Temperature Effects on Electrode Processes. I. The Entropy of the Reversible Oxidation and Reduction of Alternant Aromatic Hydrocarbons

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The temperature dependence of the reversible electrode potentials for the oxidation and reduction of alternant aromatic hydrocarbons (AAH) was determined using phase selective second harmonic a.c. voltammetry. The value of dE^{rev}/dT, which is equal to ΔS, was found to vary for the reduction of planar AAH in a manner predictable from the distribution of charges in the ions. Triphenylene, the ions of which have disperse charge showed a very low temperature dependence of E^{rev} for the reduction process while anthracene reduction was accompanied by the highest value. The charges in the ion radicals of anthracene are concentrated in the 9,10-positions. Substitution of phenyl groups on the 9- or 9,10-positions of anthracene brought about essentially no effect on dE^{rev}/dT for the reduction processes. It was proposed that the entropy of solvation is greater the more localized the charge is. The oxidation processes were less amenable to study but it was possible to draw conclusions for the processes involving the phenyl substituted anthracenes. Oxidation of 9,10-diphenylanthracene was accompanied by a temperature effect of similar magnitude as for the reduction process while the entropy effect was greater for the oxidation of 9-phenylanthracene. The interpretation of these data is that in the case of the 9-phenylanthracene cation radical, solvation is strongest at the unsubstituted 10-position. The results indicate that entropy studies can give added detail to the study of electrode processes.

The effect of the temperature on the values of reversible electrode potentials has been investigated to a very limited extent. The early work of Hoijtink[1] using *d.c.* polarography indicated that aromatic hydrocarbon reduction potentials change about 0.4 mV/K near room temperature. Van Duyne and Reilley[2] investigated both the oxidation and reduction of several organic compounds and found values of dE^{rev}/dT, where E^{rev} is the reversible potential defined in eqn. (1), in good agreement to those reported earlier.[1] In (1) f and D refer to

$$E^{rev} = E^{\circ} - (RT/nF)\ln (f_R/f_O)(D_O/D_R)^{\frac{1}{2}} \qquad (1)$$

activity coefficients and diffusion coefficients, respectively, and the subscripts refer to the reduced (R) and oxidized (O) forms of the species undergoing electron transfer. A much more comprehensive study of the temperature effects in inorganic electrode processes has been reported.[3] The values reported in the latter study are much larger, typically ± 1 mV/K.

We have undertaken a systematic investigation of the temperature dependence of reversible organic electrode processes in order to determine the factors contributing to ΔS for these reactions. The relationship between ΔS and E^{rev} is given by eqn. (2)

$$E^{rev} = (1/nF)(T\Delta S - \Delta H) = T(dE^{rev}/dT) - \Delta H/nF \quad (2)$$

providing that the diffusion coefficient and activity coefficient ratios are unity and temperature independent and that ΔH is independent of the temperature in the range of measurements. These assumptions are reasonable under the low concentration conditions involved in E^{rev} measurements over small temperature intervals. The most precise measure of

the reversible potential can be obtained by phase selective second harmonic a.c. voltammetry (PSSHAC).[4] Use of the latter technique should have a distinct advantage over either of the previous polarographic[1] or cyclic voltammetric[2] methods. Consequently, we anticipated obtaining precise values of dE^{rev}/dT without the necessity to use wide temperature ranges. As the first step in our investigation, we chose to study the reactions of the alternant aromatic hydrocarbons (AAH) since the voltammetry of these compounds has been intensively investigated[5] and the structural simplicity of the compounds suggests that they may serve as model systems by which to compare results from more complex processes.

RESULTS

Reversible potential measurements. Due to the importance of precision in the determination of E^{rev}, the measurement method will be discussed in some detail here rather than in the experimental part. Although the precision of the measurement of d.c. peak potentials has been improved dramatically by recent work employing derivative techniques,[6,7] phase selective second harmonic a.c. voltammetry[4] remains the method of choice for the measurement of E^{rev} values. The reason for this is that at low voltage sweep rates the d.c. waves can be influenced by such undesirable factors as electrode edge effects and convection as well as by chemical follow-up reactions. At higher sweep rates, necessary to avoid these problems, the uncompensated solution resistance becomes a significant problem. Although it is possible to overcome the latter problem, a large number of measurements at different concentrations is still necessary to obtain a single E^{rev}.[7,8] On the other hand, the preferred mode of the a.c. measurements is to use low d.c. voltage sweep rates and the second harmonic signal is affected to a minimal extent by either uncompensated resistance or double layer charging current.

