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Entropy of Electrochemical Formation of *p*-Semiquinones in Dimethylformamide

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Entropy of formation of anion radicals at the mercury electrode in dimethylformamide for 1,4-benzoquinone, 1,4-naphthoquinone, 9,10-anthraquinone, and 5,12-tetracenequinone has been determined from the temperature dependences of the reversible half-wave potentials using a nonisothermal cell. The linear relationship between the entropy and the calculated spin density at the oxygen atom of semiquinones was established. Similarly the linear correlation of the literature reaction entropy for electrooxidation of a few heteroaromatic compounds versus the experimental spin density at a heteroatom (N, S or Se) from ESR measurements was also observed.

(Keywords: Electrochemistry; Entropy of formation; Radical cations; p-Semiquinones; Spin density)

Die Entropie der elektrochemischen Bildung von p-Semichinonen in Dimethylformamid

Die Bildungsentropie von Anionenradikalen an der Quecksilberelektrode wurde in Dimethylformamid für 1,4-Benzochinon, 1,4-Naphthochinon, 9,10-Anthrachinon und 5,12-Tetracenchinon aus der Temperaturabhängigkeit der reversiblen Halbwellenpotentiale unter Benutzung einer nichtisothermen Zelle bestimmt. Es wurde eine lineare Abhängigkeit zwischen der Entropie und der berechneten Spindichte am Sauerstoffatom der Semichinone festgestellt. Eine ähnliche lineare Korrelation konnte für die Literaturdaten von Reaktionsentropien der Elektrooxidation einiger heteroaromatischer Verbindungen gegenüber den experimentellen Spindichten am Heteroatom (N, S, Se; ESR-Messungen) beobachtet werden.

Introduction

The entropy change during the electrode process of organic aromatic compounds was measured only in a few cases. *Savèant* and coworkers investigated the entropy factor in two successive electron transfers for a series of nitroaromatic compounds[1,2]. Lately *Svaan* and *Parker* have measured the entropy of formation of ion radicals of alternant aromatic hydrocarbons[3] and heteroaromatic compounds[4, 5] in acetonitrile (*ACN*). They have used a nonisothermal electrochemical cell, similar as in works of *Weaver* and his group[6—8] and next other authors[9, 10], who determined the reaction entropy ΔS_r° (i.e. the difference between the ionic entropies of the reduced and oxidized forms of the redox couple) for the electroreduction of various complexes. The ΔS_r° values can be easily evaluated by the measurement of the temperature coefficient of the equilibrium electrode potential in such a cell, after neglection of the potential contributions from the temperature gradients across the both liquid junction and mercury in the working electrode. The validity of the necessary assumptions has been discussed in[6].

According to all above mentioned authors the reaction entropy reflects mainly the change in the solvation of ions. Thus the knowledge of the entropy for electrochemical formation of aromatic radical ions can be important for the detailed understanding of not only the thermodynamics of the redox process but also of the solvent structural changes accompanying the electron transfer, which determine the kinetics[8, 11].

The entropy of formation at the electrode of the anion radicals for a series of *p*-quinones is given in this paper.

Materials and Methods

Dimethylformamide (*DMF*) (Reachim) was dried with calcium hydride and then distilled under argon reduced pressure. The middle 60% of the distillate was shaken with active neutral alumina and distilled once more in the same manner. Tetraethylammonium perchlorate (*TEAP*) was prepared and vaccum dried as in our previous paper[12]. 1,4-Benzoquinone (*BQ*) (Schuchardt), 1,4-naphthoquinone (*NQ*) (Loba-Chemie), 9,10-anthraquinone (*AQ*) (POCh) and 5,12-tetracenequinone (*TQ*) (Aldrich) were purified by vacuum sublimation.

The concentrations of the depolarizer and the supporting electrolyte were 0.5 m*M* and 0.1 *M*, respectively.

Polarographic waves were recorded with a Radelkis OH-105 apparatus using the most extended potential scale. Half-wave potentials were determined for at least seven curves at each temperature, the standard deviations being less than or equal to 1 mV.

Measurements were performed in a three electrode cell consisting of a dropping mercury electrode and a Hg pool as a counter electrode. The temperature of the cell was varied in the range of 20 to 50 °C using a constant temperature (± 0.1 °C) water, which was pumped through a jacket surrounding the cell. The reference electrode consisted of a silver wire in a freshly prepared solution containing 0.09 *M* *TEAP* and 0.01 *M* $AgNO_3$ in *DMF*[13] enclosed in a glass tube with a fritted glass disc at the end and maintained at a constant room temperature using a cooling coil. This assembly was connected with the main compartment by the 30 cm long glass tube[3] with a *Luggin* capillary at the end.

All solutions were deaereted by pure argon gas which was presaturated by bubbling through the solvent.

