MULTIPLE CHAIN TERMINATION BY NITROXYL RADICALS DURING THE OXIDATION OF METHYL LINOLEATE IN MICELLES AS A METHOD OF IDENTIFICATION OF HYDROPEROXIDE

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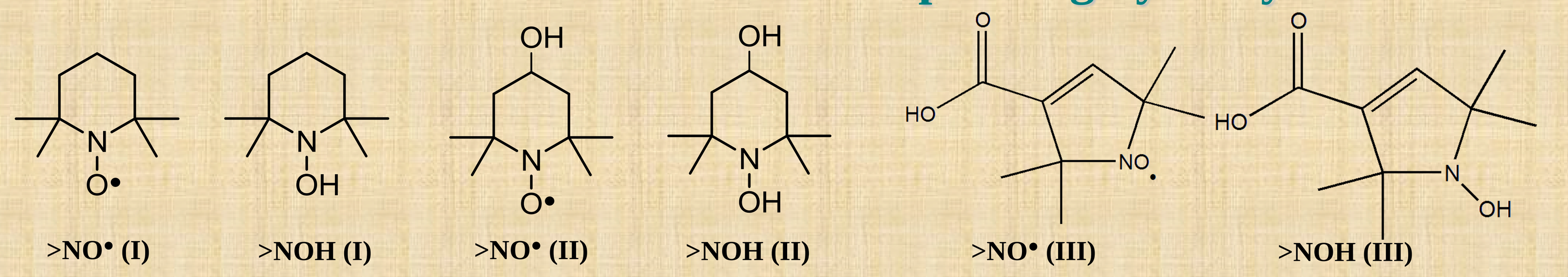
Objective: Establishing of the mechanism of radical chain oxidation of methyl linoleate (LH) in solutions and micelles in the presence of stable nitroxyl radicals.

Methods: Oxygen monitoring: capillary micro-volumetry (in solutions), Biological oxygen monitor (YSI Model 5300A – in micelles); ESR-spectroscopy (CMS 8400, Adani); Gas chromatography (Perkin Elmer, Clarus 600); Kinetic modeling (Kinetics-2012); Quantum-chemical analysis (DFT B3LYP/6-311++G[d,p])

Conditions: solution of LH in chlorobenzene or aqueous micelles at 37.0 ± 0.1 ºC.
Initiators: 2,2'-Azobis(2,4-dimethyl)valeronitrile (AMNV) and 2,2'-Azobis(2-methylpropionamidine)dihydrochloride (AAPH).
Surfactant: Triton X-100