A description of PSSHAC response for reversible and reacting organic redox systems has recently been presented.[9] In this work we have used three criteria to verify that the potentials measured are in fact E^{rev}. The first two, the independence of the measured values on frequency and phase (either the in phase I or quadrature Q component zero current crossing potentials) follow from the recommendations of Bond and Smith.[4] The third criteria, the indepen-

dence of the measured values on the substrate concentration was adopted in order to attempt to circumvent any possible problems due to product adsorption or solution equilibria. Unless otherwise noted, the data reported is for the Q component zero current crossing potentials and tests have been made relating to the other criteria.

In the most favorable cases we find that our measurement precision approaches ± 0.1 mV in the E^{rev} values and the error seldom exceeds ± 0.2 mV. This represents a significant improvement over that reported by Bond and Smith (± 0.5 mV) using Fast Fourier Transform procedures.[4] The importance of measurement precision can be appreciated by considering the error in 2 point slopes as a function of the precision and the temperature range for the case where the slope is equal to 0.2 mV/K. If the precision is ± 0.1 mV a temperature range of only 20 degrees is necessary for 5 % accuracy in the slopes. The temperature ranges necessary to retain this accuracy with measurement precision of ± 0.2, ± 0.5 and ± 2.0 mV are equal to 40, 100 and 400 degrees, respectively. The generally accepted measurement precision for d.c. peak potentials, not including the recent derivative work, is of the order of ± 5 mV which would require a 1000 degree temperature range in order to measure slopes to within 5 %. The most significant consequence of the high precision that we observe is that we can restrict our measurement to temperatures close to the ambient value and thereby avoid all of the extreme problems associated with low temperature measurements.

The reference electrode for variable temperature E^{rev} measurements is another factor which requires special attention. The problem in this case is that it is desirable that the temperature dependence reflects only dE^{rev}/dT of the process being studied and that the reference electrode temperature remains constant. No matter what the experimental arrangement there will necessarily be a temperature gradient along some part of the path between the reference and the working electrode. The latter then gives rise to a change in electrode potential caused by the temperature gradient of the liquid junction potential between the reference and working electrode compartments. To avoid the latter problem we minimized the liquid junction potential by using the same solvent and electrolyte in both compartments with the only difference being that the reference compartment was 0.002 M in $AgNO_3$. The gradient has been estimated to be about 10^{-2}

mV/K when the reference was an aqueous calomel electrode and the working compartment contained an organic solvent.[2] Thus, the gradient under the conditions of our experiments is surely much less and negligible.

With regard to electrode potential measurement precision it is important to realize that the precision observed under the best circumstances for a single series of experiments in which no changes are made in the cell or the potentiostat settings cannot be realized in the measurements made on the same system day after day. As little change as turning the power off and back on again can bring about mV changes in the measured potential. If highly accurate potentials are needed the best procedure would be to use an internal redox system as the reference.

The substances investigated. The structures of the AAH and identifying symbols are shown below. The oxidized and reduced states are indicated as $PE^{.+}$ and $PE^{.-}$, respectively, in this case for the ion radicals of perylene.

Reversible electrode potentials. The data in Table 1 illustrate a typical determination of dE^{rev}/dT. The reversible potential for the reduction of PE in acetonitrile was determined by PSSHAC voltammetry over a 40 degree temperature range. The temperature measurements were accurate to 0.1 degree. The

Table 1. A typical data set for the determination of dE^{rev}/dT. The reduction of perylene in acetonitrile.[a]

T/K	$-(E^{rev})_{exp}/mV$	$-(E^{rev})_{calc}/mV$
276.1	1971.3(0.2)	1971.4
265.9	1970.6(0.1)	1970.4
255.7	1969.2(0.1)	1969.3
246.5	1968.4(0.1)	1968.4
238.0	1967.6(0.1)	1967.5

[a] Solvent containing Bu_4NBF_4 (0.1 M) with a substrate concentration of 0.5 mM.

numbers in parentheses refer to the standard deviation in five replicate measurements. The values listed in the third column are those calculated from the linear regression correlation equation. The features of most interest in the data are that the precision in the electrode potentials was generally ± 0.1 mV and that the calculated potentials are in all cases within 0.2 mV of the experimental values. Thus, the data illustrate both the measurement precision and the linearity of the data over the entire temperature range.
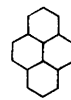
The reversible electrode potentials at 273.2 K for all of the processes investigated are tabulated in Table 2. The potentials all refer to the same
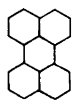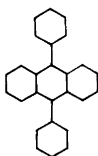

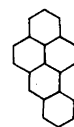Perylene (PE)   Benzoperylene (BPE)   Pyrene (PY)

