Acta Chemica Scandinavica B 38 (1984) 751−757

Temperature Effects on Electrode Processes. V. Effects of Changing the Ionic Environment on the Entropy of Formation of Ion Radicals in Acetonitrile

MORTEN SVAAN and VERNON D. PARKER

Laboratory for Organic Chemistry, Norwegian Institute of Technology, University of Trondheim,
N-7034 Trondheim-NTH, Norway

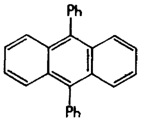
The temperature dependence of reversible electrode potentials for the formation of ion radicals from 9,10-diphenylanthracene (9,10-DPA), perylene, and triphenylene were determined in the presence of six different tetraalkylammonium salts. The reversible potentials for the formation of the ion radicals at 273.2 K were observed to be very nearly independent of the nature of the electrolyte. The entropies of formation of the ion radicals were found to depend both on the nature and the concentration of the electrolyte in acetonitrile. The most detailed studies were carried out on 9,10-DPA oxidation and reduction. At $[R_4N^+BF_4^-]$ equal to 0.033 M the entropies of formation of the cation and anion radicals were very nearly equal and the same measured in the presence of Bu_4N^+ and Et_4N^+. Upon increasing the electrolyte concentration $-\Delta S_{273.2}$ was observed to increase for the formation of the cation and decrease for the formation of the anion radical in the presence of both R_4N^+. Similar effects were observed during the redox reactions of 9-phenylanthracene. Ion pair formation was observed to be negligible during the formation of the ions of 9-phenyl- and 9,10-diphenylanthracene.

The effect of substrate structure on the entropy of formation of ion radicals in acetonitrile has been reported.[1-4] The entropy changes were calculated from the temperature coefficients (dE^{rev}/dT) of the reversible electrode potentials measured by phase selective second harmonic a.c. voltammetry using relationship (1). The processes which have been studied include (i) the oxidation and reduction of alternant aromatic hydrocarbons,[1] (ii) the oxidation of heteroaromatic compounds,[2] (iii) the reduction of nitrobenzenes,[3] and (iv) the reduction of aromatic ketones related to benzophenone.[4] All of the studies were carried out in acetonitrile in the presence of $Bu_4N^+BF_4^-$ (0.10 M). In these studies values of $-\Delta S_{273.2}$ ranging from 0.87 to 25.3 cal/K mol were found.[1-4] It was concluded that the predominant factor responsible for the relative magnitudes of the entropy changes is the loss in entropy of the solvent during solvation of the ion radicals.

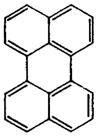
$$\Delta S = F(dE^{rev}/dT) \tag{1}$$

What the previous studies[1-4] did not address in any manner was the effect of changes in the medium on the entropies of formation of the ion radicals. It might be anticipated that changes in both the supporting electrolyte and the solvent might have profound effects upon the entropies of formation of the ion radicals.

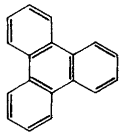
In this paper we report the results of our studies on the effect of tetraalkylammonium salts on the entropies of formation of ion radicals of some alternant aromatic hydrocarbons. The three substrates, 9,10-diphenylanthracene (*1*), perylene (*2*) and triphenylene (*3*) were chosen for



1



2



3

0302-4369/84 $2.50
© 1984 Acta Chemica Scandinavica

the following reasons. Formation of both the anion and cation radical of 9,10-DPA can be studied in acetonitrile. The entropy of formation of triphenylene anion radical is the smallest (−0.87 cal/K mol) value that we are aware of while that for perylene is intermediate between the smallest and largest reported[1] for the anion radicals of alternant aromatic compounds. (By small or large we mean the numerical value of the entropy of formation which is expected to be negative for the formation of both anion and cation radicals. We have previously[1,2] incorrectly used positive signs for the entropies of formation of cation radicals.) Perylene and triphenylene anion radicals have planar structures and thus solvation energies will not reflect steric factors as might be expected for those of the ion radicals of 9,10-DPA[1] and for the other aromatic substrates that have been studied.[2-4] The other variables that we have made use of are the nature and the concentration of supporting electrolytes.