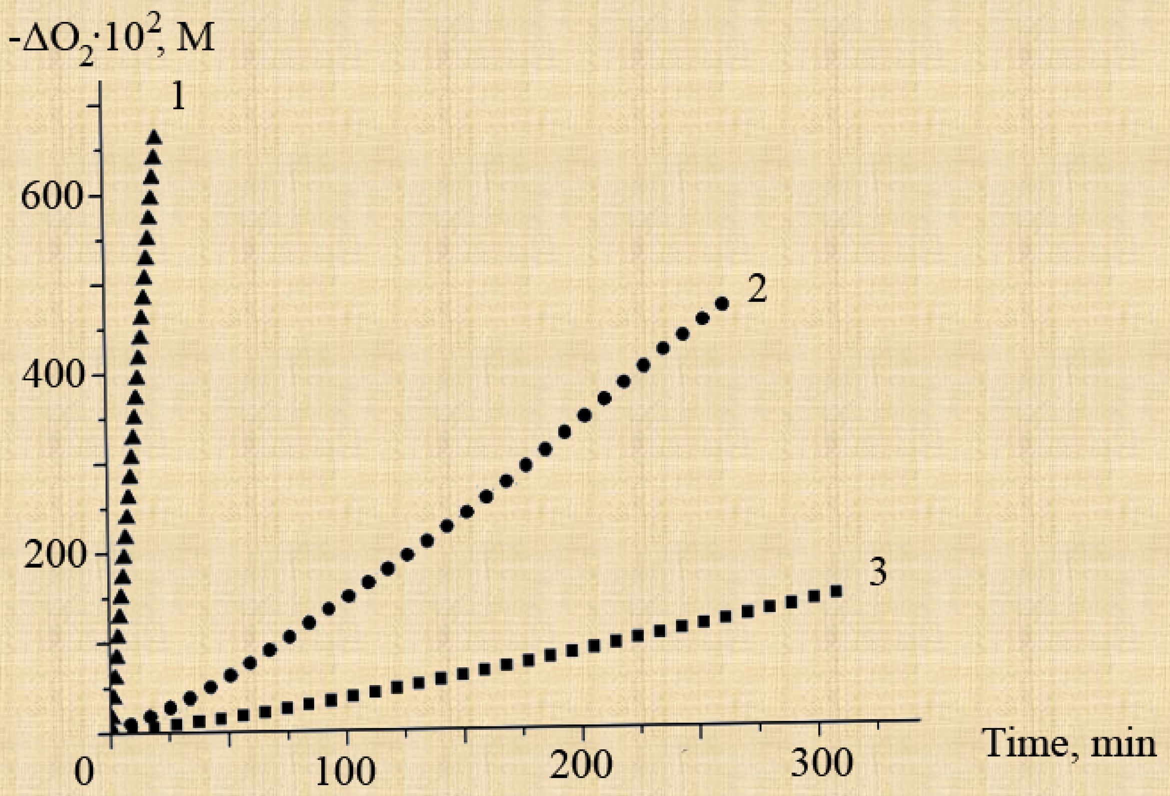
LH oxidation conditions in micelles: aqueous phosphate buffer with pH = 7.4 at 37 °C