9,10-Diphenylanthracene (DPA)   9-Phenylanthracene (PA)   Benzopyrene (BPY)

Anthracene (AN)   Triphenylene (TR)

Table 2. Reversible reduction potentials and the temperature dependence for alternant aromatic hydrocarbons and cation radicals.[a]

Substance	$E^{rev}_{273.2\,K}$ [b]/V	$(dE^{rev}/dT)/(mVK^{-1})$
Triphenylene	−2.750	−0.0378
Perylene	−1.971	−0.101
Benzoperylene	−2.174	−0.107
Benzopyrene	−2.146	−0.116
Pyrene	−2.383	−0.119
9-Phenylanthracene (PA)	−2.220	−0.192
Anthracene	−2.257	−0.197
9,10-Diphenylanthracene (DPA)	−2.179	−0.197
DPA cation radical	+0.932	+0.240
PA cation radical	+0.972	+0.553
Perylene cation radical	+0.737	+1.223

[a] All measurements were with a gold electrode at a substrate concentration of 0.5 mM. [b] The zero current crossing potential of the quadrature component.

Ag/Ag$^+$ reference electrode in acetonitrile and the precision is ±0.2 mV.

The temperature dependence of reversible electrode potentials. Values of dE^{rev}/dT for all of the processes studied are summarized in Table 2. In all cases the slopes are negative for reductions and positive for oxidations. The magnitudes of the values of the slopes for the reduction of AAH show no relationship to the reversible electrode potentials. However, there does appear to be a definite relationship between the charge distributions in the AAH ions and dE^{rev}/dT. The most symmetrical molecule, TR, produces ion radicals in which the charge is uniformly spread out over the structure and gave rise to the lowest temperature dependence of the reduction potentials. Anthracene, the ion radicals of which have the charge concentrated in the 9,10-positions, gave rise to significantly greater slopes. Substitution of phenyl groups in the 9 (PA) or 9,10 (DPA) positions of anthracene was observed to have very small effects on both E^{rev} and dE^{rev}/dT for the reduction reactions. The value of dE^{rev}/dT for the oxidation of DPA was only slightly greater than that for the reduction which suggests that the same factors are responsible for the temperature effects in this case. However, for both PA and PE the

Table 3. Concentration and phase effects on the observed temperature dependence of the oxidation of perylene.[a]

[Perylene]/mM	Component [b]	$E^{rev}_{273.2\,K}$ [c]/V	$(dE^{rev}/dT)/(mVK^{-1})$
Oxidation process			
0.125	Q	+0.771	+0.897
0.25	Q	+0.768	+1.005
0.50	Q	+0.767	+1.223
0.50	I	+0.773	+1.169
Reduction process			
0.125	Q	−1.963	−0.0976
0.25	Q	−1.970	−0.100
0.50	Q	−1.971	−0.101
0.50	I	−1.971	−0.0991

[a] Conditions were the same as for the data in Table 1. [b] The quadrature (Q) or the in phase (I) component of the PSSHAC output. [c] The zero current crossing potential of the quadrature component measured at 5 − 6 temperatures and the value given is taken from the linear regressions correlation at 273.2 K.

Table 4. Concentration and phase effects on the observed temperature dependence of the reversible oxidation potential of 9-phenylanthracene.[a]

[PA]/mM	Component[b]	$E^{\text{rev}}_{273.2\,\text{K}}$ [c]/mV	$(\text{d}E^{\text{rev}}/\text{d}T)/(\text{mV K}^{-1})$
0.50	I	972.2	+0.556
0.50	Q	971.3	+0.553
0.25	Q	972.7	+0.555
0.125	Q	969.8	+0.559

[a] Conditions were the same as those for the data in Table 1. [b] The quadrature (Q) or in phase (I) component of the PSSHAC output. [c] See Table 3.

magnitudes of $\text{d}E^{\text{rev}}/\text{d}T$ are significantly greater for the oxidations than the reductions, by a factor of 10 in the latter case. It was not possible to obtain reliable data for the oxidation of the remaining AAH.

