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Temperature Effects on Electrode Processes. II. The Entropy of Formation of Ion Radicals of Heteroaromatic Compounds

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The temperature dependence of reversible electrode potentials, measured by phase selective second harmonic *a.c.* voltammetry, for the formation of ion radicals of hetroaromatic compounds structurally related to anthracene was determined in order to obtain entropies of formation. All compounds investigated had the anthracene nucleus with the 9 and 10 positions occupied by heteroatoms, S, O, N or Se. The entropy for the formation of the anion radical of phenazine (9 = N = 10) in acetonitrile was observed to be equal to −4.7 cal/K mol, a value in close agreement with that for anthracene anion radical indicating little influence of the nitrogen atoms on the charge distribution of the anion radical. The entropies of formation of cation radicals of the hetroaromatics were very much greater than expected for the anthracene cation radical ranging from +10.0 to +25.3 cal/K mol. Enthalpy changes and reversible potentials, relative to those for the reduction of anthracene, were observed to be linearly related with a slope of 0.907 and a correlation coefficient of 0.999. The deviation of the slope from unity shows the importance of entropy changes in the redox processes.

We have recently shown that the entropy changes during reversible electrode processes (1) are closely

$$A \pm e^- \rightleftarrows B^{\mp} \tag{1}$$

related to the charge distributions in the ion radicals formed upon charge transfer to or from alternant aromatic hydrocarbons (AAH).[1] The entropy changes were determined from the temperature coefficients of the reversible electrode potentials assuming that the enthalpy changes were constant over the small temperature ranges employed, as indicated in eqn. (2). Appreciable charge

$$\mathrm{d}E^{\mathrm{rev}}/\mathrm{d}T = \Delta S/nF \tag{2}$$

delocalization is a characteristic of the ion radicals of AAH and the ΔS values observed were relatively small.

Reversible electrode potentials are often correlated with gas phase ionization potentials and electron affinities as well as with molecular orbital parameters.[2-12] Invariably, entropy effects are considered to be negligible, a reasonable approximation for the gas phase reactions but somewhat questionable for the corresponding redox potentials measured in solution. To illustrate this point we have calculated the enthalpy changes relative to that for the reduction of triphenylene from the data previously reported[1] using eqn. (3)

$$\Delta\Delta H = -nF(\Delta E^{\mathrm{rev}}) + T\Delta\Delta S \tag{3}$$

(Table 1). The column headed $T\Delta S$ gives the contribution of entropy to the free energy changes in the reactions at 273.2 K. Correlation of E^{rev} with $\Delta\Delta H$, when expressed in the same units, results in a slope of 0.98 and a correlation coefficient of 0.998. At the level of accuracy achievable in gas phase measurements, the error introduced by the entropy effects for the redox reactions of AAH is of little consequence. However, such correlations have been reported for aromatic compounds in general that do not belong to any closely related group such as the AAH.[8] Correlations have also been reported for non-aromatic nitrogen containing compounds in which the charges on the resulting radical cations are surely localized on the heteroatoms.[7] Reasonably good correlations are found in practice and it is of interest to examine why this is so. Is it that

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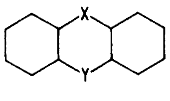
Table 1. Relative contributions of enthalpy and entropy for the formation of alternant aromatic hydrocarbon anion radicals in acetonitrile.[a]

AAH	$E^{\mathrm{rev}}_{273.2}$/mV[b]	$-\Delta S_{273.2}$[c]	$-T\Delta S$/kcal mol^{-1}	$-\Delta\Delta H$[d]
Triphenylene	0 (0)	0.87	0.238	0
Perylene	779 (18.0)	2.33	0.637	18.4
Benzoperylene	576 (13.3)	2.47	0.675	13.7
Benzopyrene	604 (13.9)	2.67	0.729	14.4
Pyrene	367 (8.5)	2.74	0.749	8.97
9-Phenylanthracene	530 (12.2)	4.43	1.21	12.0
Anthracene	493 (11.4)	4.54	1.24	11.1
9,10-Diphenylanthracene	571 (13.2)	4.54	1.24	12.9

[a] Electrode potential and entropy data from Ref. 1. [b] Reversible electrode potentials relative to the reduction potential for triphenylene, numbers in parentheses are in kcal/mol. [c] The entropy change in cal/K mol from Ref. 1. [d] The enthalpy change relative to that for triphenylene reduction in kcal/mol.

entropy effects are negligible as commonly assumed? Or, do systematic errors in solution or gas phase data cause a cancellation of the entropy effects? A third intriguing possibility is that changes in ΔH are paralleled by corresponding changes in ΔS resulting in good correlations with significant errors in the slopes when they are assumed only to arise from the ΔH contribution.

We now report the second stage of our investigations of entropy effects on electrode processes. We have chosen another rather closely related series of compounds of structure *1* in order to test the effect of heteroatoms introduced into aromatic systems on the entropy changes of the redox reactions. The compounds are related to anthracene and X and Y are O, S, Se, N, N – H and N – Me. The electrochemistry of these compounds has been investigated intensively in recent years.[13-24] It was hoped that this investigation would provide answers to some of the questions posed in the previous paragraph.



