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Temperature Effects on Electrode Processes. III. Electronic and Steric Effects on the Entropy of Formation of Nitrobenzene Anion Radicals

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The effect of multiple substitution and alkyl substituents on the reversible electrode potentials was determined for the reduction of nitrobenzenes in acetonitrile. The entropy of formation of the anion radicals was observed to be influenced both by steric and electronic effects of the alkyl substituents. The effect of multiple substitution was observed to be dependent upon substitution pattern. The entropies of formation of the anion radicals of dinitrobenzenes were observed to be −7.8 (1,3), −5.3 (1,2) and −5.1 (1,4) as compared to −11.7 cal/K mol for the formation of nitrobenzene anion radical. Mono-, di- and trinitromesitylene anion radical formations were observed to be accompanied by entropy changes of −15.1, −11.0 and −6.8 cal/K mol. The larger entropy values due to steric interactions are further demonstrated by the series, 2,5-dimethyl (−13.0), 2,4,6-trimethyl (−15.1), 2,4,6-triethyl (−19.9), 2,4,6-tri-isopropyl (−21.7) and 2,4,6-tri-*tert*-butyl (−18.6). The steric effect is explained by the decrease in charge delocalization as the nitro groups are forced out of the planes of the benzene rings by the interactions with the *ortho* substituents. Entropy changes and enthalpy changes are correlated with molar extinction coefficients.

In previous papers in this series we have demonstrated that reversible electrode potentials for both the oxidation and the reduction of aromatic compounds can be measured to a very high degree of precision. This enabled us to carry out precise determinations of the temperature coefficients which are related to the entropy of formation of the radical ions by eqn. (1).[1,2] Both studies provided

$$dE^{rev}/dT = \Delta S/nF \quad (1)$$

strong evidence that the origin of the entropy changes is dominated by the reorganization of the environment around the species undergoing electron transfer as the charge is transfered. The study concerned with the redox reactions of alternant aromatic hydrocarbons led to deductions concerning the relationship between the entropy change and the charge distribution in the absence of any steric and substituent effects.[1] The study concerned with the oxidation and reduction of compounds with the anthracene skeleton in which the 9 and 10 positions are substituted with heteroatoms brought in another factor, *i.e.* the ease with which the systems can form planar ion radicals, the most favorable situation for charge delocalization.[2] As the heteroatoms became larger the entropy changes were observed to be larger indicating more concentration of charge on the heteroatoms which in turn requires a greater reorientation of the environment during electron transfer.

Neither of the systems studied so far[1,2] were amenable to the assessment of polar effects, which might contribute to solvation of the neutral as well as the charged species. As the starting point for a systematic investigation of polar and steric effects on the entropy changes of reversible electrode processes, we chose to study the reduction of nitrobenzenes. These compounds are particularly suitable since the anion radicals are stable, steric effects can be tested for by *ortho* substitution, polar effects can be analyzed by *meta* and *para*

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Table 1. The temperature dependence for the reversible reduction potentials of nitrobenzenes in acetonitrile.[a]

Compound No.	Substitutents	$\frac{-dE^{rev}/dT}{mV\,K^{-1}}$	$-E^{rev}_{273.2}$/mV
1	0	0.507	1295
2	2-Methyl	0.569	1327
3	3-Methyl	0.496	1324
4	4-Methyl	0.477	1360
5	2,5-Dimethyl	0.556	1464
5a	2,3-Dimethyl	0.597	1417
6	2,4,6-Trimethyl	0.655	1622
7	2,4,6-Triethyl	0.864	1619
8	2,4,6-Tri-isopropyl	0.941	1617
9	2,4,6-Tri-*tert*-butyl	0.805	1662

[a] In solvent containing Bu_4NBF_4 (0.1 M). Measurements by phase selective second harmonic *a.c.* voltammetry at a mercury electrode at temperatures ranging from about 255 to 295 K.

Table 2. The temperature dependence of the reversible reduction potentials of di- and trinitrobenzenes in acetonitrile.[a]

Compound No.	Nitro Substituents	Other Substituents	$\frac{-dE^{rev}/dT}{mV\,K^{-1}}$	$-E^{rev}_{273.2}$/mV
10	1,2	0	0.228	1018
11	1,2	4-Methyl	0.194	985
12	1,3	0	0.338	1097
13	1,3	4-Methyl	0.376	1119
14	1,3	2,5-Dimethyl	0.408	1150
15	1,3	4,6-Dimethyl	0.392	1254
16	1,3	2,4,6-Trimethyl	0.476	1411
17	1,3	2,4,6-Tri-*tert*-butyl	0.669	1466
18	1,4	0	0.219	873
19	1,3,5	2-Methyl	0.117	902
20	1,3,5	2,4,6-Trimethyl	0.295	1209

[a] The measurement conditions were the same as described in Table 1.

substitution, and the effect of multiple substitution can be studied.

