Temperature Dependence of Radical-Anion Salts Disproportionation. The Nature of Radical-Anion and Dianion Aggregation with the Various Alkali Cations

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Abstract: A potentiometric technique is described for determining the temperature dependence of difference between the first and second redox potentials of electron acceptors ($\epsilon_2 - \epsilon_1$). Since $\epsilon_2 - \epsilon_1$ gives $\Delta G°$ of the disproportionation, $2Ar^-\cdot,Cat^+ \rightleftarrows Ar + Ar^{2-},2Cat^+$, the obtained data yield $\Delta H°$s and $\Delta S°$s for those reactions. The described method was applied to the disproportionation of salts of perylene (Pe) radical anions in THF with Li^+, Na^+, K^+, and Cs^+ counterions, respectively. The results revealed interesting structural differences in the behavior of sodium perylenide in THF when compared with its lithium, potassium, and cesium salts.
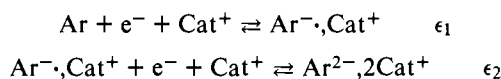
The equilibria and kinetics of radical anions disproportionations were extensively studied in our laboratory.[1-4] We found that the interaction of radical anion with cation and the kind of aggregation taking place between cations and a dianion greatly affect these equilibria. These effects could be better understood if the thermodynamic parameters of the disproportionation, i.e., the respective $\Delta H°$s and $\Delta S°$s, were available. The temperature dependence of such disproportionations was investigated only for two systems: the radical anions of tetraphenylethylene[1a,1d] and of cyclooctatetraene.[5] More extensive information on this subject is therefore desirable.

Potentiometric Technique

We developed now a simple potentiometric technique that allows us to determine the $\Delta H°$s and $\Delta S°$s of radical anions disproportionation. The apparatus used in these studies is shown in Figure 1. It consists of two bulbs linked by an U-tube with two glass sinter plates sealed in. Platinum electrodes are inserted into each bulb, and these are connected to the terminals of a Fluke 871-A, dc differential voltmeter of an infinite resistance.

A solution of an investigated salt of a radical anion mixed with equimolar amount of the parent hydrocarbon was introduced into one of these bulbs, while a 1:1 mixture of the radical anion and dianion salts dissolved in the same solvent was placed in the other. Typically 10^{-3} M solutions were employed. The U-tube was filled with a relatively concentrated solution of a readily dissociated salt sharing a common cation with the studied solutions, e.g., $NaBPh_4$ when sodium salts were investigated or $CsB(CN)Ph_3$ when we studied Cs salts. The evacuated and sealed off unit was immersed in a Dewar filled with ethanol and the difference of potentials between the two half-cells determined as a function of temperature. The measured potential was highly reproducible, being constant at any fixed temperature for many hours. The measurements were performed at a series of temperatures rising from −55 to +25 °C, and then again at a series of falling temperatures. The results of both series were concordant.

Assuming that the potential of the liquid junction is negligible, we identify the measured potential differences with $\epsilon_2 - \epsilon_1$

$$Ar + e^- + Cat^+ \rightleftarrows Ar^-\cdot,Cat^+ \qquad \epsilon_1$$

$$Ar^-\cdot,Cat^+ + e^- + Cat^+ \rightleftarrows Ar^{2-},2Cat^+ \qquad \epsilon_2$$

Here, Ar, $Ar^-\cdot,Cat^+$ and $Ar^{2-},2Cat^+$ denote the investigated aromatic hydrocarbon and its radical anion and dianion salts, respectively.

Experimental Section

The apparatus and its operation are described in the preceding section. In this investigation we studied disproportionation of perylene radical anions in THF with Li^+, Na^+, K^+, and Cs^+ counterions. The purification of the solvent and of the hydrocarbon followed the now well-known high-vacuum technique.[6] The Na and K salts of radical anions and dianions were prepared by reducing the hydrocarbon with mirrors produced by the conventional technique. Cesium azide was used in preparation of Cs mirror. Lithium salts were prepared by contacting the hydrocarbon solutions with chunks of metallic lithium, its surface being cleaned by allowing the chunks to react with THF solution of perylene, discarding the products, and washing the shiny surface with purified THF.

