

Comparative Numerical Study on The Action of Tocopherols as Antioxidant in Methyl Linoleate Peroxidation Reaction.

Levon A. Tavadyan¹, Avet A. Khachoyan¹, Gagik A. Martoyan¹, Afaf Kamal-Eldin²

¹Institute of Chemical Physics NAS of Armenia, Yerevan, Republic of Armenia,

²Dept. of Food Science Swedish Univ. of Agric Sci., Uppsala, Sweden

Tocopherols (Toc) are main antioxidants that exist in cellular membranes and edible oils and protect lipids from peroxidation and oxidation damage. The objective pursued in this work is to compare the antioxidant action of different tocopherols (α -Toc, β -Toc, γ -Toc, δ -Toc) using value numerical analysis with revealing of the role and kinetic significance of individual steps and chemical species. The reaction mechanism of methyl linoleate peroxidation reaction by α -tocopherol inhibition, constructed earlier by us, was chosen as a starting kinetic model. In the case of β -, γ -, δ -tocopherols, the rate constants of the corresponding reactions were changed, and steps were excluded or added according to the chemism of autooxidative conversions of the corresponding tocopherols. The kinetic models adequately and numerically describe the existing experimental results. Value numerical analysis allowed revealing the following differences in the antioxidant activities of various tocopherols.

- ❖ At relatively high initial concentrations of tocopherols ($[\text{TH}] > 2 \times 10^{-3}$ M, an order of antioxidant activity, $\alpha < \beta < \gamma < \delta$, opposite to antiperoxyradical scavenging activity is observed and is explained by several reasons:
 - a. This series is mainly conditioned by the increase of the role of prooxidant action of the autoinitiation reaction with the participation of hydroperoxide molecules (LOOH) and tocopherols.
 - b. In this series, the increase of the rate constant magnitudes of the dominant reactions of the chain propagation with the participation of tocopheroxyl radicals (T^\bullet) leading to tocopherol-mediated-peroxidation reaction is compensated by the increase of the concentration of peroxy radicals participating in the cross reaction of the chain termination with T^\bullet
- ❖ At low concentrations, $[\text{TH}]_0 < 4 \times 10^{-4}$ M, the reverse to antioxidant activity of tocopherols takes place in the series $\alpha > \beta > \gamma > \delta$. Under these conditions the dominant reaction of the chain propagation is the reaction $\text{LOO}^\bullet + \text{LH} \rightarrow \text{LOOH} + \text{L}^\bullet$. The given series of the decrease of antioxidant activity is conditioned by the methyl linoleate peroxidation reaction chain length

growth and inessential pro-oxidant action on the peroxidation reaction with the participation of LOOH molecules and tocopherols.