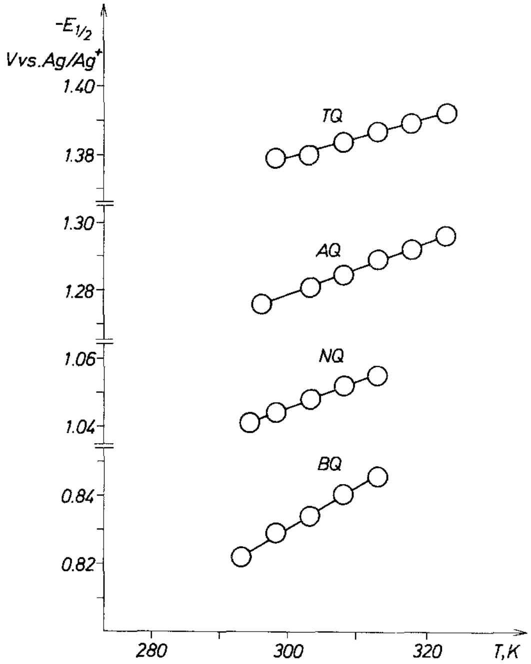


Fig. 1. Temperature dependences of the half-wave potentials for the reduction of *p*-quinones in *DMF*. The correlation coefficients of linear regression are given in Table 1

Numerical calculations for the *TQ* radical anion were made with an ODRA-1305 computer, using the method of *Hückel* and *McLachlan* with the same parametrization as in our previous paper[12].

Results and Discussion

Polarographic reduction of all quinones under investigation involves two one-electron steps. The first one is reversible and the radical anions do not form polarographically detectable ion pairs with the $(C_2H_5)_4N^+$ cations[12, 14, 15], so the half-wave potentials are good estimates of the standard potentials of quinone—semiquinone couples.

The variations in measured half-wave potentials with the temperature are shown in Fig. 1. The inspection of this figure indicates that the linear dependences exist for the four quinones under study. Thus the reaction entropy can be expressed by the temperature coefficient of the half-wave potential:

$$\Delta S_r^\circ = n F \mathrm{d} E_{1/2} / \mathrm{d} T \qquad (1)$$

where F is the Faraday constant and $n = 1$ is the number of electrons transfered.

The measured values of $\mathrm{d}E_{1/2}/\mathrm{d}T$ (with the errors determined on the basis of *Student*'s distribution with confidence level 0.95) and the calculated reaction entropies for all systems under investigation are summarized in Table 1. All values of $\mathrm{d}E_{1/2}/\mathrm{d}T$ and reaction entropies are negative as expected for the reduction processes of neutral molecules with the formation of radical anions which are more strongly solvated than the parent molecules, and thus a greater degree of solvent ordering in the vicinity of the depolarizer will be generated during the electron transfer. Such a result is in full agreement with the conclusions obtained from the entropy measurements for other aromatic compounds[3—5] as well as from investigation of the solvent effect on the redox potentials of quinones[12].

Table 1. *Temperature dependence of the half-wave potentials and reaction entropy for the reduction of p-quinones in DMF*

Quinone	n[a]	r[b]	$-\mathrm{d}E_{1/2}/\mathrm{d}T$ mV K^{-1}	$-\Delta S_r^\circ$ Jmol^{-1}K^{-1}	ρ_0[c]
BQ	5	0.999	1.2 ±0.1	116	0.196
NQ	5	0.999	0.8 ±0.1	77	0.167
AQ	6	0.999	0.74 ± 0.05	71	0.146
TQ	6	0.997	0.59 ± 0.07	57	0.138

[a] Number of data sets (different temperatures).
[b] Correlation coefficient of $E_{1/2}$ on T.
[c] Spin density at oxygen atom of semiquinone, calculated as in Ref.[12].

The reaction entropy of quinones in *DMF* is much higher than observed for alternant aromatic hydrocarbons[3] and comparable with that of heteroaromatic compounds (e.g. $\mathrm{d}E_{1/2}/\delta T = -0.557\,\mathrm{mV\,K^{-1}}$ for benzophenone in *ACN*[5]). Moreover, the values of ΔS_r° decrease with an increase in number of rings in the conjugated system. *Svaan* and *Parker* proposed a correlation between the entropy of formation of the anion radical and the parameter describing the localization of the charge on it. This parameter was calculated for the alternant hydrocarbons radicals as a sum of the squares of spin densities for all non-ring juncture positions, but only a qualitative correlation was found[3].

For the case of semiquinones the highest spin density is positioned at the oxygen atom of the carbonyl group and the interaction of the charge in this position mainly determines the solvation process as was suggested on the basis of ESR as well as the electrochemical measurements (c.f. the

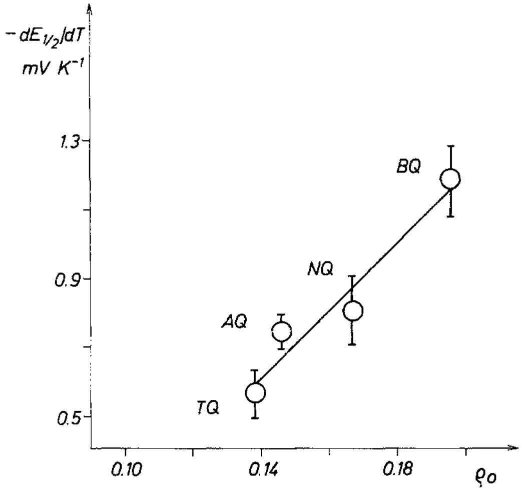
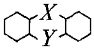


