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TETRAANIONS OF ACEPLEIADYLENE AND PYRENE? AN ELECTROCHEMICAL STUDY

John Mortensen, Jürgen Heinze*

Institut für Physikalische Chemie der Universität Freiburg,
Albertstrasse 21, D-7800 Freiburg

Summary: Acepleiadylene can be electrochemically reduced to its tetraanion at -57°C using THF as solvent and $LiBPh_4$ as supporting electrolyte.
(E_1^o = -1.85V, E_2^o = -2.51V, E_3^o = -3.11V, E_4^o = 3.14V vs. Ag/AgCl).
All attemps to generate the tetraanion of the isoelectronic pyrene under different conditions failed.

Acepleiadylene (1) is an isomer of pyrene (2). Both compounds are reported to form tetraanions through a four-electron redox process via alkali-metal reduction[1,2]. Müllen et al.[1] succeeded in generating the tetraanion of 1 by reduction with Li in THF at -80°C. Rabinovitz et al.[2] described the formation of 2^{4-} at 20°C using Na in THF as reduction agent. The arguments concerning the generation and stability of these supercharged species rest exclusively on spectroscopic and chemical findings. Corresponding electrochemical measurements, which could independently confirm these results, have not previously been carried out. We have studied the electrochemical reduction of 1 and 2 by arranging almost the same experimental conditions described in previous works [1,2]. Surprisingly, only 1 gives a tetraanion, whereas 2 yields a dianion.

As protic and electrophilic impurities, which are normally present in the solution, will react with highly charged anions in electrochemical experiments the whole system including the cell must be purified very carefully to fulfill superdry conditions [3,4]. Given these prerequisites we have used THF as solvent and Na- or $LiBPh_4$ [5] as supporting electrolytes. Both electrolytes exhibit typical ion-pairing effects which will decrease at low temperatures as a consequence of the increasing solvent permittivity. In general the Li-cation will be more strongly solvated than sodium. Therefore, the background limit for an Li-salt is more negative than for an Na-electrolyte. We observed at 0°C the reduction of Na at -2.87V vs. Ag/AgCl and of Li at -3.07V [6]. On the other hand, the Li-cation will shield the negative charges in the aromatic anions more easily than Na on account of its small radius. This behavior should be predominant at supercharged anions. Combining these effects led us to expect that tetraanions should be generated most easily in the presence of Li-cations at very low temperatures.

At first, we studied the electroreduction of **1** and **2** in THF in the presence of $NaBPh_4$ by cyclic voltammetry (Pt-working electrode). In both cases two well-separated reversible one-electron transfer steps are observed (Table 1). Lowering the temperature to -50°C the Na-reduction background limit shifts negatively as well as the dianion redox-potentials. Neither a tetraanion wave nor trianion wave are visible in the whole temperature range. Furthermore, the apparent potential of the Na^+ reduction lies in the vicinity of the $\mathbf{2}^{1-}/\mathbf{2}^{2-}$ redox potential (ΔE = 150 mV), not of the corresponding $\mathbf{1}^{1-}/\mathbf{1}^{2-}$ value (ΔE = 500 mV), which obviously excludes the existence of the tetraanion of **2** under the given conditions.

Table 1: Reduction Potentials of **1** and **2** THF ($NaBPh_4$, $LiBPh_4$) vs. Ag/AgCl [a)]

		1				**2**			
Supp. el.		25°C	0°C	-30°C	-60°C	25°C	0°C	-30°C	-60°C
$NaBPh_4$	R/R^-	-1.83	-1.835	-1.84	-1.84	-2.27	-2.28	-2.28	
	R^-/R^{2-}	-2.34	-2.365	-2.40	-2.51	-2.73	-2.77	-2.81	
$LiBPh_4$	R/R^-		-1.84	-1.84	-1.85		-2.29	-2.29	-2.29
	R^-/R^{2-}		-2.49	-2.50	-2.51		-2.91	-2.93	-2.97
	R^{2-}/R^{3-}				-3.11 b)				
	R^{3-}/R^{4-}				-3.14 b)				

a) Experimental data were obtained using a three-electrode cell compartment [3,4]; Electrode potentials were controlled by a PAR Model 173 potentiostat.

b) Potentials were computed by digital simulation.

