Two-Electron Stepwise Redox Processes in the Boron Subhalide Cluster Series

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Many redox active compounds have more than two oxidation states [1,2]. This gives rise to several electron transfer steps. The relative thermodynamics of these steps controls whether intermediate oxidation states are stable or subject to disproportionation. In the case of three redox states, for example, two electrons can be transferred. Only if the second electron transfer is thermodynamically more favourable than the first one, disproportionation occurs. In this case, a single voltammetric two-electron signal is observed. Such "potential inversion" cases are usually linked to the occurrence of considerable structural changes upon oxidation or reduction [1,3].

We investigated a series of binary boron halide cluster compounds, the boron subhalides $\mathrm{B}_n\mathrm{Hal}_n$ ($n = 10, 9, 8, 6$) by cyclic voltammetry and chronocoulometry in acetonitrile or dichloromethane [4,5], and expected increasing effects of the molecular structure on the electrochemical processes with decreasing cage size. In this contribution particular emphasis will be placed on the $\mathrm{B}_6\mathrm{Hal}_6^{2-}$ dianions [6], of which only a single oxidation peak had been reported before the present study.

Either the neutral clusters or their dianions were used as the starting compounds. In all cases, a considerable splitting of the redox potentials of the two redox steps neutral/radical anion and radical anion/dianion of up to 1 V were observed. Although X-ray analyses of several radical anions from this series of compounds (see, e.g. [7]) show characteristic differences to the starting compounds, potential inversion was never observed.

On the other hand, the electrochemical experiments revealed that the neutral clusters, which are of the hypercloso type, are readily reduced to the radical anions by a homogeneous chemical process in the organic electrolytes, giving rise to characteristic voltammograms. Furthermore, in some cases the "curve crossing" phenomenon in cyclic voltammograms is observed.

Electrochemical and chemical parameters were estimated from the experimental curves by means of comparison to computer simulations and will be discussed in terms of cage size and halide properties.

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