Entropy Change Associated with the Charge Transfer Reation of Various Quinones in Aprotic Solvents

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Temperature dependence of the cathodic reduction potentials of various *p*-benzoquinone derivatives have been determined in five aprotic solvents, benzonitrile, acetonitrile, propylene carbonate, *N,N*-dimethylformamide, and dimethyl sulfoxide. As for the first electron transfer reactions, the free energy of transfer between any two of solvents has been found to be less than 1.0 kcal $\mathrm{mol^{-1}}$, which is much smaller than the solvation enthalpy of ordinary anions. As a result, the transfer entropy is compensated almost perfectly by the transfer enthalpy. The compensation effect also appears in the transfer energies of the second electron transfer reaction though not perfect.

In the previous paper,[1] we have stated that the free energy of transfer of quinone/quinone anion radical systems in several aprotic solvents is negligibly small. This statement was derived from the experimental fact that the first electrode potential ($E_1°$) of various quinones determined in a solvent M, aligns on a straight line of unit slope when they are plotted against those determined in another solvent N.

The fact is expressed as the following equation,

$$E_1°(\mathrm{i,M})=E_1°(\mathrm{i,N})+\mathrm{const.} \tag{1}$$

where i expresses individual substrate and M and N specify two different solvents. Eq. 1 is of course an empirical equation and $E°$ values are apparent ones. Formally speaking, however, the equation should also hold for the absolute potentials though their numerical values are unknown.

$$E_1°(\mathrm{i,M})_{\mathrm{abs}}=E_1°(\mathrm{i,N})_{\mathrm{abs}}+K \tag{2}$$

Our conclusion was that K appearing in Eq. 2 is very small and is within the experimental uncertainty. In this paper, we will add a quantitative base for the above conclusion by analyzing the entropy change in the redox reaction of various quinone derivatives.

The entropy change associated with the electrode reactions of aromatic compounds has been studied extensively by Svaan and Parker[2] and more recently by Jaworsky[3,4] and also by Nagaoka et al.[5] Entropy change of various quinone derivatives in the gas phase electron attachment is discussed by Heinis et al.[6]

Experimental

A nonisothermal cell arrangement[2,3] was used for determining the temperature coefficient of electrode potentials. In one compartment of the cell, the temperature of which was varied in the range of 10—50 °C at a step of 10 °C, a set of test electrodes were placed. The other compartment, in which a reference electrode was placed, was kept at a fixed temperature (25±0.1 °C) and the temperature gradient was set up over the length of a liquid bridge connecting the two compartments. Potential sweep technique (sweep rate : 0.1 V $\mathrm{s^{-1}}$) was employed for the potential determination at various temperatures. The potential values were determined as the mean of cathodic peak potential and its anodic counterpart. Test solutions contained 0.1 mol $\mathrm{dm^{-3}}$ $\mathrm{Et_4NClO_4}$ and 5×10^{-3} mol $\mathrm{dm^{-3}}$ of a given substrate. The working electrode was a Pt wire (0.5 mm in diameter and 0.5 cm in length) and the counter electrodes was a Pt plate. The reference electrodes used were low-chloride calomel electrodes whose potentials are dependent on the perchlorate concentration.[7] These electrodes were prepared individually for each solvent system using the respective solvent.

Since all solvents studied are hygroscopic in nature and moistening of the test solution affected strongly the measurement, a special caution was necessary for avoiding the moistening. All the solvents used were dehydrated with $\mathrm{CaH_2}$ or molecular sieves overnight and distilled just before use. Water content was checked by gas chromatography to be less than the limit of detection (8×10^{-4} mol $\mathrm{dm^{-3}}$). The measurements carried out in the course of ascending temperature were repeated in the reverse course of descending temperature so as to confirm the agreement of the two values. The temperature coefficient thus determined has an uncertainty of ±0.02 mV $\mathrm{K^{-1}}$.