Structural formulas of >NO• used and corresponding hydroxylamines >NOH



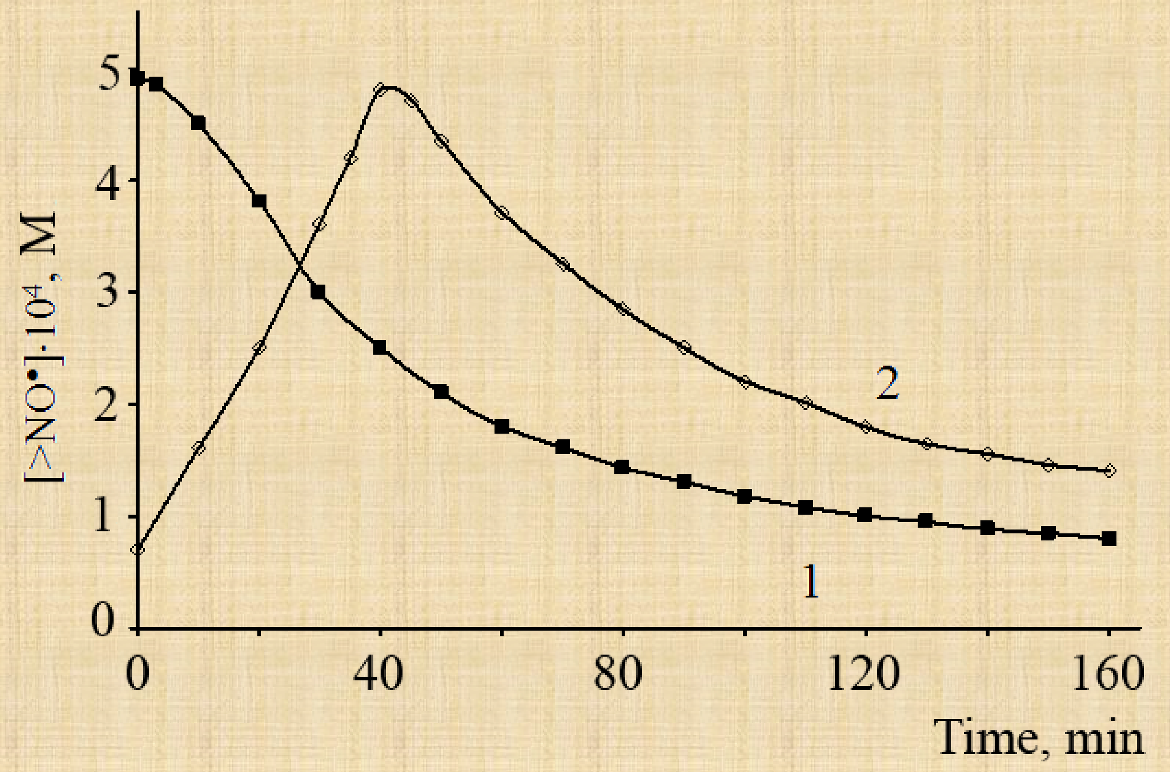
Oxidation in solution

Typical kinetics of oxygen absorption during the LH oxidation in chlorobenzene



[LH] = 2.4 M, P_{O2} = 20 kPa; [>NO• (I)], M: 0 (*1*), $3.31{\cdot}10^{-5}$ (*2*), $8.2{\cdot}10^{-5}$ (*3*); $W_i = 3.6{\cdot}10^{-8}$ M·s^{-1}

>NO• consumption and accumulation out of the corresponding hydroxylamine during the LH oxidation in chlorobenzene



[LH] = 2.4 M; $W_i = 2.4{\cdot}10^{-7}$ M·s^{-1}; P_{O2} = 20 kPa;
1 – $[>NO^•(II)]_0 = 4.9{\cdot}10^{-4}$ M; *2* – $[>NOH(II)]_0 = 5.0{\cdot}10^{-4}$ M.

Process rate does not measure up the non-inhibited reaction rate after the theoretical induction time (τ_{ind}). Thus, for curve *3* τ_{ind} is about 20 min, while after 200 min oxidation proceeds with a constant rate which is almost three times lower than the non-inhibited process rate.

Chromatography analysis results given below shows that only part of the added nitroxyl radical is consumpted during the induction period:

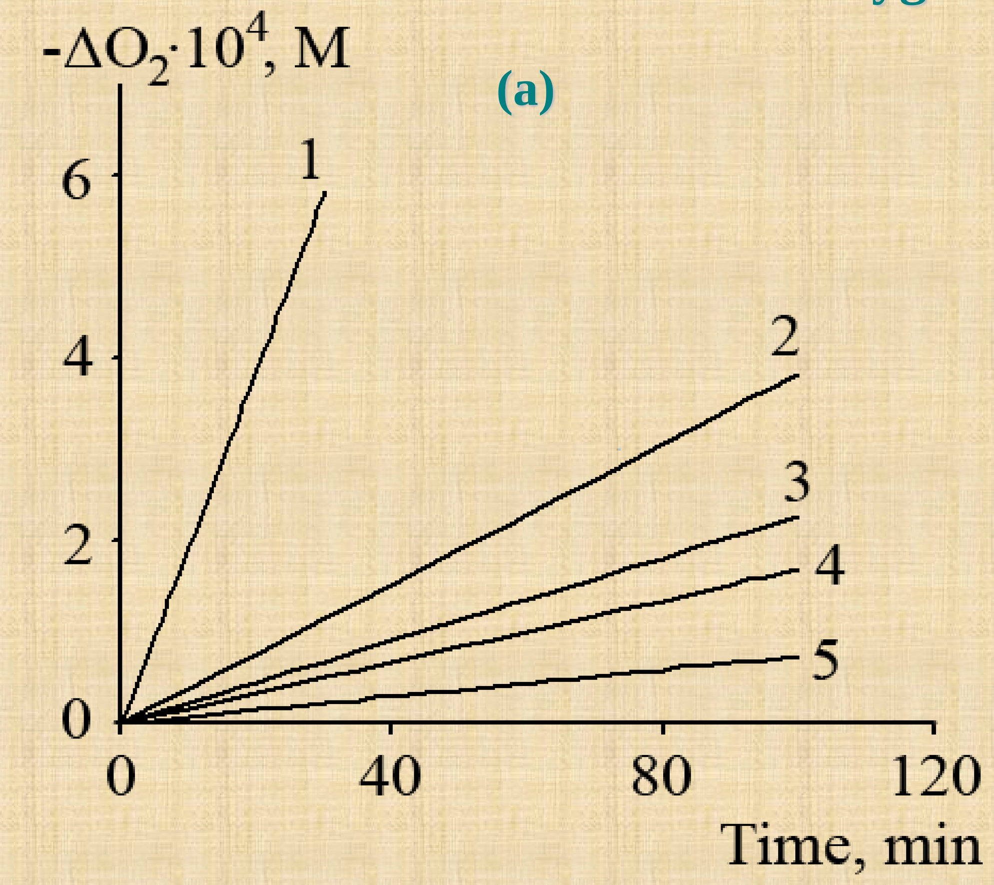
$[>NO^•(I)]{\cdot}10^4$, M	τ_{ind}, min	Consumption, %
0.8	37.6	68.12
1.6	74.1	69.80
2.4	110.0	61.99