Fig. 2. Plot of — d $E_{1/2}$/d T for p-semiquinones vs. spin density at the position of the oxygen atom in the radical anion

Table 2. *Temperature dependences of the reversible potentials for oxidation of heteroaromatic compounds from Ref.*[4]*, experimental hyperfine splitting constants* a^X *and spin densities* ρ_X

No.	Compound 	X	Y	$-\mathrm{d}E^{\mathrm{rev}}/\mathrm{d}T$ mV K^{-1}	$a^{X\mathrm{a}}$ mT	Ref.[b]	ρ_X[c]
					$X = \mathrm{N}$		
1	Phenazine	N	N	0.205[d]	0.515[e]	16	0.185
2	*DMDHP*[f]	NCH_3	NCH_3	0.434	0.686	17	0.247
3	Phenoxazine	NH	O	0.627	0.790	18	0.284
4	Phenothiazine	NH	S	0.626	0.650	19	0.234
5	N-Methylphenothiazine	NCH_3	S	0.530	0.750	20	0.270
					$X = \mathrm{S}$		
6	Phenoxathiine	S	O	0.824	1.191	21	0.357
7	Thianthrene	S	S	1.098	0.915	21	0.274
					$X = \mathrm{Se}$		
8	Phenoxaselenin	Se	O	1.046	3.95	22	0.321

[a] ESR measurements in *ACN*, nitromethane and nitroethane for compounds 1–4, 5–7 and 8, respectively.

[b] References for ESR measurements.

[c] Spin densities are calculated using eq.: $a^X = Q^X \cdot \rho_X$ with the following parameters: $Q^{\mathrm{N}} = 2.78\,\mathrm{mT}$ from Ref.[19], $Q^{\mathrm{S}} = 3.34\,\mathrm{mT}$ from Refs.[19,21] and $Q^{\mathrm{Se}} = 12.3\,\mathrm{mT}$ from Ref.[22].

[d] $\mathrm{d}E^{\mathrm{rev}}/\mathrm{d}T$ for the reduction process.

[e] a^{N} value for the radical anion.

[f] *DMDHP* is 9,10-dimethyl-9,10-dihydrophenazine.

discussion in Ref. [12]). Thus the spin density at the position of oxygen atom, ρ_0, can be used for the correlation with the obtained reaction entropies, similarly as just the ρ_0 values could describe the sensitivity of the half-wave potential to the solvent effect[12]. The proposed relationship is indeed remarkable with a correlation coefficient of linear regression $r = 0.970$, as is shown in Fig. 2.

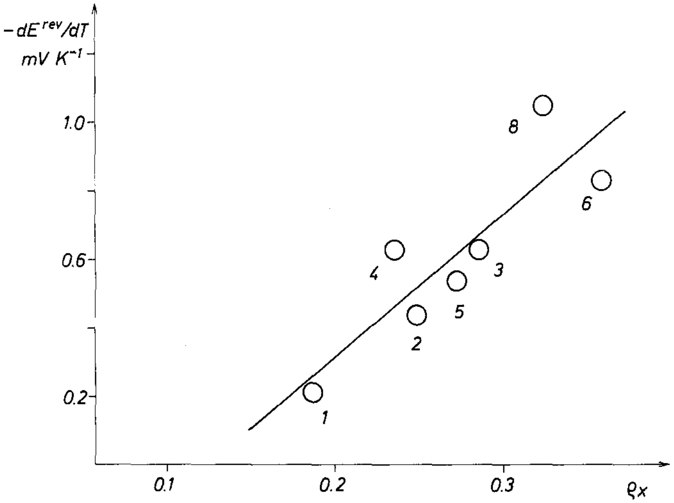


Fig. 3. Relationship between dE^{rev}/dT from Ref.[4] and spin density ρ_X from Table 2; numbers of compounds as in Table 2

A similar approximation can be also used for describing the change in the reaction entropy for the electrooxidation of a few compounds related to anthracene (but with the heteroatoms N, S, O and Se at 9 and 10 positions) reported by *Svaan* and *Parker*[4] and discussed only qualitatively as related to the ease of the formation of a planar structure, favorable for the delocalization of the charge at the radical cation. Taking into account the experimental hyperfine splitting constants (hsc) for ^{14}N, ^{33}S and ^{77}Se atoms in ESR measurements (collected in Table 2) and its simple proportionality to spin density, it is possible to find the experimental spin densities, ρ_X, at the heteroatom X which has the highest spin density in the radical. The ρ_X values (Table 2) correlate with the entropy factor, as is shown in Fig. 3. Only the point for thianthrene considerably deviates from the correlation line. It should be mentioned here that in the more advanced theory of calculating the hsc values the spin densities at carbon atoms adjacent to the heteroatom are also taken into account[21,23,24], but the lack of these quantities from experiment does not allow to improve the observed correlation.

From this it follows that the polarographic method can be useful in determining the entropy of formation of semiquinones at the electrode, ΔS_r°, which in turn is important in comprehending the role of solvent in the electroreduction process. Further investigations including other solvents are in progress.

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