Results and Discussion

The temperature coefficients of electrode potentials as well as derived values of entropy change for both the first and second electron transfer reactions of 13 quinones in 5 aprotic solvents are compiled in Table 1. Jaworski's data[4] are also listed for reference. It is evident that our data are always smaller than his by a factor of 2 to 4. We cannont understand why such big differences appeared. Thermal diffusion of silver ion, which was used by him as the potential reference, might be the source of the discrepancy. Enthalpy data were calculated by assuming zero free energy change for the reaction of *p*-benzoquinone **1** in every solvent studied.[8]

Before discussing the nature of the present data, it will be worthwhile to check the reliability of our measurements. Svaan and Parker,[2] who studied the problem with various types of compounds, reported that $\Delta S_1°$ values of dinitrobenzenes ranged from −5.05 (1,4-dinitrobenzene, $T\Delta S_1°=-1.50$ kcal $\mathrm{mol^{-1}}$; 1 cal=4.184 J) to −9.41 e.u. (2,5-dimethyl-1,3-dinitrobenzene, $T\Delta S_1°=-2.80$ kcal $\mathrm{mol^{-1}}$). Our values for various

Table 1. Temperature Coefficients of Reduction Potentials of Various Quinones

Compd[a]	Solvent[b]	$\mathrm{d}E_1/\mathrm{d}T$	$\mathrm{d}E_2/\mathrm{d}T$	$-T\Delta S_1^\circ$	ΔH_1[c]	$-T\Delta S_2^\circ$	ΔH_2
		(mV K^{-1})		(kcal mol^{-1})			
1	BN	0.82	2.21	5.6	−5.6	15.2	−0.1
	AN	0.62	3.13	4.3	−4.3	21.5	−0.9
		(1.5±0.2)[d]					
	PC	0.44	1.28	3.0	−3.0	8.80	2.0
		(1.4±0.1)[d]					
	DMF	0.38	1.01	2.6	−2.6	6.94	14.8
	DMSO	0.42	1.58	2.9	−2.9	10.9	10.3
		(1.6±0.3)[c]					
2	BN	0.71	3.36	4.9	−12.2	23.1	−12.1
	AN	0.23	1.47	1.6	−9.1	10.1	−1.1
	PC	0.26	2.03	1.8	−9.6	14.0	−7.2
	DMF	0.24	1.62	1.6	−9.4	11.1	3.2
	DMSO	0.11	1.45	0.78	−8.09	9.96	3.0
3	BN	0.48	2.44	3.3	−15.0	16.8	−9.2
	AN	0.18	1.39	1.2	−13.4	9.55	−3.32
	PC	−0.05	1.96	−0.4	−11.7	13.5	−9.1
	DMF	−0.09	1.09	−0.6	−11.7	7.49	1.15
	DMSO	−0.03	1.22	−0.2	−11.2	8.38	−0.86
4	BN	0.18	1.42	1.2	−25.1	9.77	−13.2
	AN	−0.05	1.15	−0.4	−23.2	7.90	−12.6
	PC	−0.17	1.39	−1.2	−21.7	9.55	−15.0
	DMF	−1.42	1.05	−9.76	−13.5	7.21	−10.5
5	BN	0.69	1.87	4.7	−2.3	12.9	6.1
	AN	0.67	2.02	4.6	−2.6	13.9	5.2
	PC	0.78	0.87	5.4	−3.5	6.0	7.3
	DMF	0.29	1.28	2.0	−0.2	8.80	25.1
	DMSO	0.40	1.52	2.7	−0.9	10.4	12.1
6	BN	0.69	3.69	4.7	−0.2	25.4	−4.0
	AN	0.60	4.62	4.1	−7.8	31.8	−13.1
	DMF	0.28	0.96	2.0	1.6	6.6	15.0
	DMSO	0.43	1.66	2.9	0.8	11.4	13.1
7	BN	0.86	3.66	5.9	−0.9	24.8	−6.2
	AN	0.53	2.11	3.7	0.6	14.5	4.4
		(1.1±0.2)[d]					
	PC	0.78	1.60	5.4	−1.2	11.0	2.5
		(1.1±0.1)[d]					
	DMF	0.45	1.29	3.1	0.9	8.86	14.2
	DMSO	0.18	1.22	1.2	3.0	8.38	14.7
		(1.2±0.1)[d]					
8	BN	0.58	2.51	4.0	−5.3	17.3	−2.7
	AN	0.28	1.65	2.0	−3.7	11.3	2.8
	PC	0.14	2.96	0.95	−2.7	20.3	−10.9
	DMF	0.28	1.28	1.9	−4.0	8.80	8.5
	DMSO	0.24	1.26	1.7	−3.6	8.66	7.4
9	BN	0.73	3.90	5.0	2.0	26.8	−5.1
	AN	0.83	2.07	5.7	0.7	14.2	7.6
	PC	0.70	1.80	4.8	1.5	12.4	4.7
	DMF	0.41	1.29	2.8	3.4	8.86	16.7
	DMSO	0.24	1.32	1.6	4.4	9.07	15.6
10	BN	0.87	2.33	6.0	4.7	16.0	8.2
	AN	0.41	1.92	2.8	7.1	13.2	9.3
		(1.0±0.1)[d]					
	PC	0.34	2.58	2.3	7.6	17.7	−0.2
		(1.0±0.1)[d]					
	DMF	0.24	1.15	1.7	7.9	7.90	18.7
	DMSO	0.51	1.50	3.5	6.0	10.3	15.8
		(1.1±0.2)[d]					
11	BN	0.85	1.96	5.9	5.7	13.5	10.4
	AN	0.51	1.71	3.5	7.1	11.7	12.7
	PC	0.37	2.43	2.6	8.0	16.7	1.4
	DMF	0.21	2.27	1.5	8.6	15.6	11.5
	DMSO	0.35	1.19	2.4	7.8	8.18	18.4

