

Temperature Effects on Electrode Processes. VI. Solvent Effects on the Entropies and Reversible Potentials for the Formation of Ion Radicals of Organic Compounds

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The entropies of formation of anion and cation radicals of organic compounds were determined from the temperature coefficients of the reversible potentials for reduction and oxidation, respectively, in a number of aprotic solvents. The reversible potentials measured at 273.2 K were independent of the solvent, to within about ± 50 mV, while substantial differences were observed in the entropies. The change in the entropy of formation of an ion radical with solvent was observed to depend strongly on the structure of the substrate. It was concluded that there is a steric factor, originating in the relative accessibility of the appropriate end of the solvent dipole to interaction with the ion radical, involved in addition to those factors specific to the reorganization of the solvent. The results are compared to literature values for spherical inorganic ions in which the steric effect is either absent or of much less importance. The sum of the entropies of formation of the anion and cation radicals of 9,10-diphenylanthracene was observed to be independent of the solvent although large variations were observed in the individual values.

In our previous studies of the entropies of formation of ion radicals of aromatic compounds we have restricted the measurements to acetonitrile solutions.¹⁻⁵ We have recently shown that both the nature of the supporting electrolyte and the salt concentration have significant effects upon the entropies of formation of the ion radicals.⁵ In this paper we examine the effect of changes in the aprotic solvent on the entropies of formation of a variety of anion and cation

radicals which have previously been studied in acetonitrile.

A great deal of work has been carried out on thermodynamic measurements on solutions of inorganic ions in aprotic solvents.⁶ The partial molal entropy, S_{ion}° is identical to the entropy of solvation, $\Delta S_{\text{solv}}^{\circ}$, and this is comprised of three terms (1);⁶

$$\Delta S_{\text{solv}}^{\circ} = \Delta S_{\text{D}}^{\circ} + \Delta S_{\text{O}}^{\circ} + \Delta S_{\text{F}}^{\circ} \quad (1)$$

where $\Delta S_{\text{D}}^{\circ}$ is an entropy increase caused by the disordering of the solvent, $\Delta S_{\text{O}}^{\circ}$ is an entropy decrease resulting from the ordering of the solvent molecules around the ions, and $\Delta S_{\text{F}}^{\circ}$ is an entropy decrease caused by the loss of the degrees of freedom of the gaseous ions. In making comparisons of the entropies of formation for particular ions in various solvent environments the last term in (1) does not change and we are then concerned with the changes in the other terms as in eqn. (2).

$$\Delta \Delta S_{\text{solv}}^{\circ} = \Delta \Delta S_{\text{D}}^{\circ} + \Delta \Delta S_{\text{O}}^{\circ} \quad (2)$$

The entropy of orientation of the solvent molecules about an ion will depend upon the extent and the number of molecules that are involved and will always be a negative quantity.⁶ It has been argued⁶ that the entropy of orientation of solvent molecules around an ion can be expected to be approximately constant for solvents with not too widely differing dipole moments. The basis for this proposal is that a solvent having a

high dipole moment exhibits strong ion-solvent interactions in the first solvation sphere, but relatively weak interactions further out in solution, while solvents with low dipole moments exhibit weaker interactions in the first solvation sphere, but that the electrical field due to the ion will be felt at greater distances. These two effects might be expected to be manifested in a leveling effect. If this is the case, eqn. (2) reduces to (3)

$$\Delta\Delta S_{\text{soliv}}^{\circ} = \Delta\Delta S_{\text{D}}^{\circ} \quad (3)$$

since the last term is a constant. This then implies that the most important factor in determining the relative entropies of formation in a number of solvents will be the relative extent to which ions disorder the various solvents.

