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The pecking order of free radicals and antioxidants: lipid peroxidation, alpha-tocopherol, and ascorbate.

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Abstract

Free radicals vary widely in their thermodynamic properties, ranging from very oxidizing to very reducing. These thermodynamic properties can be used to predict a pecking order, or hierarchy, for free radical reactions. Using one-electron reduction potentials, the predicted pecking order is in agreement with experimentally observed free radical electron (hydrogen atom) transfer reactions. These potentials are also in agreement with experimental data that suggest that vitamin E, the primary lipid soluble small molecule antioxidant, and vitamin C, the terminal water soluble small molecule antioxidant, cooperate to protect lipids and lipid structures against peroxidation. Although vitamin E is located in membranes and vitamin C is located in aqueous phases, vitamin C is able to recycle vitamin E; i.e., vitamin C repairs the tocopheroxyl (chromanoxyl) radical of vitamin E, thereby permitting vitamin E to function again as a free radical chain-breaking antioxidant. This review discusses: (i) the thermodynamics of free radical reactions that are of interest to the health sciences; (ii) the fundamental thermodynamic and kinetic properties that are associated with chain-breaking antioxidants; (iii) the unique interfacial nature of the apparent reaction of the tocopherol free radical (vitamin E radical) and vitamin C; and (iv) presents a hierarchy, or pecking order, for free radical electron (hydrogen atom) transfer reactions.

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