Table 1. (Continued)

Compd[a)]	Solvent[b)]	dE_1/dT	dE_2/dT	$-T\Delta S_1°$	ΔH_1[c)]	$-T\Delta S_2°$	ΔH_2
		(mV K^{-1})		(kcal mol^{-1})			
12	BN	0.65	2.09	4.5	8.2	14.4	10.6
	AN	0.32	1.61	2.2	9.8	11.1	13.1
	PC	0.47	1.63	3.2	8.7	11.2	8.5
	DMF	−0.34	0.87	−2.3	14.0	6.0	21.3
	DMSO	0.53	1.14	3.7	8.5	7.83	18.8
13	BN	0.51	1.76	3.5	12.6	12.1	13.9
	AN	0.35	1.45	2.4	13.2	9.96	15.4
	DMF	0.19	0.86	1.3	15.3	5.9	22.7

a) Compounds. **1**: 1,4-benzoquinone (BQ), **2**: 2,5-dichloro BQ, **3**: tetrachloro-BQ, **4**: 2,3-dicyano-5,6-dichloro-BQ, **5**: Me-BQ, **6**: 2,5-diMe-BQ, **7**: 1,4-naphthoquinone (NQ), **8**: 2,3-dichloro-NQ, **9**: 2-Me-NQ, **10**: 9,10-anthraquinone (AQ), **11**: 2-Me-AQ, **12**: 1-amino-AQ, **13**: 1,4-diamino-AQ. b) Solvents, BN: Benzonitrile, AN: Acetonitrile, PC: Propylene carbonate, DMF: *N*,*N*-dimethylforamide, DMSO: Dimethyl sulfoxide. c) Enthalpy data were calculated by assuming tentatively the free energy change associated with the firsr electron transfer reactions of para benzoquinone to be always zero.[8)] d) Values in the parenthesis were cited from Jaworski.[3)]

quinones are very close to those of dinitrobenzenes. On the other hand, Jaworski's values are very large and almost near our $\Delta S_2°$ vlaues.

The entropy change associated with the charge transfer reaction is mostly determined from the potential difference in a nonisothermal cell. It should be noted that such a measurement unavoidably involves irreversible entropy production intrinsic to the transport phenomena, heat flow and Soret effect.[9)] Fortunately, de Bethune[10)] showed that, if the potential determining electrode reactions are regarded as reversible, the irreversible entropy productions can be ignored and the standard entropy change can be safely determined. Actually, however, it is also true that many organic compounds do not behave reversibly at electrodes. Quinones are no exception. This is particularly true for the second electron transfer reaction between anion radicals and their dianions as has been described in the previous paper. Accordingly, our attention will mainly be focused on the first electron transfer reactions.

