (IV) and (III) to give concentrations of 4×10^{-3}M of both the latter. The spectrum of this solution was recorded. Electrolysis was conducted for an additional 3·22 min on the bulk solution and an aliquot portion (150 μl) was diluted as before. The spectrum of the latter solution was recorded. The electrolysis and spectral measurements were conducted once more as before in order to obtain data for a third value of the equilibrium constant.

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