The degree of reduction was controlled spectrophotometrically, and the composition determined from the absorbance at the appropriate λ_{max}s of perylene radical anion and dianion.

Results

The results obtained for the perylene (Pe) system in tetrahydrofuran (THF) with Li^+, Na^+, K^+, and Cs^+ cations are summarized in Table I. The listed K_{dispr}s are calculated from the relation $-RT \ln K_{dispr} = F(\epsilon_1 - \epsilon_2)$. The respective van't Hoff plots, as well as the plots of $\epsilon_2 - \epsilon_1$ vs. T, are exemplified by Figure 2. Slopes of the former curve give $\Delta H°_T$, whereas $\Delta S°_T$s are calculated from the slopes of the latter curve, both pertaining to the appropriate temperature range. The experimental uncertainties are 0.1–0.2 kcal/mol for the $\Delta H°_T$s and about 1 eu for the $\Delta S°_T$s. This might lead to a slight difference between the K_{dispr} listed in Table I and its value calculated from the relation $-RT \ln K_{dispr} = \Delta H° - T\Delta S°$. Both plots are linear over the whole investigated temperature range of −55 to +25 °C for the Na^+, K^+, and Cs^+ salts, whereas Figure 2 shows a pronounced curvature in the $\epsilon_2 - \epsilon_1$ vs. T plot and a slight curvature in the van't Hoff plot for the Li^+ salt. The thermodynamic parameters obtained from these plots are collected in Table II.

Discussion

The investigated disproportionations refer to ion pairs. The concentration of free ions is depressed by their relatively high concentration and the presence of salts sharing common cation with the radical anions. All these reactions are endothermic, the electron–electron repulsion in the dianions being the main factor contributing to the endothermicity. The endothermic character of disproportionation of some radical anions was previously reported by other investigators[7-9] and by our group.[1a,d] The striking increase of $\Delta S°$ for the Na^+ system
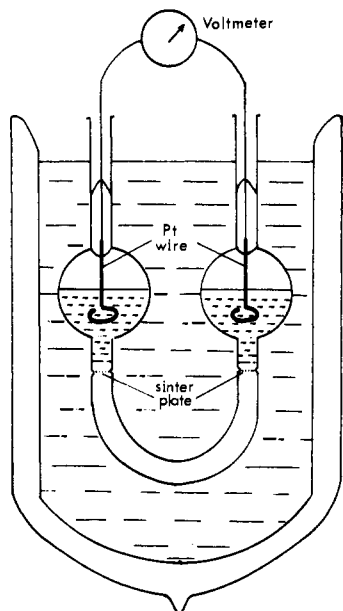
Figure 1. Schematic drawing of the apparatus used to determine the temperature dependence of $\epsilon_2 - \epsilon_1$.

Table I. Temperature Dependence of $\epsilon_2 - \epsilon_1$ for the Reductions in THF of $Pe + e^- + Cat^+ \rightleftarrows Pe^-,Cat^+$ (ϵ_1); $Pe^-,Cat^+ + e^- + Cat^+ \rightleftarrows Pe^{2-},2Cat^+$ (ϵ_2)[a]