RESULTS AND DISCUSSION

When a change is made in either the nature or the concentration of the supporting electrolyte the measurement of a reversible electrode potential cannot be expected to give results identical to those obtained before the change was made. This is because the liquid junction potential between the reference electrode and the solution in which the measurement is being made will change.[5] In our previous work we have minimized the effect of liquid junction potentials by using the same solvent (acetonitrile) containing the same electrolyte ($[Bu_4NBF_4]=0.10$ M). In order to continue this practice for the work described here it would have been necessary to prepare a new reference electrode each time the conditions were changed. This was deemed to be impractical and we have used the same reference electrode as was used in the previous work.[1-4]

In this study, we have used six different tetraalkylammonium salts as supporting electrolytes. The data in Table 1 are reversible reduction potentials for the three substrates measured in the presence of all or some of the electrolytes. The data in the second column are the mean values and standard deviations for the reversible potentials measured in the presence of all six salts in acetonitrile. The standard deviations are in all cases close to 20 mV. The third column gives the same values with the data for the solutions containing Bu_4NBF_4 excluded. In this case the standard deviations are only of the order of 8 mV. The reason for this is that the Bu_4NBF_4 data are those that have been reported previously[1] based on work that was carried out about three years ago and we found that during this time there has been a drift in the potential of the reference electrode.

The data in Table 1 indicate that there is no serious problem with the change in liquid junction potential with the changing of the nature of the tetraalkylammonium ion in acetonitrile. However, it is convenient to use an internal reference potential to avoid the complication. We elected to use the reversible potential for the reduction of triphenylene measured under the same conditions as that standard. Data for all the electrolytes referred to that potential are collected in the last column on Table 1. The standard deviations observed were 8 and 6 mV for the reduction of 9,10-DPA and perylene, respectively.

The data in Tables 2 and 3 show the effect of the nature of the supporting electrolyte on the entropies of formation of the anion radicals as well as the reversible potentials. Both of the

Table 1. Reversible electrode potentials for the reduction of some alternant aromatic hydrocarbons in acetonitrile.[a]

Substrate	$-E^{rev}_{273.2}$[b]	$-E^{rev}_{273.2}$[c]	$E^{rev}_{273.2}$[d]
9,10-DPA	2.210(17)	2.216(8)	0.577(8)
Perylene	2.011(21)	2.019(7)	0.775(6)
Triphenylene	2.786(19)	2.794(8)	0.000

[a] All measurements by phase selective second harmonic *a.c.* voltammetry as described in Ref. 1. [b] In the presence of all six electrolytes (0.10 M) used in Tables 2 and 3. [c] The same as in *b* omitting the data for Bu_4NBF_4. [d] The same as in *b* referred to the reversible potential for the reduction of triphenylene.

Table 2. The effect of tetraalkylammonium fluoroborate salts on the entropy of formation of alternant aromatic hydrocarbon anion radicals in acetonitrile.[a]

Electrolyte	$-\Delta S_{273.2}$[b]	$-E^{\text{rev}}_{272.2}$/mV
9,10-DPA as substrate		
Bu_4NBF_4	3.67	0.571
Pr_4NBF_4	3.52	0.575
Et_4NBF_4	3.44	0.571
Perylene as substrate		
Bu_4NBF_4	1.46	0.779
Pr_4NBF_4	1.47	0.778
Et_4NBF_4	1.80	0.770
Triphenylene as substrate		
Bu_4NBF_4	0.00 (0.87)[c]	0.000 (2.750)[c]
Pr_4NBF_4	0.00 (2.31)[c]	0.000 (2.797)[c]
Et_4NBF_4	0.00 (2.74)[c]	0.000 (2.800)[c]

[a] Measurements according to the procedure described in Ref. 1. The supporting electrolyte concentration was 0.10 M in all cases. [b] In cal/K mol and is equal to $(dE/dT)F$ in appropriate units where E^{rev} is relative to the reduction of triphenylene under the same conditions. [c] The values in parentheses are those obtained in the experiments.

