Carotene and Limonene Cooxidation: Experimental Study and Computer Simulation

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The question of whether β-carotene is a negative or a positive oxidation catalyst for lipids was discussed for a long time. The investigations of the influence of β-carotene on lipid oxidation demonstrate that its role as an antioxidant depends on the environment[13] and that its inhibition activity is related to both oxygen concentration and to the presence of other antioxidants. In this study limonene (4-isopropenyl-1-methyl-1-cyclohexene) (LH) was chosen as a model lipid.

Kinetics of limonene (R+) (LH) and β-carotene (A) oxidation by molecular oxygen and effect of β-carotene on the limonene autoxidation was investigated. Oxygen uptake, peroxide accumulation, and β-carotene consumption were measured at different initial β-carotene concentration and partial oxygen pressure, and kinetic characteristics of individual LH and A autoxidations and their cooxidation were determined.

β-Carotene exhibits high activity in the reactions with peroxyl and C-centered radicals. The reversible reaction of oxygen addition to β-carotene-derived C-centered radicals (A^*), fast cross-disproportionation reactions of A^* and peroxyl polyene radicals (AO_2^*) are responsible for the pronounced effect of oxygen partial pressure on the kinetics of β-carotene consumption and its antioxidant efficiency in the limonene autoxidation.

The mechanism of limonene and β-carotene oxidation covering the main pathways for formation, transformation and decay of free radicals has been formulated. The rate constants for the elementary reactions of both limonene and β-carotene with initiator and substrate derived C-centered (L*, A*) and peroxyl radicals (LO2*, AO2*) in solution were determined. Computer modeling has been used to solve numerically the reaction kinetics combining the experimental kinetic parameters and the literature data on the corresponding rate constants. The model proposed enables analysis of the kinetics of β-carotene consumption and oxygen uptake under various conditions as well as the assessment of the influence of β-carotene on oxidation of limonene and other substances, which is in considering agreement with the experimental data obtained.