

Single Two-Electron Transfers in the Electrochemical Oxidation and Reduction of Carotenoids

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With most molecules, the second electron is more difficult to add (or to remove) than the first, resulting, in cyclic voltammetry, in two successive one-electron reversible waves. The reason for this behavior is the large coulombic repulsion between the two injected charges, which is only partially compensated by the increase of the solvation free energy upon going from the starting molecule to the radical mono-ion and then to the di-ion. However, it has been shown for several systems that the removal of the second electron could be significantly easier than the first one [1-3]. In most of such systems the removal of the second electron is accompanied by important structural changes, often involving the release of steric constraints [1]. Such inverted redox potentials are also observed in carotenoid molecules for which no major structural changes are expected [2,3]. Cyclic voltammetry of several symmetrical carotenoid molecules revealed the inversion of the standard potentials of the first and second electron transfers in the oxidation of beta-carotene (1) and 15,15'-didehydro-beta-carotene (2) as well as in the reduction of canthaxanthin (3). At the same time, the reduction of carotenoids (1) and (2) as well as the oxidation of (3) did not reveal the this potential inversion. The factors that control potential inversion in carotenoid systems, and more generally in symmetrical molecules containing long polyene chains, were investigated by quantum chemical calculations. Geometry optimizations and energy calculations were performed with the Gaussian 98 package. Solvation free energies were calculated on the gas phase optimized conformations according to the self consistent reaction field method using the polarized continuum (overlapping spheres) model. Two main factors that control the potential inversion in the symmetrical polyene chain compounds were identified. One is the localization of the charges in the di-ion towards the ends of the molecule at a large distance from one another, thus minimizing coulombic repulsion. The same effect favors the solvation of the di-ion providing additional stabilization. In contrast, the charge in the ion radical is delocalized over the whole molecular framework, thus disfavoring its stabilization by interaction with the solvent. The combination of the two solvation effects allows potential inversion to occur as opposed to the case where the two electrophores are linked by a saturated bridge where potential inversion cannot

occur. Localization of the charges in the di-ion, and thus potential inversion, is favored by the presence of electron-accepting terminal groups for reductions (as the two carbonyl groups in canthaxanthin) and of hole-accepting terminal groups for oxidations (as in beta-carotene).

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