Table 3. The effect of tetraalkylammonium iodide salts on the entropy of formation of alternant aromatic hydrocarbon anion radicals in acetonitrile.[a]

Electrolyte	$-\Delta S_{273.2}$[a]	$-E^{\text{rev}}_{272.2}$/mV
9,10-DPA as substrate		
Bu_4NI	4.46	0.587
Bu_3NMeI	3.56	0.569
Bu_2NMe_2I	4.43	0.586
Perylene as substrate		
Bu_4NI	1.49	0.782
Bu_3NMeI	1.95	0.765
Bu_2NMe_2I	2.19	0.778
Triphenylene as substrate		
Bu_4NI	0.00 (1.14)[b]	0.000 (2.793)[b]
Bu_3NMeI	0.00 (1.44)[b]	0.000 (2.780)[b]
Bu_2NMe_2I	0.00 (1.59)[b]	0.000 (2.798)[b]

[a] As in Table 2. [b] The numbers in parentheses are the experimental values, all others are referred to the value obtained during the reduction of triphenylene under the same conditions.

quantities are referred to the reduction of triphenylene under the particular set of reaction conditions. This not only eliminates from consideration the effect of the liquid junction potentials for the various solutions but also the temperature coefficients of the latter. The most significant feature of the data is that the entropies of formation of the anion radicals of 9,10-DPA and perylene are very nearly independent of the nature of the supporting electrolyte cation but appear to be slightly larger when the counter ion is iodide instead of BF_4^-. Also, there does appear to be a small increase in the value of $-\Delta S_{273.2}$ for the formation of perylene anion radical as the tetraalkylammonium ion becomes smaller. The ionic radii of Et_4N^+, Pr_4N^+ and Bu_4N^+ have been estimated to be equal to 2.79, 3.36 and 3.83 Å, respectively.[6] It has been shown that the degree of ion pairing of dianions derived from aromatic hydrocarbons with tetraalkylammonium ions increases with decreasing ionic radii of R_4N^+.[7] This is expected to be a more or less general phenomenon and has been amply demonstrated for the pairing of aromatic hydrocarbon anions with alkali metal ions in less polar solvents.[8] Thus, a possible interpretation of the increase in $-\Delta S_{273.2}$ for the formation of perylene anion radical as the tetraalkylammonium ion gets smaller is that ion-pairing accompanies ion radical formation. This then requires that ion-pairing increases as the R_4N^+ becomes smaller and that the entropy of formation is more negative when ion-pairing is more pronounced. This interpretation requires that the degree of ion-pairing to the anion radical of 9,10-DPA is less dependent upon the nature of R_4N^+.

The same trends in the data are observed when the unsymmetrical tetraalkylammonium salts are the supporting electrolyte (Table 3). In these cases the ionic radii are not known but it can be inferred from the results of a heterogeneous charge transfer kinetic study[9] that the ionic radii decrease as butyl groups of Bu_4N^+ are successively replaced by methyl.

The data in Table 4 show the effect of $[R_4NBF_4]$ on the entropy of formation of both the cation and anion radicals of 9,10-DPA. The corresponding data for the reduction of triphenylene are also included. The values of $-\Delta S_{273.2}$ were very nearly independent of

Table 4. The effect of the nature and concentration of the electrolyte on the entropies of formation of the cation and anion radicals of 9,10-diphenylanthracene in acetonitrile.[a]