As are seen in Table 1, the variation of $-T\Delta S_1°$ of each individual substrate makes it rather complicated to find some systematic correlation with their molecular characteristics. A notable thing appearing in this table is that there are some compounds which have a positive entropy value. The entropy change for gaseous electron attachment reaction of various quinones have been reported by Heinis et al.[6)] According to them, the values are all negative irrespective of the nature of substituents. It is interesting to note that the positive values in Table 1 always appear in the reaction of chlorinated compounds.[11)] We have mentioned[1)] that there is a significant contrast between the solvation behavior of chlorinated and nonchlorinated compounds. Heinis et al. also noticed a similar substituent effect of Cl in the correlation between electron affinity and electrode potential.[6)] To the extension that the solvent is considered as a dielectric continuum, the entropy change should have a negative value. Since the reaction entropy reflects the difference in the structure ordering around the product and reactant, a positive entropy change will indicate that the degree of order is higher with the neutral reactant molecule than that of the charged product. This point is worthy of a more detailed analysis in future studies. Regarding this, there is another point to be noted, though qualitative, that variation of $T\Delta S_1°$ of chlorinated compounds in a given solvent seems to be discriminated from other nonchlorinated compounds. As is seen in Fig. 1, $-T\Delta S_1°$ of chlorinated compounds in a given solvent (solvent is

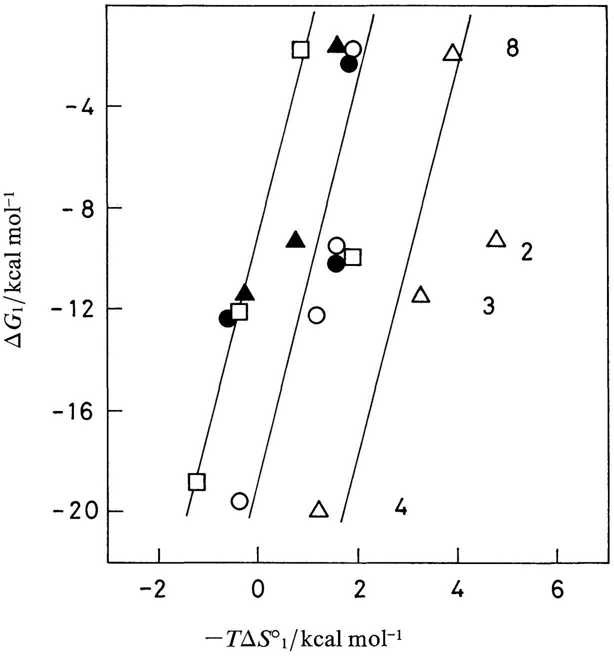

Fig. 1. Entropy change in the first electron transfer reaction of chlorinated compounds. ΔG_1's are relative values referred to 1,4-benzoquinone. Numerical figures indicate compound number given on the margin of Table 1. Symbols specify solvents used. △: BN, □: PC, ○: AN, ●: DMF, ▲: DMSO.

specified by different symbols), increases with decreasing number of chlorine (or cyano group) substitution; **4**>**3**>**2**>**8**. In addition, if we ignore the point for **4** in DMF, which has an anomalously large positive value and is omitted from the figure, $T\Delta S_1^\circ$ seems to be roughly proportional to ΔG_1.[8] On the other hand, no such simple correlation seems to exist in nonchlorinated compounds. Qualitatively, irrespective of the nature of substrates, $-T\Delta S_1^\circ$ in DMF (●) and DMSO (▲) exhibit smaller values than those in other solvents, particularly in BN (△). Regarding this, it will be worth noting the work of Hupp and Weaver,[12] who studied the entropy change in the redox system of some coordinated transition metal compounds. They showed that, in accordance with the simple Born equation, the reaction entropy changes linearly with the reciprocal of ionic radius. In the present case, however, no such a simple correlation was observed and the entropy change seems to be insensitive to the size of substrate studied.[13] The different size dependence appeared in transition metals and quinone systems may be attributed to the difference in the surrounding conditions of charge in molecule. In case of metal complexes, the charge of the central metal ion is separated by ligands from the surrounding solvent molecules and the polarizing force will be directly affected by the size of ligands. On the other hand, in the case of quinone anion radical, most of the negative charge is localized on carbonyl oxygen and the charge density at oxygen will be independent of the size of aromatic ring. The solvation at carbonyl oxygen mainly contributes to entropy change and relatively small size effect would be expected for quinone systems. The spherical symmetry of the metal complexes and planer structure of the quinones should also be accounted for.