We considered the proposals outlined above in relation to the results that we have previously presented.¹⁻⁵ There should be a corollary between the high-low dipole moment leveling effect and a steric effect toward solvation. For example, an ion which is sterically unhindered toward solvation might be expected to interact more strongly in the first solvation sphere, but to exhibit the effect of its electric field beyond the first solvation layer to a lesser extent than an ion which does not allow the dipoles of the solvent molecules to interact as strongly because of steric hindrance to solvation. This would appear to be equivalent to changing the degree of interaction

with a given ion by changing the dipole moment of the solvent molecules. However, we have observed substantial steric effects on the values of the entropies of formation of ions of two different series of compounds, nitrobenzenes³ and aromatic ketones related to benzophenone.⁴ In both cases the anion radicals of the compounds within the series are very closely structurally related differing only in substitution patterns on the phenyl rings. In these cases it is clear that there is not a leveling effect as expected from the discussion above.

It was the purpose of this investigation to determine the effect of changes in the aprotic solvent on the entropies of formation of a variety of ion radicals of aromatic compounds.

RESULTS AND DISCUSSION

The first series of measurements were made on the reduction of the alternant aromatic hydrocarbons; 9,10-diphenylanthracene (9,10-DPA), anthracene, perylene and triphenylene. Entropies of formation and reversible electrode potentials for these compounds in four different solvents, acetonitrile (MeCN), *N,N*-dimethylformamide (DMF), propylene carbonate (PC) and pyridine (PYR), are listed in Table 1. It was not possible to make measurements on triphenylene in PYR because the very negative potentials

Table 1. The entropies and electrode potentials for the formation of anion radicals of alternant aromatic hydrocarbons in aprotic solvents.^a

Substrate	MeCN ^b (37.45) ^b	$-\Delta S_{273,2}/(\text{cal/K mol})$ $-E_{273,2}^{\text{rev}}/V$ vs. Ag/Ag ⁺			PYR ^e (13.24)	Mean ^f
		DMF ^c (38.93)	PC ^d (64.4)			
9,10-DPA	4.54 2.179	6.78 2.106	7.15 2.090	9.73 2.118	2.123(0.039)	
Anthracene	4.54 2.257	5.44 2.316	6.53 2.284	8.07 2.286	2.286(0.024)	
Perylene	2.33 1.971	3.48 1.918	5.28 2.010	7.59 1.889	1.947(0.054)	
Triphenylene	0.87 2.750	0.00 2.739	-0.84 2.792		2.760(0.028)	

^a All measurements were by phase selective second harmonic *a.c.* voltammetry at a mercury or gold electrode in solvent containing Bu₄NBF₄ (0.10 M). ^b Acetonitrile. ^c *N,N*-dimethylformamide. ^d Propylene carbonate. ^e Pyridine. ^f The mean and standard deviation in $-E_{273,2}^{\text{rev}}$ in all the solvents.

required are outside of the available range in that solvent. The magnitudes of the entropies do not appear to be simply related to any physical or chemical property of the aprotic solvents. The numbers in parentheses at the head of each solvent column are the values of the solvent dielectric constants which do not appear to bear any relationship with the entropies. The data are arranged according to increasing values of $-\Delta S_{273.2}$ for 9,10-DPA. This arrangement was arbitrary but it is a means of analyzing for relative trends in the data. The same trend in the data with changes in the solvent were found for the reduction of anthracene and perylene. On the other hand, $-\Delta S_{273.2}$ for triphenylene was observed to vary in the opposite sense as the solvent was changed from MeCN to DMF to PC. It is also significant to note that a small positive value of the apparent entropy of formation was found when the solvent was PC.

It should be pointed out that the same reference electrode that has been used in all of the previous studies in acetonitrile¹⁻⁵ was used in this work. This electrode consists of Ag/Ag⁺ (2.0 mM) in MeCN-Bu₄NBF₄ (0.10 M). In the previous paper in which the effect of changes in the supporting electrolyte was studied, it was proposed that liquid junction potentials between the solutions and the reference electrode could account for some of the apparent variations in the observed entropies.⁵ It was suggested that this

complication could be avoided by expressing all electrode potentials vs. the reversible electrode potential for the reduction of triphenylene under the particular set of conditions. The reason for suggesting this reaction as standard was that $-\Delta S_{273.2}$ had been observed to be equal to only 0.87 cal/K mol in MeCN-Bu₄NBF₄ (0.10 M) which is by far the smallest numerical value observed for any of the processes that have been studied.