Electrolyte	Process[b]	$-\Delta S_{273.2}$[a] at electrolyte concentration 0.033 M	0.066 M	0.100 M	0.133 M
Bu_4NBF_4	TR Reduction[d]	1.82	1.50	0.87	0.56
Bu_4NBF_4	Oxidation	6.57	7.82	8.67[e]	9.02
Et_4NBF_4	Oxidation	6.46	8.00	8.53	8.60
Bu_4NBF_4	Reduction	6.48	5.84	4.54	4.34
Et_4NBF_4	Reduction	6.64	6.18	4.54	4.29
$-\Delta S$ (sum)[c]	Bu_4NBF_4	13.1	13.7	13.2	13.4
$-\Delta S$ (sum)[c]	Et_4NBF_4	13.1	14.2	13.1	12.9

[a] As in Table 2. [b] Oxidation is for cation radical formation and reduction for the formation of the anion radical. [c] Refers to the sum of the entropies of formation of the cation and anion radicals measured under the same conditions. [d] Values obtained for the reduction of triphenylene. [e] This value is greater than originally reported.[1]

Table 5. The effect of the nature and the concentration of the electrolyte on the entropies of formation of the cation and anion radicals of 9-phenylanthracene in acetonitrile.[a]

Electrolyte	Process[b]	$-\Delta S_{273.2}$[a] at electrolyte concentration 0.033 M	0.066 M	0.100 M	0.133 M
Bu_4NBF_4	Oxidation	8.60	10.4	12.1	12.5
Et_4NBF_4	Oxidation	8.56	9.32	9.80	10.3
Bu_4NBF_4	Reduction	6.43	5.63	4.43	4.29
Et_4NBF_4	Reduction	6.92	5.51	4.61	4.38
$-\Delta S$ (sum)[c]	Bu_4NBF_4	15.0	16.1	16.5	16.7
$-\Delta S$ (sum)[c]	Et_4NBF_4	15.5	14.8	14.4	14.6

[a] As in Table 2. [b] Oxidation is for cation radical formation and reduction for the formation of the anion radical. [c] Refers to the sum of the entropies of formation of the cation and anion radicals under the same conditions.

whether R_4N^+ was Bu_4N^+ or Et_4N^+. At low $[R_4N^+]$ the entropy of formation for the anion radical and the cation radical were identical within experimental error. At the electrolyte concentration was increased, that for the cation became more negative and that for the anion less negative. The overall result is that the sum of the entropies of formation of the cation and anion radicals of 9,10-DPA in acetonitrile are a constant independent of the electrolyte concentration. The mean of the eight values of $-\Delta S$(sum) was observed to be equal to 13.3 cal/K mol with a standard deviation of ±0.4.

In order to determine whether or not the remarkable results for the redox reactions of 9,10-DPA, described above, are a coincidence it was necessary to carry out a similar set of experiments with a different substrate. Unfortunately, the only other substrate that we have found that we can make measurements on both the formation of the anion and the cation radical is 9-phenylanthracene (PA). It has not been possible to study the formation of the other alternant aromatic hydrocarbon cation radicals due to experimental difficulties such as product adsorption on the electrode.[1] The entropies of formation are summarized in Table 5. When the electrolyte was either Bu_4NBF_4 or Et_4NBF_4, any trends in $-\Delta S$ (sum) were small. The observed values were 16.1±0.8 and 14.8±0.5 cal/K mol when the electrolyte was Bu_4NBF_4 or Et_4NBF_4, respectively.

If the ion radicals are involved in association reactions with the electrolyte counter ions, the reversible potential for oxidation, E^{rev}(ox), is expected to shift to less positive values as a consequence of reaction (2) while the reversible reduction potentials, E^{rev}(red), will shift to less negative values as the supporting electrolyte concentration is increased as a consequence of reaction (3). Since reaction (2) would be expected to be of less importance than reaction (3),