The electroreduction of aromatic nitro compounds has received a great deal of attention over the years. In recent years they have been studied in aprotic solvents[3] and liquid ammonia.[4] They have served as substrates for the investigation of ion-pairing[5] and for the determination of disproportionation parameters.[6,7] The electron transfer rate constants, both homogeneous exchange[8,9] and heterogeneous at electrode[8,10-12], have been obtained for a variety of nitrobenzenes. The literature concerning these topics is extensive and only the most pertinent papers have been cited here.

RESULTS AND DISCUSSION

The phase selective second harmonic *a.c.* reversible potential determinations for compounds *1–20* were determined over about a 40 K temperature range and the data are summarized in Tables 1 and 2. In general the temperature coefficients obtained by correlation of E^{rev} *vs.* T were based on measurements at from 5 to 6 temperatures spaced between about 255 and 295 K. The measurements provide dE^{rev}/dT to ± 0.01 mV/K which corresponds to an error of ± 0.2 cal/K mol in ΔS. A vast amount of data was gathered and processed and for reasons of space economy, none

Table 3. Entropy and relative enthalpy changes for the formation of methyl substituted nitrobenzene anion radicals.

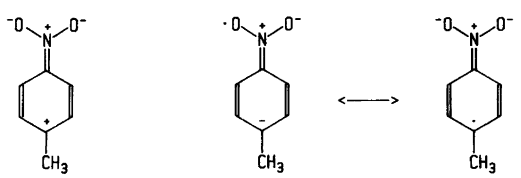
Compound No.	Substituents	$-\Delta S_{273.2}$/cal K^{-1} mol^{-1}	$\Delta\Delta H$/kcal mol^{-1} [a]
1	0	11.7	0
2	2-Methyl	13.1	0.36
3	3-Methyl	11.4	0.75
4	4-Methyl	11.0	1.69
5	2,5-Dimethyl	13.0	3.54
5a	2,3-Dimethyl	13.8	1.69
6	2,4,6-Trimethyl	15.1	6.61

[a] Relative to that for formation of nitrobenzene.

of the raw data will be reported here. Examples of the temperature coefficient determinations have been presented in other papers in this series.[1,2]

Temperature coefficients and reversible electrode potentials for the reduction of alkyl substituted nitrobenzenes and di- and trinitrobenzenes are summarized in Tables 1 and 2. Entropy changes along with enthalpy changes, relative to the reduction of nitrobenzene taken as the standard reaction, are tabulated in groups of similar structural features in Tables 3 to 7. The entropy changes will be discussed first and the relative enthalpy changes are used in comparisons of correlations of reversible potentials and entropy changes with parameters obtained in other types of experiments.

The relative importance of steric and polar effects on the magnitude of the entropy change during the reduction of nitrobenzenes can be assessed from the first four entries in Table 3. As expected, the *ortho* methyl substituent in *2* brings about an increase in the entropy change during reduction relative to unsubstituted nitrobenzene. On the other hand, methyl groups in the *meta* (*3*) or *para* (*4*) positions have the opposite effect. The resonance structures *21* – *23* give an indication of the stabilizing or destabilizing of charge in the neutral (*21*) and anion radical (*22*↔*23*) forms of *4*. Structure *21* suggests that charge separation is enhanced by methyl substitution and to the extent that this contributes to solvation would enhance the latter. On the other hand, the electron donating methyl group would clearly be expected to repel negative charge in the ring and cause the charge to be more localized on the nitro group than in the anion radical of benzene. The same direction in effects are expected when the methyl groups are either *meta* or *ortho* to the nitro group but the magnitude of the effect is expected to be diminished in both cases relative to the *para* substituent, because of weaker polar interactions of *meta* substituents and diminished polar interaction of the *ortho* substituent due to steric interference of planarity. Since the entropy changes are lower for *meta* and *para* methyl substituted nitrobenzenes we conclude that the overriding polar effect is on the solvation of the neutral molecules rather than on that for the corresponding anion radicals. In any event, the contribution of the polar effect to the entropy changes is small with those for *3* and *4* not being very much out of the range of experimental error from that observed for the reduction of nitrobenzene. The small influence of a *meta* methyl substituent is also evident in comparing the entropy change for the reduction of *2* with that of *5*, the values are nearly within experimental error of being identical. The steric effect of two *ortho* methyl groups is apparently greater than twice that of a single one. The decrease in the entropy change in going from *1* to *6* is greater than twice that in going from *1* to *2* in spite of the presence of the *para* methyl substituent which influences the entropy change in the opposite direction.