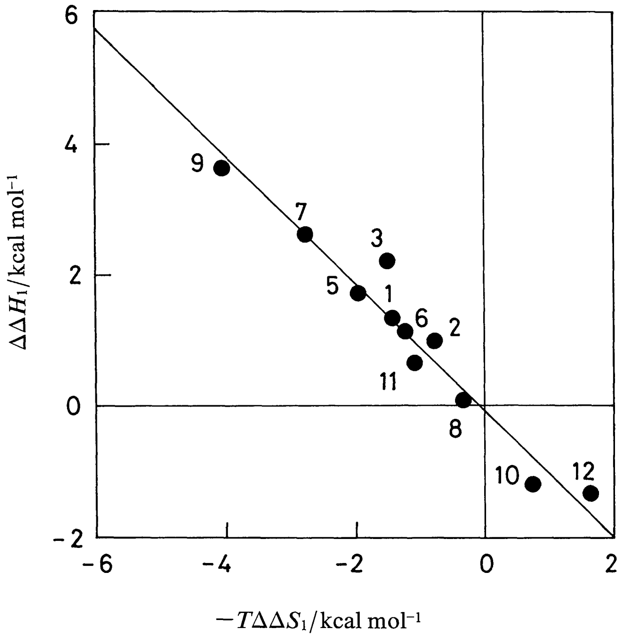

Fig. 2. Correlation between two transfer energies of the first electron transfer reaction transferred from AN to DMSO.

Although individual values of $T\Delta S_1^\circ$ vary in a rather complicated fashion, we can find a very simple rule for the transfer entropies, i.e., the difference in two different solvents. A typical example is shown in Fig. 2, where the transfer entropy, $-T\Delta\Delta S_1^\circ$ from AN to DMSO is plotted against the corresponding transfer enthalpy, $\Delta\Delta H_1$.[8] One can readily see that a compensation effect exists between two energies, $T\Delta\Delta S_1^\circ$ and $\Delta\Delta H_1$, for the transfer process concerned. More or less similar correlations were found for every combination of two solvents. Since the compensation between $T\Delta\Delta S_1^\circ$ and $\Delta\Delta H_1$ arises when the free energy of transfer is almost null, the results obtained here provide a strong support to our previous conclusion.

The compensation effect can be analyzed in a little more detail. Table 2, which lists the least square parameters in the following equation, was prepared for this purpose.

$$T\Delta\Delta S_1^\circ = a\Delta\Delta H_1 + b$$

Generally speaking, when the compensation is perfect and the potential of the reference electrode is invariable throughout the different solvents studied, the slope "a" should be unity and the intersect "b" must be zero. If, on the other hand, the transfer free energy is not zero but is a constant, b will have a finite value. Of course, the potential of the reference electrode cannot be regarded to be invariable because the perchlorate activity will vary slightly from solvent to solvent. According to Parker,[14]

Table 2. Parameters Appearing in the Compensation Equation,[8] $T\Delta\Delta S_1^\circ = a\Delta\Delta H_1 + b$

Solvent couple from	Solvent couple to	a/kcal mol^{-1}	b/kcal mol^{-1}	Correlation coefficient
AN	BN	0.94±0.09	0.54±0.15	0.954
PC	BN	0.83±0.10	0.72±0.23	0.943
DMF	BN	0.86±0.06	1.01±0.23	0.980
DMSO	BN	0.82±0.12	1.01±0.31	0.913
PC	AN	0.86±0.06	0.06±0.07	0.980
DMF	AN	0.95±0.05	0.14±0.15	0.988
DMSO	AN	0.99±0.08	0.07±0.14	0.973
DMF	PC	1.01±0.02	0.19±0.07	0.998
DMSO	PC	0.97±0.07	0.01±0.14	0.981
DMSO	DMF	0.91±0.08	−0.16±0.10	0.969