$$\text{cation radical} + BF_4^- \rightleftarrows \text{ion-pair} \quad (2)$$

$$\text{anion radical} + R_4N^+ \rightleftarrows \text{ion-pair} \quad (3)$$

the largest effect is expected to be found in E^{rev} (red). The data in Table 6 are for measurements on the oxidation and reduction of PA in acetonitrile at 273.2 K. With both electrolytes E^{rev} (ox) was observed to shift to more positive values as $[R_4NBF_4]$ was increased. This is in the oppositive direction expected to result from reaction (2) and leads to the conclusion that the shift is due to changes in the liquid junction potential. Thus, the changes that are observed in E^{rev} (red) cannot be related to the effect of reaction (3). The last column in Table 6 gives the numerical sum of E^{rev} (ox) and $-E^{rev}$ (red). Although there is some deviation in the values, there are no clear trends with increasing $[R_4NBF_4]$. On this basis, we conclude that the ion-pairing equilibria (2) and (3) have a negligible effect on the observed entropies of formation of both the cation radicals and the anion radicals.

We have been unable to arrive at a satisfactory explanation of the constant values of $-\Delta S$ (sum) (Tables 4 and 5) based on the expected changes in solvation of the anion and cation radicals as the

Table 6. Reversible potentials for the formation of the cation and anion radicals of 9-phenylanthracene in acetonitrile.[a]

Electrolyte	$E^{rev}(ox)^b$	$-E^{rev}(red)^b$	$E^{rev}(sum)^c$
Bu_4NBF_4(0.033 M)	0.986	2.302	3.288
Bu_4NBF_4(0.067 M)	0.990	2.291	3.281
Bu_4NBF_4(0.100 M)	1.005	2.284	3.289
Bu_4NBF_4(0.133 M)	1.006	2.279	3.285
Et_4NBF_4(0.033 M)	0.983	2.304	3.287
Et_4NBF_4(0.067 M)	0.988	2.291	3.279
Et_4NBF_4(0.100 M)	0.990	2.284	3.274
Et_4NBF_4(0.133 M)	0.997	2.280	3.277
			mean 3.283(0.006)

[a] For measurements at 273.2 K. [b] The reversible potentials for oxidation (ox) and reduction (red). [c] $E^{rev}(sum)=E^{rev}(ox)+(-E^{rev}(red))$.

electrolyte concentration changes. Little is known about the detailed structure of aprotic solvents[10] and much less on the effect of tetraalkylammonium salts on this structure. Thus, a microscopic explanation of this phenomenon must wait for advances in the general knowledge of the structure and properties of aprotic solvents. On the other hand, a macroscopic description may be of use. Since we conclude that the sum of the reversible potentials is affected negligibly by the supporting electrolyte concentration and if we assume that ΔH for the redox reactions does not change with the electrolyte concentration, $\Delta\Delta G$ (the change in ΔG brought about by the concentration change) is related to ΔS by eqn. (4). Thus as

$$\Delta\Delta G = T\Delta\Delta S \tag{4}$$

$$\mathrm{A} \rightleftarrows \mathrm{A}^{\cdot +} + \mathrm{e}^{-} \tag{5}$$

$$\mathrm{A} + \mathrm{e}^{-} \rightleftarrows \mathrm{A}^{\cdot -} \tag{6}$$

$[\mathrm{R_4NBF_4}]$ is increased ΔG for reaction (5) becomes more positive while that for reaction (6) becomes less positive (A is either 9,10-DPA or PA) when the reactions are carried out in acetonitrile. Thus, increasing $[\mathrm{R_4NBF_4}]$ in acetonitrile brings about a change in the solvent-electrolyte structure which makes formation of the cation radicals more difficult and the formation of the anion radicals more favorable. The magnitude of the effects are very nearly equal.