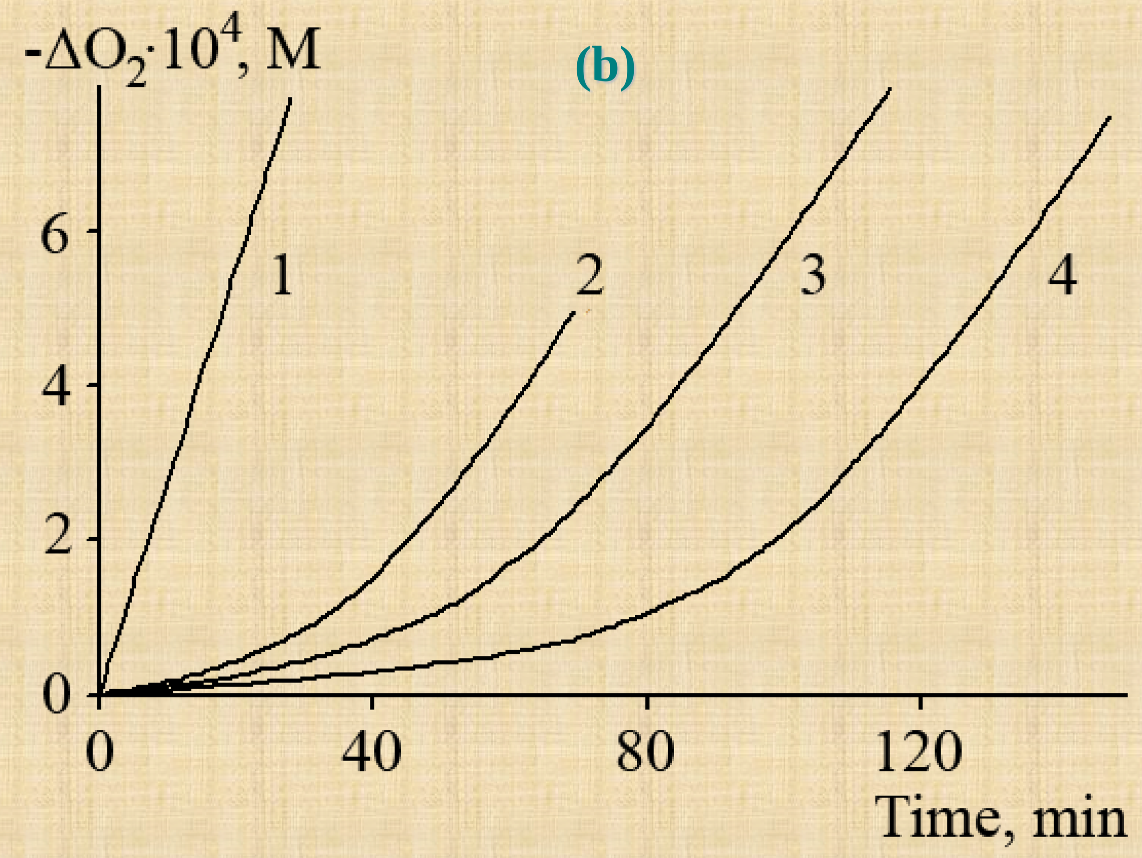
$W_i = 3.6{\cdot}10^{-8}$ M·s^{-1}; experiment time is 240 min.