With the possible problem of liquid junction potentials in mind, the trend in the data and even the apparent positive entropy of formation is understandable. We do not believe that $\Delta S_{273.2}$ is positive in this case and attribute the observation as an artefact arising from the temperature coefficient of the liquid junction potential between the reference electrode and PC-Bu₄NBF₄ (0.10 M). Here again, it would be possible to avoid the complications due to the liquid junction potential by using the reduction of triphenylene as the reference process. In Table 1 and those that follow we have not done this since we were unable to make measurements in two of the solvents used, PYR and CH₂Cl₂. However, conversion to that scale is readily made for MeCN and PC and not necessary for DMF since the observed value of $\Delta S_{273.2}$ was 0.

The data in Table 2 obtained for the reduction of benzophenones and related compounds even more clearly show that there is no property of the

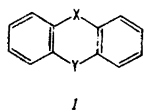
Table 2. The entropies and electrode potentials for the formation of anion radicals of aromatic ketones in aprotic solvents.^a

Substrate	$-\Delta S_{273.2}/(\text{cal/K mol})$ $-E_{273.2}^{\text{rev}}/V$ vs. Ag/Ag ⁺		PC ^a	PYR ^a	Mean ^a
	MeCN ^a	DMF ^a			
2,2'-Dimethylbenzophenone	14.4	11.8	9.27	12.9	2.164(0.019)
	2.149	2.192	2.160	2.156	
Benzophenone	12.8	10.5	11.8	16.3	1.983(0.012)
	1.967	1.980	1.990	1.993	
4,4'-Dimethylbenzophenone	10.8	11.0	8.65	11.9	2.115(0.040)
	2.066	2.157	2.100	2.137	
Fluoren-9-one	9.82	10.3	10.2	13.0	1.569(0.067)
	1.661	1.561	1.554	1.499	
1,4-Dibenzoylbenzene	8.69	9.32	9.62	12.0	1.579(0.056)
	1.661	1.569	1.541	1.545	

^a As in Table 1.

solvents that can be directly related to the entropies. For the solvent series, MeCN-DMF-PC, $\Delta S_{273.2}$ was observed to be nearly independent of solvent for fluoren-9-one, to decrease along the series for 2,2'-dimethylbenzophenone, to increase along the series for 1,4-dibenzoylbenzene and vary randomly for the benzophenone and 4,4'-dimethylbenzophenone. None of this behaviour is predictable from the results obtained on the alternant aromatic compounds in Table 1.

Similar comments could be made concerning the data obtained for the reduction of nitrobenzenes summarized in Table 3. In this case the variations are somewhat greater in some cases, in particular for the reduction of 2,4,6-triethylnitrobenzene. In all cases where data are available in Tables 1, 2 and 3, $-\Delta S_{273.2}$ is greater in the less polar solvent PYR than in the others. However, since there is a very big difference in



dielectric constants for PC as compared to MeCN and DMF, there is no general correlation between solvent polarity and the entropy of formation of the anion radicals.

The data in Table 4 is for the oxidation of heteroaromatic compounds related to anthracene. In the case of thianthrene, X=Y=S, there is a substantial decrease in $-\Delta S_{273.2}$ along the series, MeCN-DMF-PC, and the value for CH₂Cl₂ is the largest observed to date for the redox reactions of aromatic compounds in aprotic solvents. At the other end of the scale, for X=Y=N-Me, an increasing trend in the entropy of formation of the cation radical is observed and the value of CH₂Cl₂ is larger than the others. The changes along the series of polar solvents are small for the other two substrates and the values in CH₂Cl₂ are substantially larger than those in MeCN-DMF-PC.