T, °C	$-(\epsilon_2 - \epsilon_1)$, mV	k_{dispr}	T, °C	$-(\epsilon_2 - \epsilon_1)$, mV	K_{dispr} K_{dispr}
		System Li$^+$			
−55	573.5	5.2×10^{-14}	−10	564.5	1.5×10^{-11}
−50	573.5	1.0×10^{-13}	−5	562.5	2.5×10^{-11}
−45	573.0	2.0×10^{-13}	0	560.0	4.4×10^{-11}
−40	572.5	3.9×10^{-13}	+5	557.5	7.4×10^{-11}
−35	571.5	7.4×10^{-13}	+10	554.5	1.3×10^{-10}
−30	570.5	1.4×10^{-12}	+15	551.5	2.1×10^{-10}
−25	569.5	2.5×10^{-12}	+20	549.0	3.4×10^{-10}
−20	568.5	4.5×10^{-12}	+25	546.0	5.6×10^{-10}
−15	566.5	8.2×10^{-12}	+28	544.0	7.4×10^{-10}
		System Na$^+$			
−57	549.5	1.4×10^{-13}	−10	412.0	1.2×10^{-8}
−49	530.5	1.1×10^{-12}	0	385.5	7.4×10^{-8}
−40	505.0	1.1×10^{-11}	+10	360.0	3.8×10^{-7}
−30	475.5	1.3×10^{-10}	+20	336.0	1.6×10^{-6}
−20	442.5	1.5×10^{-9}	+25	327.0	2.9×10^{-6}
		System K$^+$			
−55	404.5	4.2×10^{-10}	−5	354.0	2.1×10^{-7}
−45	397.0	1.6×10^{-9}	0	350.0	3.4×10^{-7}
−35	386.0	6.5×10^{-9}	+5	345.5	5.3×10^{-7}
−25	374.5	2.3×10^{-8}	+15	337.0	1.2×10^{-6}
−15	364.0	7.4×10^{-8}	+25	328.0	2.8×10^{-6}
		System Cs$^+$			
−55	338.0	1.5×10^{-8}	−5	307.5	1.6×10^{-6}
−45	331.0	4.7×10^{-8}	0	304.0	2.4×10^{-6}
−34	322.0	1.6×10^{-7}	+5	301.0	3.4×10^{-6}
−25	317.5	3.4×10^{-7}	+15	292.5	7.5×10^{-6}
−15	312.5	7.6×10^{-7}	+25	283.5	1.6×10^{-5}

[a] The $\epsilon_2 - \epsilon_1$ values are rounded up to the nearest 0.5 mV.

when compared with other cation systems calls for comments. Apparently Li$^+$ ions are fully solvated by THF whether associated with Pe$^-$· or Pe^{2-}. This is most evident at the lowest
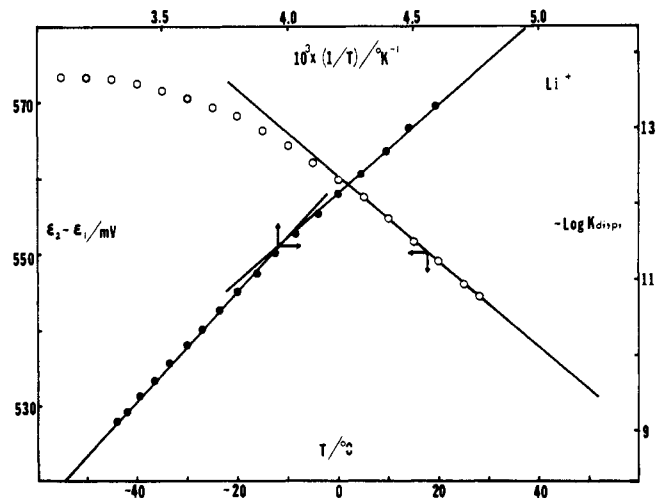

Figure 2. Plots of log K_{dispr} vs. $1/T$ and $\epsilon_2 - \epsilon_1$ vs. T for Pe$^-$·,Li$^+$ in THF.

Table II. $\Delta H°$ and $\Delta S°$ for the Disproportionation in THF $2Pe^-,Cat^+ \rightleftarrows Pe + Pe^{2-},2Cat^+$ (K_{dispr})[a]

Cation	Temp range, °C	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, eu
Li$^+$	−55 to −40	13.2	0.0
Li$^+$	0 to +25	16.14	11.9
Na$^+$	−55 to +25	26.9	65.8
K$^+$	−55 to +25	14.15	22.2
Cs$^+$	−55 to +25	11.0	15.0

[a] ΔH from van't Hoff plot; ΔS from a plot $\epsilon_2 - \epsilon_1$ vs. T.

temperatures, a slight desolvation on disproportionation seems to take place at higher temperatures. The K$^+$ and Cs$^+$ ions seem to be poorly solvated (probably externally) in either associates. Hence, the disproportionation in these systems leads only to a small gain in entropy. On the other hand, the Na$^+$ ions seem to be fully solvated when associated with Pe$^-$· but become partially desolvated on forming Pe^{2-},2Na$^+$ aggregates. This accounts for the large $\Delta S°$ as well as for the substantial increase in $\Delta H°$. Thus, the peculiar behavior of the Na$^+$ salts, reported previously,[2,4a] is rationalized.

References and Notes

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