Concentration and phase effects on electrode potential measurements. The unusually large values of $\text{d}E^{\text{rev}}/\text{d}T$ for the oxidation of PE and PA suggest that there may be complicating factors associated with the electrode processes. The data in Tables 3 and 4 in which measurements were conducted at different concentrations were gathered in order to determine whether or not the unusually large temperature effects can be attributed to the entropies of the charge transfer reactions. Looking first at the data for the reduction of perylene, we see that $\text{d}E^{\text{rev}}/\text{d}T$ is essentially independent of the concentration of PE and does not depend upon whether the E^{rev} values were derived from I or Q components of the a.c. current. On the other hand, during the oxidation of PE, $\text{d}E^{\text{rev}}/\text{d}T$ is definitely concentration dependent and also depends upon whether the data refers to the I and Q component. In view of the foregoing, we conclude that the oxidation process for PE is accompanied by complicating features not present during the reduction and thus the unusually large value of $\text{d}E^{\text{rev}}/\text{d}T$ for the oxidation process cannot be attributed solely to an entropy effect. On the other hand, $\text{d}E^{\text{rev}}/\text{d}T$ observed during the oxidation of PA is both concentration and phase independent. Thus, in this case it appears to be safe to conclude that this process involves a greater entropy change than is observed with the reduction of PA or any of the other AAH.

Further Comments. A referee pointed out that a temperature gradient will give rise to some potential difference which varies with the gradient. In our opinion, the data provide evidence that any such effect is negligible and that the values of $\text{d}E^{\text{rev}}/\text{d}T$

are true reflections of ΔS. An indication of this is the very similar absolute values of ΔS observed for the oxidation and reduction of DPA, $+5.53$ and -4.54. Any gradient error would effect the positive and negative values in opposite directions.

DISCUSSION

The reduction of a neutral AAH is accompanied by a decrease in entropy whereas the reduction of the corresponding cation radicals brings about an increase in entropy. The values calculated from $\text{d}E^{\text{rev}}/\text{d}T$ for the various processes are summarized in Table 5.

Values were obtained for processes involving both the reduction and the oxidation of DPA. It is instructive to examine the entropy values for these processes first in order to suggest the primary

Table 5. Entropies and molecular orbital charge localization parameters of alternant aromatic hydrocarbon reduction processes.[a]

Substance	$\Delta S^{\circ}_{273.2\,\text{K}}/$ cal K^{-1}mol^{-1}	Q[b]
Triphenylene	−0.87	0.056
Perylene	−2.33	0.075
Benzoperylene	−2.47	0.068
Benzopyrene	−2.67	0.097
Pyrene	−2.74	0.104
9-Phenylanthracene	−4.43	—
Anthracene	−4.54	0.122
9,10-Diphenylanthracene	−4.54	—
DPA cation radical	+5.53	—
PA cation radical	+11.6	—
Perylene cation radical	(+22.4)	—

[a] Electrochemical data from Table 2. [b] Measure of charge localization as defined by eqn. (3).

factors involved. It has been suggested that the solvation energies of the positive and negative ions of AAH should be equal or very nearly so.[5,10] The latter then suggests that if the entropy of the corresponding electrode processes is a direct reflection of the solvation energies of the ions that ΔS for the reduction of the neutral AAH and that for the reduction of the corresponding cation radical should be equal but opposite in sign. Since the reduction of the neutral AAH is accompanied by the formation of the AAH anion radical and ordering of solvent in the solvation process, a decrease in entropy is expected. Conversely, reduction of the cation radical involves a decrease in solvation and a corresponding decrease in ordering of the solvent. One might also expect that in addition to the magnitude of the solvation energies, the entropy should be affected by the distribution of charges in the ions. In this respect, the positive and negative ions of AAH are ideal for comparison since molecular orbital theory predicts the charge distributions should be identical.[11] Turning now to the ΔS values observed for the reduction of DPA and DPA$^{\cdot +}$ we find the predictions based on solvation being the primary factor in determining the entropy value to be fulfilled. The values observed, -4.54 and $+5.53$ indicate that the entropy changes can be attributed to the solvation and desolvation processes, respectively. The fact that ΔS is numerically greater for the reduction of DPA$^{\cdot +}$ could be a consequence of the fact that the dipolar aprotic solvent, acetonitrile, is more effective in solvating cations than anions.[12] In any case, the values for the two processes are very similar but opposite in sign. Therefore it appears to be justifiable to discuss ΔS values in terms of solvation effects, at least in the polar solvent, acetonitrile, where ion association is minimal.[13]