An alternative explanation of the changes in $-\Delta S_{273.2}$ with electrolyte concentration is that it is an artefact brought about by changes in liquid junction potentials and the corresponding temperature coefficients. This explanation requires that the effect be independent of the nature of the substrate. This was not observed to be the case. The changes in $-\Delta S_{273.2}$ during reduction of TR, 9,10-DPA and PA as $[\mathrm{Bu_4NBF_4}]$ was changed from 0.033 to 0.133 M were 1.26, 2.14 and 2.05 cal/K mol, respectively. On the other hand, the relative values of $-\Delta S_{273.2}$ for TR, 9,10-DPA and PA at the extremes of $[\mathrm{Bu_4NBF_4}]$ for the same processes were 3.25, 1.49 and 1.50, respectively. This suggests that the relative values depend upon the magnitude of $-\Delta S_{273.2}$ and increase as the latter decreases. This is the trend expected if the effect is due to liquid junction potentials and the corresponding temperature coefficients.

We conclude that neither the explanations put forth in the previous paragraphs can account for the observed changes in the apparent values of $-\Delta S_{273.2}$. However, it appears that changes in the liquid junction potential may account for a large proportion of the observed changes. The problem is circumvented by considering $-\Delta S_{273.2}$ relative to that observed in the reduction of TR. The data expressed in this manner are gathered in Table 7. The most noteworthy feature of these data is that $-\Delta S_{273.2}$ is dependent upon $[\mathrm{Bu_4NBF_4}]$ but far less markedly than when the observed values are considered directly.

Our overall conclusion is that changes in the supporting electrolyte and the salt concentration can have significant effects on the entropies of formation of anion and cation radicals generated in polar aprotic solvents. Detailed explanations for these effects are not possible at this time. Because of the existance of such effects, the effect of substrate structural changes must be analyzed in the absence of any changes in the medium in which the ion radicals are generated.

Table 7. The effect of electrolyte concentration on the relative entropies of formation of the cation and anion radicals of 9,10-diphenylanthracene and 9-phenylanthracene in acetonitrile.[a]

	$-\Delta S_{273.2}$[a] at electrolyte concentration			
Process	0.033 M	0.066 M	0.100 M	0.133 M
9,10-DPA reduction	4.66	4.34	3.67	3.78
9,10-DPA oxidation	8.38	9.32	9.54	9.58
PA reduction	4.61	4.13	3.56	3.73
PA oxidation	10.4	11.9	13.0	13.1

[a] For measurements in the presence of $\mathrm{Bu_4NBF_4}$ referred to the corresponding values for the reduction of triphenylene.

Since most of the available data[1-4] are for reactions in acetonitrile-Bu_4NBF_4(0.10 M), this is an appropriate standard system for new studies.

EXPERIMENTAL

All experimental procedures and data handling were described earlier.[1]

Acknowledgement. We thank Dr. Robert Eliason for many helpful discussions during the preparation of the manuscript.

REFERENCES

1. Svaan, M. and Parker, V. D. *Acta Chem. Scand. B 35* (1981) 559.
2. Svaan, M. and Parker, V. D. *Acta Chem. Scand. B 36* (1982) 351.
3. Svaan, M. and Parker, V. D. *Acta Chem. Scand. B 36* (1982) 357.
4. Svaan, M. and Parker, V. D. *Acta Chem. Scand. B 36* (1982) 365.
5. Butler, J. N. In Delahay, P., Ed., *Advances in Electrochemistry and Electrochemical Engineering,* Wiley-Interscience, New York 1970, Vol. 7, Chapter 2.
6. Coetzee, J. F. and Cunningham, G. P. *J. Am. Chem. Soc. 87* (1965) 2529.
7. Jensen, B. S. and Parker, V. D. *J. Am. Chem. Soc. 97* (1975) 5619.
8. Szwarc, M. *Carbanions, Living Polymers and Electron Transfer Processes,* Interscience, New York 1968.
9. Ahlberg, E. and Parker, V. D. *Acta Chem. Scand. B 37* (1983) 723.
10. Reichardt, C. *Solvent Effects in Organic Chemistry,* Verlag Chemie, Weinheim/Bergstr. 1979, Chapter 2.

Received January 4, 1984.