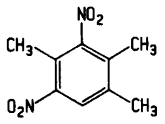
21 *22* *23*

The steric and polar contributions to the entropy change upon the reduction of nitrobenzenes can be incorporated into an empirical equation (2), as can be seen from Table 8, to predict ΔS for nitro, 1,3-

dinitro and 1,3,5-trinitro compounds. In (2) A_z is the entropy change when the nitro compound is

$$\Delta S = A_z + \{0.69(\text{cal/K mol})B + 0.23(\text{cal/K mol})C - 2.08(\text{cal/K mol})D - 5.53(\text{cal/K mol})E\}/z \quad (2)$$

unsubstituted and z is the number of nitro groups. The number of *ortho* and *para* methyl groups are designated by B and that of *meta* by C. The number of nitro groups with one *ortho* methyl and with two *ortho* methyls are specified by D and E, respectively. Thus, structure *24* would be treated in the following manner:



24

$A_z = \Delta S$(*m*-dinitrobenzene)
$z = 2$
$B = 2$, $C = 1$, $D = 1$, and $E = 1$.

The experimental ΔS values for the compounds listed in Table 3 are compared to those calculated using (2) in the upper half of Table 8. With the exception of the value for the reduction of *5a*, the calculated values are within 0.1 cal/K mol of the experimental ones.

Before leaving the mononitrobenzene derivatives and going in more detail into the significance of eqn. (2), we can examine the steric effect of *ortho* substituents a little more closely. The data in Table 4, summarize the effect on ΔS when the 2,6-alkyl substituents are made progressively larger. The entropy change becomes progressively larger as the alkyl groups are changed from methyl to ethyl to isopropyl, in which case the maximum value observed in this study, −21.7 cal/K mol, was recorded. This is qualitativelly the expected trend. As the alkyl group gets larger, the overlap of *p* orbitals on nitrogen with the pi system of the ring becomes progressively less with the charge of the anion radical becoming more and more localized on the nitro group. However, reaction of compound *9* in which the nitro group is flanked by two large *tert*-butyl groups exhibited a smaller entropy change, −18.6 cal/K mol. This result would appear to be inconsistent with our model where localization of charge is accompanied by a more ordered environment and hence a greater loss in entropy. However, when we examined space-filling models of structure *9* we found that the nitro group is effectively buried in the bulky *tert*-butyl groups and solvation cannot possibly be as localized as in the other structures in Table *4*. Thus, the ordering of the solvent around the periphery of the buried nitro group is less than in cases where the solvation can be

Table 4. Entropy and relative enthalpy changes for the formation of 2,4,6-trialkylnitrobenzene anion radicals.

Compound No.	Substituents	$-\Delta S_{273.2}$/cal K^{-1} mol^{-1}	$\Delta\Delta H$/kcal mol^{-1}
6	2,4,6-Trimethyl	15.1	6.61
7	2,4,6-Triethyl	19.9	5.23
8	2,4,6-Tri-isopropyl	21.7	4.69
9	2,4,6-Tri-*tert*-butyl	18.6	6.58

Table 5. Entropy and relative enthalpy changes for the formation of dinitrobenzene anion radicals.