It has earlier been noted that reversible reduction potentials of aromatic compounds become more negative as the dielectric constant of the solvent decreases.⁷ Our data do not agree with this conclusion since we see no real trends in the reversible potentials. The last columns of Tables 1-4 give the average potentials for each of the processes in all of the solvents in which measurements were made. The standard deviations in the reversible potentials were somewhat less for the heteroaromatic compound oxidation (Table 4) and the alternant aromatic hydrocarbon reduction (Table 1) than for the reduction of aromatic ketones (Table 2) and the reduction of aromatic

Table 3. The entropies and electrode potentials for the formation of anion radicals of aromatic nitro compounds in aprotic solvents.^a

Substrate	$-\Delta S_{273.2}/(\text{cal/K mol})$ $-E_{273.2}^{\text{rev}}/\text{V vs. Ag/Ag}^+$		PC ^a	PYR ^a	Mean ^a
	MeCN ^a	DMF ^a			
2,4,6-Triethylnitrobenzene	19.9	16.0	12.8		
	1.619	1.728	1.648		1.665(0.056)
2,4,6-Trimethylnitrobenzene	15.1	16.3	14.2		
	1.622	1.657	1.622		1.634(0.020)
Nitrobenzene	11.7	16.0	9.78	16.2	
	1.259	1.317	1.328	1.337	1.310(0.035)
1,3-Dinitrobenzene	7.79		5.44	7.98	
	1.097		1.121	1.204	1.141(0.056)
1,2-Dinitrobenzene	5.26		5.83		
	1.018		1.107		1.063(0.063)
1,4-Dinitrobenzene	5.05	6.71	5.88	7.89	
	1.000	1.218	1.194	0.975	1.097(0.127)

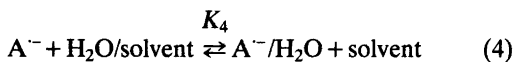
^a As in Table 1.

Table 4. The entropies and electrode potentials for the formation of cation radicals of heteroaromatic compounds in aprotic solvents.^a

X ^b	Y ^b	$-\Delta S_{273.2}(\text{cal/K mol})$ $E_{273.2}^{\text{rev}}/V$ vs. Ag/Ag ⁺		PC ^a	CH ₂ Cl ₂	Mean ^a
		MeCN ^a	DMF ^a			
S	S	25.3	20.8	14.5	31.2	1.052(0.027)
		1.021	1.063	1.042	1.083	
N-Ph	S	16.0	16.0	13.7	26.1	0.520(0.016)
		0.511	0.539	0.526	0.504	
N-Me	S	12.2	12.3		21.6	0.540(0.026)
		0.520	0.531		0.570	
N-Me	N-Me	10.0	10.6	13.1	17.5	-0.021(0.031)
		-0.060	-0.024	-0.014	0.014	

^aAs in Table 1. ^bThe heteroatoms (with substituents) in formula 1.

nitro compounds (Table 3). A possible reason for this is that the ion radicals of the first two classes of compounds do not associate appreciably with the low concentrations of water present in the solvents, while association with the more polar anion radicals (A⁻) representative of the last two classes form strong hydrogen bonded complexes. These anion radicals are involved in equilibria (4)



and appreciable fractions of the anion radical exist as the hydrogen bonded complex (A⁻/H₂O) even in the presence of low concentrations of water. Since the traces of water in the solvents are difficult to control, reaction (4) could account for some of the variations in the reversible potentials in these cases.

Table 5. A comparison of the entropies of formation of 9,10-diphenylanthracene anion and cation radicals in aprotic solvents.

Solvent	$-\Delta S_{273.2}(\text{cal/K mol})$		Sum ^a
	Anion Radical	Cation Radical	
MeCN	4.54	8.67	13.21
DMF	6.78	7.33	14.11
PC	7.15	5.97	13.12

^aThe sum of the absolute values for the formation of the anion and cation radicals.

We have previously noted that the sum of the entropies of formation of the anion and cation radicals of 9,10-DPA were independent of the concentration and the identity of the supporting electrolyte although the individual values varied substantially.⁵ The data in Table 5 show that a similar phenomenon is observed when the solvent is changed along the series, MeCN-DMF-PC. The sums are very nearly constant at 13.4 cal/K mol with a standard deviation of only ± 0.5 cal/K mol. As before, we are unable to give a microscopic rationalization for this but conclude that the formation of the anion radical becomes progressively more difficult as we go down the series while the formation of the cation radical becomes less difficult.