The distribution of charge in ion radicals of AAH is given by the squares of the atomic orbital coefficients in the highest occupied and lowest unoccupied molecular orbitals for the cation radicals and anion radicals, respectively. In order to have a measure of the localization of charge, we have summed the squares of the charges on all non-ring juncture positions according to (3), where q_i is the charge on carbon i in the AAH. For example, if an

$$Q = \sum q_i^2 \qquad (3)$$

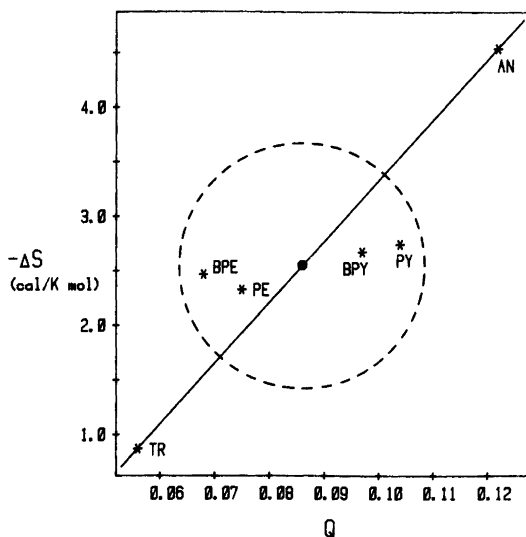AAH has 10 non-ring juncture carbon atoms and all of the charge is on a single carbon $Q = 1$ while

Fig. 1. Correlation of ΔS for the reduction of alternant aromatic hydrocarbons with the molecular orbital parameter Q. The solid octagon represents the average for the data points in the circle.

$Q = 0.1$ if the charge is equally distributed on all 10 carbons. We have calculated Q for the unsubstituted AAH anion radicals from molecular orbital data[14] and these values are summarized in Table 5. The correlation of dE^{rev}/dT vs. Q is illustrated in Fig. 1. It is obvious that a qualitative relationship exists with the value of ΔS being the smallest for the formation of the anion radical in which the charge is least localized, i.e. TR$^{\cdot -}$. The solid octagon located within the circle encompassing data for the reduction of PE, BPE, PY and BPY, represents the average value for all of the four data points in the circle.* Least squares correlation of this point with those for the reduction of AN and TR results in a slope of 55.6 and a correlation coefficient of 0.99999. Although we do not look upon the latter as a quantitative relationship, we do propose that it provides strong support for solvation being the primary factor in the entropy changes for the AAH redox reactions in acetonitrile.

The very large entropy value observed for the reduction of perylene cation radical must, be overlooked since dE^{rev}/dT was found to be concentra-

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* This representation is only to show that the average of the values in the circle fits the relationship between the extremes.

tion dependent and also was different when the E^{rev} were derived from I component data as compared to the Q component measurements. On the other hand, the large value for the reduction of $PA^{·+}$ cannot be discounted since no complications were observed in the measurements. The value of ΔS, $+11.6$ cal/K mol, is very nearly double that for the reduction of $DPA^{·+}$. Since the charge in these ions is concentrated in the 9 and 10 positions, it seems reasonable that solvation at the unsubstituted position in $PA^{·+}$ favors concentration of the charge at that position giving rise to the increased entropy effect. The latter is reasonable when one considers the steric effect of the phenyl substituents which are tilted out of the plane of the anthracene nucleus.

All of the data suggest that charge localization and the accompanying effect on the solvation process of the AAH ions are the predominant factors in determining the entropy change in the electrode processes. For the reduction of anthracene and triphenylene, the solvation energies of the anion radicals are expected to be nearly identical while the entropy is more than five times as great in the former process.

The discussion in the previous paragraphs suggests that entropy studies can be of great value in determining the details of electrode processes. Unusual solvent effects and ion association should be reflected in the entropy values for the reactions.

EXPERIMENTAL

The solvent and electrolyte handling procedures were the same as those recently described.[15] The aromatic compounds were reagent grade and recrystallized before use.

The instrumentation consisted of a PAR model 173 potentiostat driven by a HITEK model PPR1 waveform generator with the output from the PAR model 176 current follower fed into a PAR model 5203 lock-in amplifier which also served as the a.c. signal source. The output of the lock-in amplifier and the waveform generator were processed simultaneously by using both channels of the Nicolet model 2090-III digital oscilloscope. The second harmonic a.c. zero current crossing potentials were printed out by a Hewlett-Packard model 9825 desk computer after processing of the outputs of the lock-in amplifier and the waveform generator. The processing of the waveform generator output gave a determination of the voltage sweep rate and hence the mV/data point, during each potential determination.

The working electrodes were fabricated from 8 mm gold wire embedded in glass and polished to a planar surface. The reference electrode was of the type described by Moe,[16] the body of which consisted of a pyrex tube with soft glass sealed into one end providing the junction between the reference and working compartments. The length of the pyrex tube was such that about 30 cm of the length between that in contact with the working solution and the silver wire of the reference system was exposed to the atmosphere of the room. The temperature gradient was thus confined to the reference solution close to the working compartment and the temperature of the reference electrode remained constant at the ambient value.

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