KINETICS OF JOINT OXIDATION OF TRITON X-100 AND METHYL LINOLEATE

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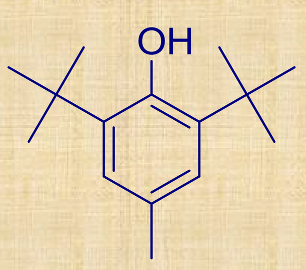
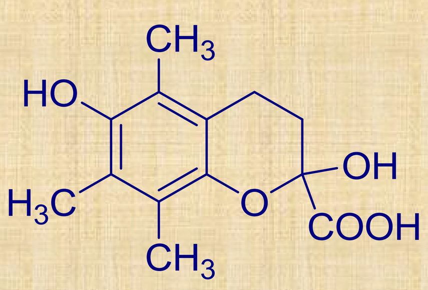
Objective:

- Experimental research of the kinetics of methyl linoleate and Triton X-100 co-oxidation in micelles;
- Determination of the mechanism of this process and analysis of the role of peroxide radicals.

Materials

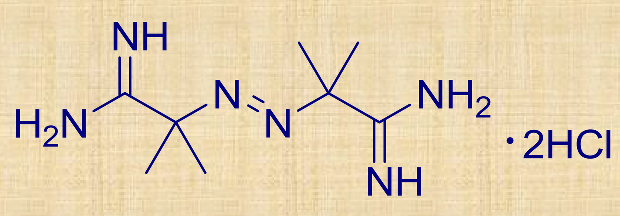


BHT

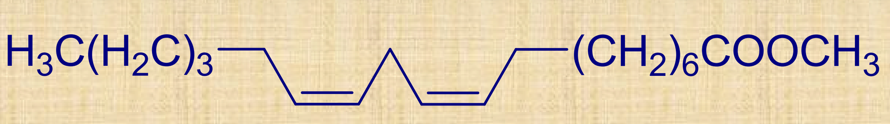


Trolox

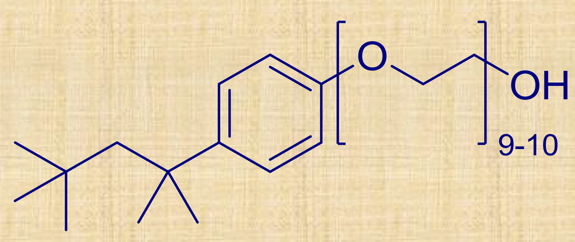
Phenols (PhOH)



AAPH, initiator



Methyl linoleate (LH_2), oxidation substrate



Triton X-100 (TH_2), detergent

Methods

- **Monitoring of oxygen consumption** (YSI 5300A Biological Oxygen Monitor)
- **Kinetic computer simulation were performed using the program Kinetic-2012 (based on the Gear method) elaborated by A. Sokolov and others.**

Experimental conditions

[LH] = 0.01-0.04 M, [Triton X-100] = 0.05-0.15 M, [AAPH] = $4\cdot10^{-4} – 5.3\cdot10^{-3}$ M air saturation, pH 7.4, 37 °C,

Calculation of inhibition coefficients (*f*)

$$R_i = \frac{2[\mathrm{PhOH}]}{\tau_{ind}} \qquad \tau_{ind} = \int_0^{\infty}\left(1-\left(\frac{R}{R_0}\right)^2\right)dt$$

The oxidation rate of Triton X-100 and LH_2 at the presence of BHT

$[BHT]\cdot10^5$, M	$W\cdot10^8$ $M\cdot s^{-1}$	
	[LH] = 0	[LH] = 0.02 M
0	2.11	11.2
0.5	1.52	1.79
1.0	1.22	1.26
2.0	1.03	8.47
3.0	1.02	9.51

$R_i = 1\cdot10^{-9}$ $M\cdot s^{-1}$, $[TH_2] = 0.1$ M.

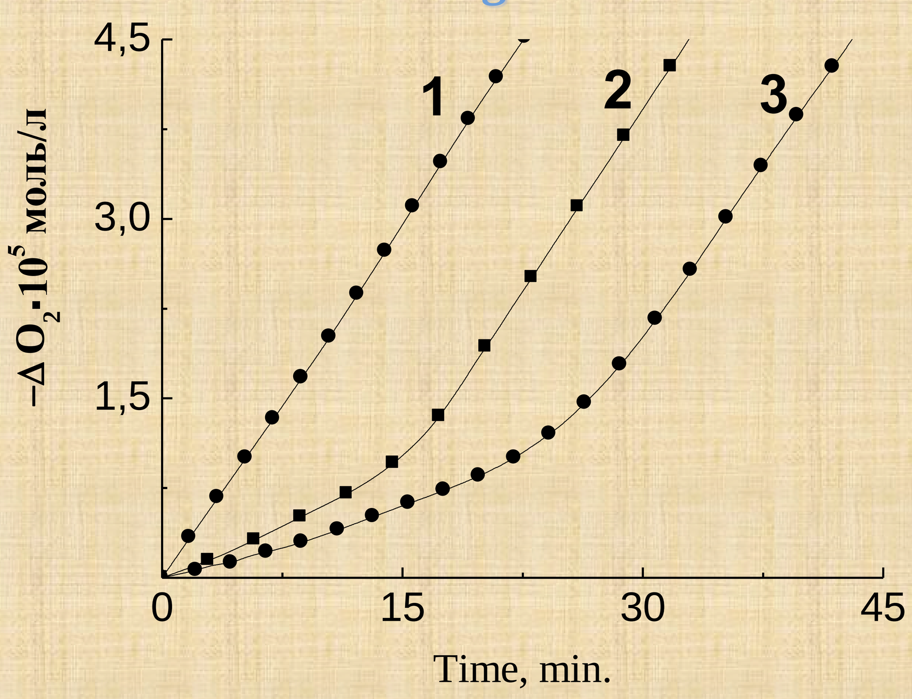
The rate constants of Triton X-100 and LH_2 co-oxidation