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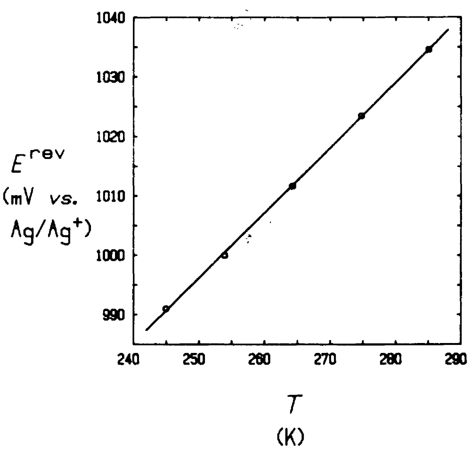


Fig. 1. Correlation of the reversible potential for the oxidation of thianthrene (0.5 mM) in acetonitrile containing Bu_4NBF_4 (0.1 M) with temperature.

RESULTS AND DISCUSSION

The temperature coefficients of the reversible electrode potentials for the reduction of phenazine and the oxidation of all of the other compounds with structure *1* studied were obtained by measurements over about a 40 K interval in acetonitrile. A typical set of data, that for the oxidation of thianthrene, is illustrated in Fig. 1. Reversible potentials calculated from correlation equations were generally within 0.2 mV of the observed values. In this case the deviation is as great as 0.5 mV at one T. The correlation coefficient in this particular case was 0.9998 and was greater than 0.999 in all correlations. The measurement precision was discussed in detail in Ref. 1. In general, the measurements provide $\mathrm{d}E^{\mathrm{rev}}/\mathrm{d}T$ to ± 0.01 mV/K which corresponds to an error of ± 0.2 cal/K mol in ΔS.

All of the experimental temperature coefficients along with the reversible potentials, ΔS and $\Delta\Delta H$ at

Table 2. Entropies and relative enthalpies of formation of ion radicals in acetonitrile for compounds with structure *1*.

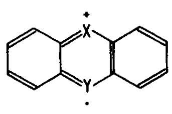
Compound Name	X	Y	$(\mathrm{d}E^{\mathrm{rev}}/\mathrm{d}T)/$ $\mathrm{mV\ K^{-1}}$ [a]	$E^{\mathrm{rev}}_{273.2}/\mathrm{mV}$ [b]	$\Delta S_{273.2}$ [c]	$-\Delta\Delta H$ [d]
Anthracene[e]	C−H	C−H	−0.197	−2257	−4.54	0
Phenazine	N	N	−0.205	−1957	−4.73	6.97
5,10-Dimethyl-5,10-dihydrophenazine	N−Me	N−Me	0.434	−60	10.0	46.7
N-Methylphenoxazine	N−Me	O	0.497	517	11.5	59.6
N-Methylphenothiazine	N−Me	S	0.530	520	12.2	59.5
Phenoxazine	N−H	O	0.627	429	14.5	56.7
Phenothiazine	N−H	S	0.626	412	14.4	56.4
N-Methylphenoxazine	O	N−Me	0.497	517	11.5	59.6
Phenoxazine	O	N−H	0.627	429	14.5	56.7
Dibenzodioxin	O	O	0.711	1191	16.4	73.8
Phenoxathiine	O	S	0.824	963	19.0	67.8
Phenoxaselenin	O	Se	1.046	926	24.1	65.6
N-Methylphenothiazine	S	N−Me	0.530	520	12.2	59.5
Phenothiazine	S	N−H	0.626	412	14.4	56.4
Phenoxathiine	S	O	0.824	963	19.0	67.8
Thianthrene	S	S	1.098	1021	25.3	67.4

[a] Data obtained in experiments similar to those described in Table 1. Negative values refer to reductions and positive to oxidations. [b] Reversible potential at 273.2 K *vs.* $\mathrm{Ag/Ag^+}$ ($\mathrm{CH_3CN}$). [c] In cal/K mol. The conversion unit for mV/K to cal/K mol is 23.06. [d] The enthalpy change relative to that for the reduction of anthracene in kcal/mol. [e] Data from Ref. 1.

273.2 K are gathered in Table 2. The pertinent data for the reduction of anthracene from Ref. 1 are included for comparison. The $\Delta\Delta H$ values are relative to that for the reduction of anthracene. The compounds are grouped according to structural similarities and some of the compounds fit in more than one series. The two compounds in the first group, phenazine and anthracene, differ from the others in that the central rings are aromatic and their reactions are the only reduction processes. The other groups have X constant while the structural feature Y is varied.

To begin with we will summarize the trends observed in ΔS and leave $\Delta\Delta H$ for later. The first two compounds are planar and the anion radicals formed upon reduction are also planar with only small structural changes expected to take place upon charge transfer. The entropy values are very similar and small in comparison to all of the others in the table. However, we recall that these values are high on the scale observed for the AAH (Table 1).[1] Following the reasoning developed earlier[1] we suggest that the charge distributions in the two anion radicals are similar with some concentration of charge in the 9,10-positions of anthracene and the corresponding 5,10-positions of phenazine. The small difference in entropy changes could reflect the fact that N is more electronegative than C.