Table 6. Standard entropies of formation of alkali metal and halide ions in aprotic solvents.^a

Ion	$-\Delta S_{298.2}(\text{cal/K mol})$		
	DMF	PC	DMSO
Li ⁺	42.5	50.2	50.6
Na ⁺	47.8	42.3	46.2
K ⁺	45.1	37.2	33.5
Cl ⁻	46.7	37.0	34.9
Br ⁻	43.3	34.4	34.7
I ⁻	35.9	35.4	30.8
mean ^b	43.6(4.2)	39.4(5.9)	38.5(8.0)

^aData from Ref. 8. ^bValues for all ions in the particular solvent.

Before discussing our data further it is instructive to consider the data in Table 6, which consists of the standard entropies of formation of alkali metal cations and halide anions in DMF, PC and dimethylsulfoxide (DMSO).⁸ The most striking feature of this data as compared to that already discussed is that there is very little variation in $-\Delta S_{298.2}$ despite the fact that the identity of the ions varies considerably. The last row of data contains the average values in each solvent along with the standard deviations. The standard deviations range from only about 10 to 20%. It is of interest to compare the data for K^+ and Cl^- which both have the argon inert gas electronic configuration. The values for these two ions in all three of the solvents are virtually identical. With the exception of the value for Li^+ in DMF and that for I^- in PC, the magnitudes of the entropies appear to decrease with increasing ionic radii. Thus, although the variations from one solvent to the next do not appear to be simply related to any physical property of the solvents, the trends in any particular solvent apart from the exceptions noted above indicate that there is a relationship between the magnitudes of the standard entropies and the solvation energies of the ions. Solvation energies for spherical inorganic ions generally decrease as ionic radii become larger.⁹

At this point, we are faced with the inevitable question: What are the fundamental differences between the aromatic ion radicals that we have studied and the inorganic ions which cause the entropies of formation of the former to vary over orders of magnitude while those for the inorganic ions vary by only a few percent? The first and most obvious difference is that the inorganic ions are spherical with equal access by the solvent in all directions while the planar or nearly planar aromatic systems have centers of charge that can only be approached from two directions. Another significant difference is that the ion radicals can to a greater or lesser extent have localized charge centers while this is not the case with the spherical inorganic ions. But, perhaps the most important difference is that the spherical inorganic ions offer no steric hindrance to solvation while this can be a predominant factor in determining the magnitude of the entropy of formation of the ion radicals. The latter has been amply demonstrated in the series involving

aromatic ketones⁴ and aromatic nitro compounds.³

Thus, we conclude that the steric factor is the most important one responsible for the variations of the entropies of formation of ion radicals within a particular solvent as well as when the solvent is changed. The dipoles of the different solvents will be more or less hindered toward reaction with the somewhat hindered sites of solvation of the ion radicals. Since the ion radicals themselves provide the greater share of the steric interactions the variations in the entropies of formation in a particular solvent as the ion radical structure is changed, is greater than the variation observed when the solvent is changed.

Although the entropies of formation of the ion radicals cannot be related to any physical or chemical property of the solvents we do meet with a measure of success when we attempt to correlate the data for the anion radicals with the B parameter developed by Swain and co-workers¹⁰ for anion solvating solvents. The B values reported for MeCN, DMF, and PYR are 0.86, 0.93 and 0.96, respectively, while that for PC has not been evaluated. There is a qualitative correlation between the entropy changes and B for 9,10-DPA, anthracene and perylene (Table 1). This is also the case for fluoren-9-one and 1,4-dibenzoylbenzene while the correlation fails with the benzophenones which are more subject to steric effects (Table 2). With the nitrobenzenes, the correct order is followed only in the case of 1,4-dinitrobenzene (Table 3). Of the cation radicals examined (Table 4), only those from thianthrene ($X=Y=S$) correlate with the solvent A factor,¹⁰ which relates to the cation solvating properties. Thus, we conclude that there are correlations but no quantitative relationships between the entropy changes and solvent A and B parameters.

EXPERIMENTAL

All experimental procedures and data handling were described earlier.¹

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