These facts similar to [Pliss E.M., Tikhonov I.V., Rusakov A.I. In: Nitroxides - theory, experiment and applications. Ed. By A. Kokorin, Rijeka: InTech, 2012. P. 263] allow to assume that >NO• regeneration in chain termination acts takes place during the LH oxidation. This assumption is also indirectly confirmed by data from the figure above which prove >NOH formation at interaction of $LO_2^•$ with >NO•.

Oxidation in micelles

Kinetics of oxygen absorption during the LH oxidation





[LH] = 0.02 M, [Triton X-100] = 0.05 M

(a) [>NO• (III)], M: 0 (*1*), $8.3{\cdot}10^{-5}$ (*2*), $1.7{\cdot}10^{-4}$ (*3*), $3.31{\cdot}10^{-4}$ (*4*), $8.2{\cdot}10^{-4}$ (*5*); $W_i = 1.1{\cdot}10^{-9}$ M·s^{-1}; $W_0 = 5.6{\cdot}10^{-7}$ M·s^{-1} (*1*), $W = 1.3{\cdot}10^{-7}$ M·s^{-1} (*2*), $W = 1.6{\cdot}10^{-8}$ M·s^{-1} (*3*).

(b) [>NOH (III)], M: 0 (*1*), $5{\cdot}10^{-6}$ (*2*), $1{\cdot}10^{-5}$ (*3*), $2{\cdot}10^{-5}$ (*4*); $W = 1.6{\cdot}10^{-8}$ M·s^{-1}.

Linear termination proceeds due to the LH dissociation via the following reaction:

$$\sim CH{=}CH{-}CH{=}CH{-}CH(OO^•){-}CH_2\sim \rightarrow$$
$$\rightarrow \sim CH{=}CH{-}CH{=}CH{-}CH{=}CH\sim + HO_2^•$$

Δ*H* (DFT B3LYP/6-311+G[d,p]) of such a process is ~40 kJ/mol, and its probability in the observed system can be high enough because of the increase of $LO_2^•$ life time in micellar systems caused by a decrease of quadratic termination rate.

Regeneration scheme in solution

(i) I (O_2, LH) → $L^•$
(1) $L^• + O_2 \rightarrow LO_2^•$
(2) $LO_2^• + LH \rightarrow LOOH + L^•$
(3) $2LO_2^• \rightarrow$ products
(4) $>NO^• + LO_2^• \rightarrow >NOH$ + products
(5) $>NOH + LO_2^• \rightarrow >NO^•$ + products
(6) $L^• + >NO^• \rightarrow >NOL$

Regeneration scheme in micelles

(i) I (O_2, LH) → $L^•$
(1) $L^• + O_2 \rightarrow LO_2^•$
(2) $LO_2^• + LH \rightarrow LOOH + L^•$
(3) $2LO_2^• \rightarrow$ products
(3`) $LO_2^• \rightarrow HO_2^•$ + product
(4) $>NO^• + HO_2^• \rightarrow >NOH + O_2$
(5) $>NOH + HO_2^• \rightarrow >NO^• + H_2O_2$
(6) $L^• + >NO^• \rightarrow >NOL$

Conclusions: It is established that a cyclic mechanism of chain termination at >NO• is observed for LH oxidation both in solution and in micelles.

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