When X is N−Me, the entropy changes during oxidation increased in going from Y = N−Me to O to S. The largest difference is the first one. In order for charge to be dispersed into the two carbon containing rings, onium structures *2* and planar



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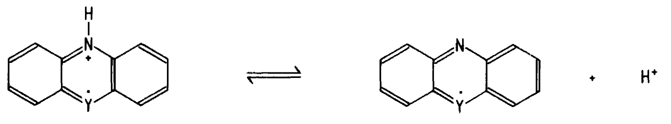
resonance forms must be favorable. The most favorable situation for bond lengths and angles in this ring system is for the parent, anthracene and the corresponding cation radical. Since $\mathrm{N^+}$ is isoelectronic with C, the smallest perturbation in geometry in structures *1* and *2*, relative to



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anthracene is when $X = Y = N - R$. This is also evident from the comparison in the previous paragraph. Thus, it appears that the entropy changes in this series can be explained by the decreasing contribution of the onium structure *2* to the overall cation radical structure as $N - Me$ is replaced by O and then S. The covalent radii of C, O, S and Se are 0.77, 0.74, 1.04 and 1.17 Å, respectively.[25] As the groups, Y, become larger achieving structure *2* becomes more difficult.

The reasoning carried through in the previous paragraph appears not to be valid for the next two compounds where $X = N - H$ and Y is either O or S. In this case the entropy changes are greater and identical within experimental error. In this case some caution must be exercized in interpreting the results in terms of structure *2*. Equilibrium (4) could contribute significantly to the overall result. The existence of cation radicals *3*, $Y = S$ [26,27] or O,[28] in acidic media was demonstrated by ESR spectroscopy. However, *3* rapidly decays in neutral media and the radical *4*, $Y = S$, has been identified by ESR measurements.[29] The occurrence of reaction (4) and the structural changes in cation radical *3* due to the weakening of the $N - H$ bond could contribute significantly to the increase in the observed entropy change. The extent to which equilibrium (4) depends on the nature of Y is not known. However, we did not observe any difference in ΔS for the oxidation of phenothiazine when the potentials were measured in acetonitrile containing trifluoroacetic acid (5 %). This suggests either that equilibrium (4) does not significantly affect the results or that the acid is not sufficiently dissociated to participate in (4).

Large changes in ΔS are observed in going down the series where $X = O$. When $Y = O$ as well, ΔS was observed to be 16.4 which is significantly greater than the case where $X = Y = N - Me$ where ΔS was found to be 10.0 cal/K mol. We can use the same reasoning as before in terms of the changing contributions of structure *2* as X and Y are changed. Further large changes in ΔS were observed in going to $Y = S$ and Se.

Large changes in ΔS are also observed when $X = S$ and the same arguments can be applied. In this series, the only compound not appearing in previous series is $X = Y = S$, thianthrene, the oxidation of which gave the largest entropy change observed in this study, 25.3 cal/K mol.

We can now return to the questions raised earlier regarding the effect of entropy changes on correlations of E^{rev} with gas phase and molecular orbital parameters. The quantity expected to relate to these parameters is ΔH rather than E^{rev}. In the case of correlations involving AAH, the effect of entropy changes was observed to be relatively small. However, the entropy changes observed for the reactions of compounds of structure *1* are very much greater than those for AAH redox reactions. In Fig. 2, $\Delta\Delta H$ is plotted *vs.* E^{rev} for all the processes described in Table 2. Both quantities are expressed in kcal/mol relative to the values for the reduction of anthracene. The slope of the correlation line was observed to be 0.907 with a correlation coefficient of 0.999. In this case it is clear that correlations of E^{rev} with any set of parameters linearly related to ΔH

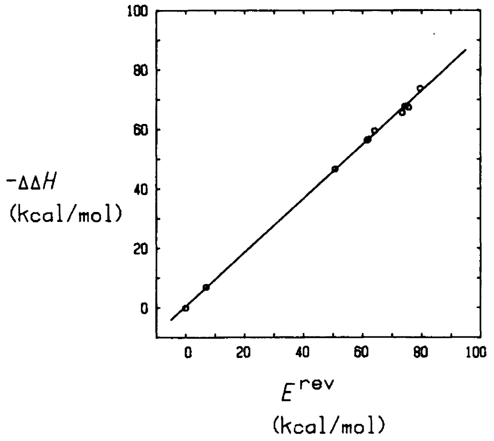

Fig. 2. Correlation of reversible potentials with enthalpy changes for redox reactions of heteroaromatic compounds.

will also appear to be linear. It is also apparent that the resulting slopes will be significantly in error if E^{rev} is assumed to reflect the value of ΔH.

In conclusion, this study has provided further evidence that the factor of overweighing importance in determining the entropy changes in reversible electrode processes is connected with the localization of charge and the accompanying changes in the ordering of the environment around the ions and the neutral molecules.

EXPERIMENTAL

The experimental procedures and data handling operations were described in detail in the first paper in this series.[1] Most of the compounds used in this study were generously provided in highly pure state by Dr. Ole Hammerich, University of Copenhagen.

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