Compound No.	Isomer	$-\Delta S_{273.2}$/cal K^{-1} mol^{-1}	$-\Delta\Delta H$/kcal mol^{-1}
10	1,2	5.26	4.63
12	1,3	7.79	3.50
18	1,4	5.05	7.91
(*11*)[a]	1,2(4-Methyl)	(4.47)	(5.17)

[a] Does not belong in the classes of any of the tables.

more localized. We have observed a similar phenomenon during the study of the entropy of the reduction of some highly substituted benzophenones.[13]

Turning our attention now to the reduction of the dinitrobenzenes, we find that regardless of the substitution pattern a significant lowering of the entropy change upon reduction is observed when a second nitro group is present. A feature of the data in Table 5 that attracts attention is that the ΔS values for 1,2 (*10*) and 1,4 (*18*) dinitrobenzene are nearly the same. This indicates that the polar effect of the nitro group, in contrast to that of the methyl group, is so strong that the steric effect is essentially overcome. Aside from this somewhat surprising feature of the data, the entropy change during the reduction of 1,3-dinitrobenzene (*12*) was intermediate between that of nitrobenzene and the other two dinitrobenzenes. This is to be expected since the *meta* substituent can only exert an inductive effect upon the charge distribution in the corresponding anion radical.

We can now return to the evaluation of polar and steric influences on the entropy change in reduction. The entropy change data for 1,3-dinitrobenzene reductions summarized in Table 6 are compared to the corresponding values calculated using eqn. (2) in the lower half of Table 8. The correspondence is just as good as was observed with the nitrobenzene derivatives with the exception of that for structure *16* where the calculated value is 1.3 cal/K mol more negative than observed. Any attempt to explain the deviation would necessarily be highly speculative and perhaps pointless. A further indication that the entropy effects in this series of reactions parallel those for the nitrobenzenes can be found by considering the differences in entropy changes for the parent compounds (3.9 cal/K mol) and the tri-*tert*-butyl substituted derivatives (3.2 cal/K mol).

The application of eqn. (2) to the reduction processes of the two series of compounds in Table 8 allows us to draw definite conclusions regarding the relative importance of polar and steric effects in determining the entropy changes. The coefficients of *B* and *C*, which relate to the polar effect of the methyl groups, are only 0.69 cal/K mol and 0.23 cal/K mol, respectively, white the corresponding factors for *D* and *E*, which take into account the steric effects, are −2.08 cal/K mol and −5.53 cal/K mol. Thus, the steric influence of an *ortho* methyl group is far greater than the polar effect of a methyl group in any position in the molecule. The signs of the multipliers are also of significance. The positive signs on the factors relating to polar effects can be taken as an indication, as discussed before, that the polar effect exerts a stronger influence on the solvation of the neutral molecule than on the anion radical. Conversely, the negative factors relating to steric effects show that the steric effect is much more important in the charge distribution, and hence solvation, of the anion radicals than of the parent substances.

Table 6. Entropy and relative enthalpy changes for the formation of alkyl substituted 1,3-dinitrobenzene anion radicals.

Compound No.	Substitutents	$-\Delta S_{273.2}$/cal K^{-1} mol^{-1}	$\Delta\Delta H$/kcal mol^{-1}
12	0	7.79	−3.50
13	4-Methyl	8.67	−3.23
14	2,5-Dimethyl	9.41	−2.72
15	4,6-Dimethyl	9.04	−0.22
16	2,4,6-Trimethyl	11.0	2.87
17	2,4,6-Tri-*tert*-butyl	15.4	2.93

Table 7. Entropy and relative enthalpy changes for the formation of methyl substituted 1,3,5-trinitrobenzene anion radicals.

Compound No.	Substituents	$-\Delta S_{273.2}$/cal K^{-1} mol^{-1}	$-\Delta\Delta H$/kcal mol^{-1}
19	2-Methyl	2.70	6.60
20	2,4,6-Trimethyl	6.80	0.64

Table 8. Comparison of experimentally determined entropy changes for mono- and dinitrobenzene reductions with those calculated using an empirical equation.

Compound No.	$-(\Delta S_{273.2})_{exp.}$/ cal K^{-1} mol^{-1}	$-(\Delta S_{273.2})_{calc.}$/ cal K^{-1} mol^{-1} [a]
1	11.7	11.7
2	13.1	13.1
3	11.4	11.5
4	11.0	11.0
5	12.8	12.8
5a	13.8	12.8
6	15.1	15.2
12	7.79	7.79
13	8.67	8.49
14	9.41	9.41
15	9.04	9.18
16	11.0	12.3

[a] Calculated from eqn. (2) in the text.