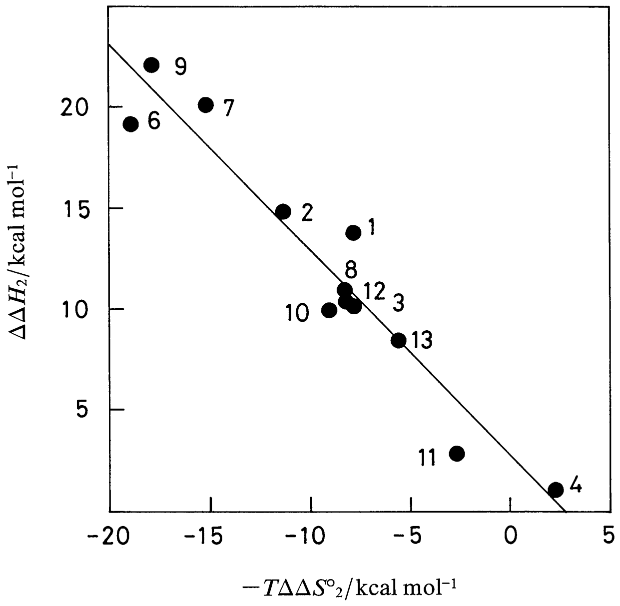

Fig. 3. Correlation between two transfer energies of the second electron transfer reaction transferred from BN to DMF.

the activity coefficient of perchlorate anion changes from −0.3 in DMSO to −0.4 in DMF. The resultant variation of the electrode potential is less than 1 mV(0.02 kcal mol^{-1}). The largest value of b in Table 2 is 1.01±0.3 kcal mol^{-1} for the transfer process from DMSO to BN. It should be noted in the first place that an enthalpy change of 1.0 kcal mol^{-1} is much smaller than the solvation enthalpy of typical anions (65 to 115 kcal mol^{-1} for I^- to F^-)[15] and is still of the order of the experimental uncertainty, which is estimated to be less than 0.3 kcal mol^{-1}.

It is interesting to note that, however, the b values seem to vary rather systematically according to the order of solvation energies observed previously for the second electrode potential, ($E_2°$): DMSO-DMF>PC>AN>BN. Final conclusions on this matter can thus be summarized as follows.

1. The free energy of transfer of the quinone/quinone anion radical system among several aprotic solvents studied here does not exceed 1.01±0.3 kcal mol^{-1} and is almost negligible.

2. There is a possibility that a very small solvent effect yet exists, however, within the limit of 1.0 kcal mol^{-1}.

A similar compensation effect can also be found in the second electron transfer reactions as is shown in Fig. 3. Except for the solvent combination of PC and DMF, we can find a fairly good linear correlation between $\Delta\Delta H_2$ and $T\Delta\Delta S_2°$ suggesting that the two transfer energies, $T\Delta\Delta S_2°$ and $\Delta\Delta H_2$, are largely though not perfectly compensating each other. As for the second electron transfer reactions, scattering of data is enhanced and it seems difficult to draw meaningful correlations.

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8) It should be noted that the entropy values here discussing are the absolute ones while those of ΔG and ΔH are relative values determined on the arbitrary assumption : ΔG_1 for the reaction of *p*-benzoquinone is always zero irrespective of solvent. As a result, ΔH values in Table 1 involve a constant difference from the absolute values. The assumption, however, does not contain any drawback since we are discussing the difference of two ΔH values ($\Delta\Delta H$).

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10) A. J. de Bethune, T. S. Licht, and N. Swendman, *J. Electrochem. Soc.,* **106**, 616 (1959).

11) There is a possibility that chloride ion is detached from the quinoid ring as a follow up reaction to the electron transfer. This will act to increase the negative entropy value, however.

12) J. T. Hupp and M. J. Weaver, *Inorg. Chem.,* **23**, 3639 (1984).

13) Estimated radius varies from 4.1 to 5.7 Å for unsubstituted benzoquinone to 9,10-anthraquinone, while corresponding variation in the entropy change ($-T\Delta S_1$) are from 5.62 to 5.97 in BN, 4.27 to 2.80 in AN, and so on (see Table 1).

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