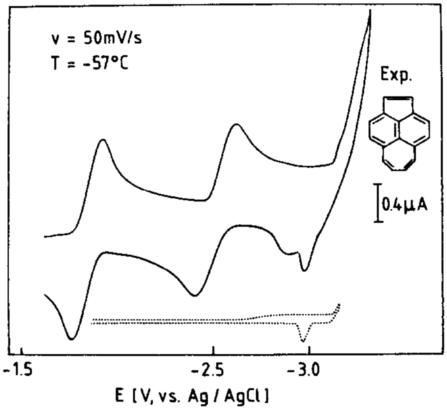

Fig. 1: ——: Experimental CV-diagram of **1** in THF/$LiBPh_4$; .....: experimental background voltammogram of $LiBPh_4$ in THF; Ref.: Ag/AgCl, working electrode: Pt.

The use of $LiBPh_4$ as supporting electrolyte enhances the gap between the dianion formation of $\mathbf{1}^{2-}$ or $\mathbf{2}^{2-}$ and the supporting electrolyte reduction. Nevertheless, in the case of **2** no further wave indicating a third or fourth electron-transfer could be observed (Table 1).

However, a modified situation results from the reduction of **1**. Already at $0^{o}C$ a slight rise of the current potential curve near -3.00V indicates a further charge-transfer step. At $-57^{o}C$ a steep single wave becomes visible below -3.10V vs. Ag/AgCl (Fig. 1). To avoid misinterpretation the background curve of the supporting electrolyte ($LiBPh_4$), whose current rises below -3.20V vs. Ag/AgCl, was subtracted from the voltammogram of **1**. The resulting difference voltammogram (Fig. 2a) was used for the further evaluation of the data. It becomes clear that the small peak in the reverse scan of the original CV of **1** (Fig. 1) is due to the reoxidation of partially reduced Li.

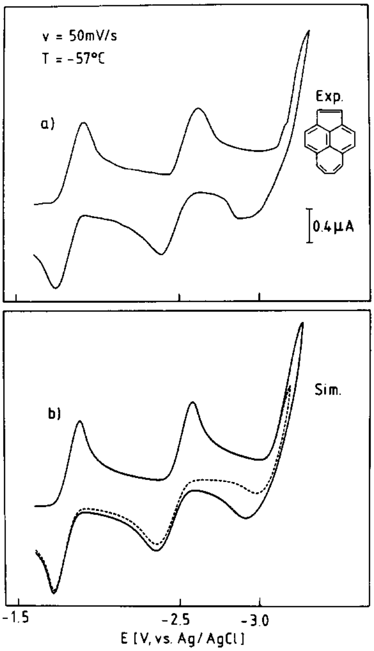

Fig. 2: Experimental and simulated CV-diagrams of **1**

a) Background corrected CV of **1**. The potential axis of the subtracted background curve was corrected for iR-effects.

b) Digital simulation (including iR-effects) of **1** (.....) assuming trianion formation, (—) assuming tetraanion formation, E^{o} values see Table 1.
($k_3^{o} = 3,1 \cdot 10^{-4}$ cm/s, $k_4^{o} = 1,3 \cdot 10^{-4}$ cm/s)

Digital simulation based on an implicit Crank-Nicolson model [7] proves that two charge-transfer steps with nearly degenerated redox potentials (Fig. 2b) lead to the tetraanion of **1**. The assumption of a trianion formation can be excluded as the digital simulation in this case indicates a very small voltammetric response, which does not fit the experimental data.

The unusual shape of the CV in the reduction range of the tri- and tetraanion is a result of the sluggishness of the heterogeneous charge transfer at such supercharged anions [8].

The very small ΔE^0-gap between the $\mathbf{1}^{2-}/\mathbf{1}^{3-}$ and $\mathbf{1}^{3-}/\mathbf{1}^{4-}$ redox couples is not, as might be assumed, an intrinsic property of the molecule but is due to the strong ion-pairing with the supercharged ions. Voluminous counterions e.g. tetrabutylammonium ions normally change the disproportionation equilibrium by several orders of magnitude [8].

The electrochemically induced tetraanion formation of **1** fully confirms the results obtained by Müllen [1]. For the reasons given above, $\mathbf{1}^{4-}$ exists only at temperatures below -40°C. The failure to generate $\mathbf{2}^{4-}$ electrochemically does not, in principle, exclude its existence, but makes its preparation under conditions reported in the literature [2] unprobable. It seems reasonable to assume that the monohydroanion, rather than the tetraanion, of **2** was formed by protonation of the dianion [9, 10].

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