We have limited data on derivatives of symmetrical trinitrobenzenes. We were unable to obtain reliable response for the parent in the series and the data for *19* and *20* (Table 7) could not be treated directly using eqn. (2). However, it is possible to treat A_z, which is ΔS of the parent, as the unknown in (2) and arrive at a value of -1.7 cal/K mol. Only one of the alternant aromatic hydrocarbon redox reactions, the reduction of triphenylene, proceeds with a lower entropy change, -0.9 cal/K mol.[1] This gives a clear indication that solvation of the anion radicals is very diffuse, and is spread out over the entire framework of the ion. It is of further interest to compare the entropy changes for mono- (*6*), di- (*16*) and trinitromesitylene (*20*) reductions. A smooth trend is observed with values of -15.1, -11.0 and -6.8 cal/K mol recorded for the compounds. This gives further justification for the application of eqn. (2) to determine ΔS for 1,3,5-trinitrobenzene.

It has been pointed out that the steric inhibition of resonance in *ortho* substituted nitrobenzene derivatives is manifested in a decrease in absorption intensity.[16] This is, of course, a reflection of the decrease in conjugation and can be expressed numerically in terms of the molar extinction coefficient, ε. Since this appears to be precisely the factor that we are attributing the relative entropy changes to, a correlation of the available data concerning this parameter is of the utmost interest. In Fig. 1, $\Delta S_{273.2}$ and $\Delta\Delta H$ for the reduction of several nitrobenzenes are plotted *vs.* ε where the latter is the extinction coefficient at the maximum of the absorption band appearing at about 250 nm for all of these compounds. The gratifying result of the correlations is that ε correlates much better with ΔS than with $\Delta\Delta H$ (or E^{rev}). The close correspondence of ΔS and ε provides further evidence for our model based upon entropy and localized charge distribution.

$$A + e^- \underset{k_s}{\rightleftharpoons} A^{\cdot -} \qquad (3)$$

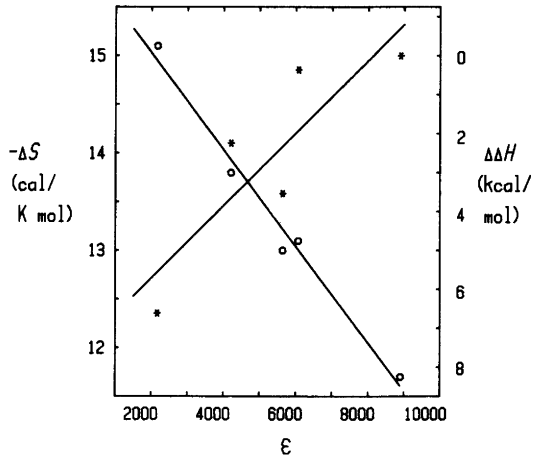


Fig. 1. Correlation of ΔS (circles) and $\Delta\Delta H$ (asterisks) for the reduction of nitrobenzenes in acetonitrile with molar extinction coefficients at the maximum of the band at about 250 nm.

The kinetics of charge transfer reactions (3) and (4) are of interest for comparison with the

$$A^{\cdot -} + A \underset{}{\overset{k_{ex}}{\rightleftharpoons}} A + A^{\cdot -} \qquad (4)$$

thermodynamic quantities for reversible electron transfer. The interesting feature of both (3) and (4) is that under the conditions of the measurements the reactions are at equilibrium and ΔG for (4) is zero. According to electron transfer theory,[17] reorientation of the environment around reactant in going to the transition state plays a dominating role in determining the rate of the reaction. In consideration of this, one might expect a direct correlation between ΔS and k_s or k_{ex}. If such a close relationship could be established it would be of great importance in the study of electron transfer kinetics. This is especially true in the case of k_s where experimentally measured rate constants are not the intrinsic values but are apparent values depending upon the electrode and double layer conditions. Unfortunately, attempts to correlate either ΔS or $\Delta\Delta H$ with available k_s or k_{ex} data were disappointing. No evidence for linear relationships could be found in any case. It is possible that these failures are due to insufficient data as well as to a rather low degree of precision in the kinetic data. Further work is called for along these lines.

The work reported here has reinforced our expectations that the measurement of entropy changes in reversible electrode processes can provide important insight into the details of the reactions.[1,2,13] We are in the progress of studying the effect of reaction conditions such as solvent and counter ion on the magnitude of the entropy changes. Work in progress or planned includes the study of the formation of multiply-charged ions and redox reactions involving other charge types.

EXPERIMENTAL

The experimental procedures and data handling operations were described in detail in the first paper in this series.[1] Nitro compounds were either commercially available or prepared and purified by standard procedures.

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