k_0, s^{-1}	$1\cdot10^{-6}$
k_{l1}, $M^{-1}\cdot s^{-1}$	$1\cdot10^{8}$
k_{t1}, $M^{-1}\cdot s^{-1}$	$1\cdot10^{8}$
k_{l2}, $M^{-1}\cdot s^{-1}$	50
k_{tl2}, $M^{-1}\cdot s^{-1}$	0.4
k_{t2}, $M^{-1}\cdot s^{-1}$	0.25
k_{lt2}, $M^{-1}\cdot s^{-1}$	0.4
k_{l3}, $M^{-1}\cdot s^{-1}$	$\approx3\cdot10^{3}$
k_{tl3}, $M^{-1}\cdot s^{-1}$	$\approx3\cdot10^{3}$
k_{t3}, $M^{-1}\cdot s^{-1}$	$\approx3\cdot10^{3}$
k_{l4}, $M^{-1}\cdot s^{-1}$	$\approx5\cdot10^{3}$ (BHT)
k_{t4}, $M^{-1}\cdot s^{-1}$	$\approx5\cdot10^{2}$ (BHT)
k_{l5}, $M^{-1}\cdot s^{-1}$	$\approx1\cdot10^{5}$
k_{t5}, $M^{-1}\cdot s^{-1}$	$\approx1\cdot10^{5}$

Proposed mechanism of methyl linoleate and Triton X-100 co-oxidation

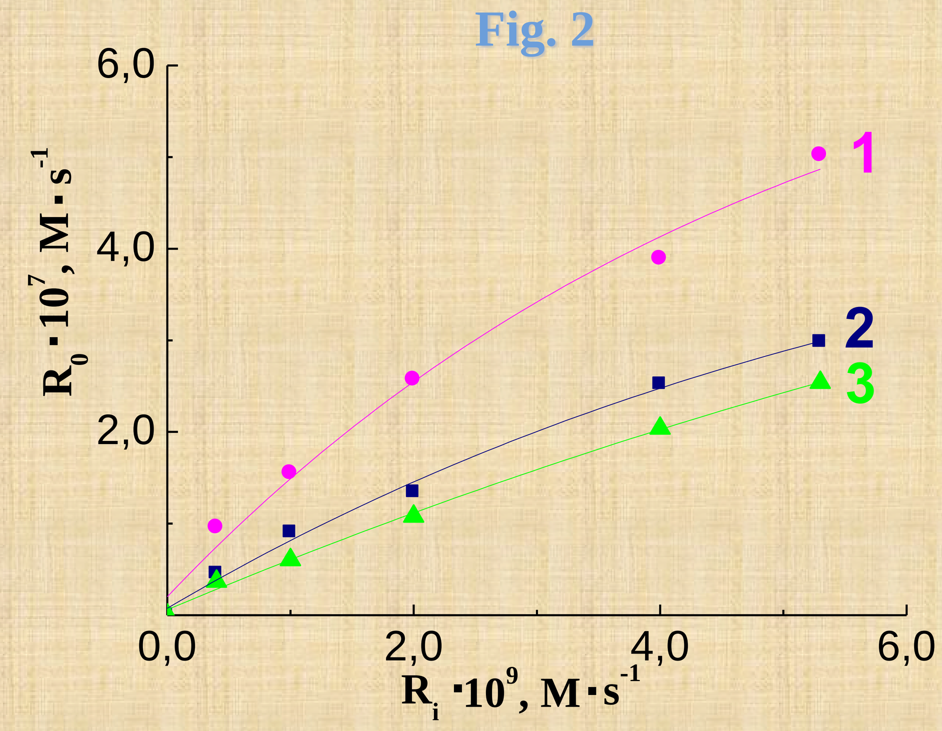
Initiator + (O_2) → $rO_2^\bullet$ + N_2 (k_0)	Initiator + (O_2) → $rO_2^\bullet$ + N_2 (k_0)
$rO_2^\bullet$ + LH_2 → $LH^\bullet$ + rOOH (k_{L0})	$rO_2^\bullet$ + TH_2 → $TH^\bullet$ + rOOH (k_{T0})
$LH^\bullet$ + O_2 → $LHO_2^\bullet$ (k_{L1})	$TH^\bullet$ + O_2 → $THO_2^\bullet$ (k_{T1})
$LHO_2^\bullet$ + LH_2 → $LH^\bullet$ + LHO_2H (k_{L2})	$THO_2^\bullet$ + TH_2 → $TH^\bullet$ + THO_2H (k_{T2})
$LHO_2^\bullet$ + $LHO_2^\bullet$ → O_2 + products (k_{L3})	$THO_2^\bullet$ + $THO_2^\bullet$ → O_2 + products (k_{T3})
$LHO_2^\bullet$ + PhOH → $PhO^\bullet$ + LHO_2H (k_{L4})	$THO_2^\bullet$ + PhOH → $PhO^\bullet$ + THO_2H (k_{T4})
$LHO_2^\bullet$ + $PhO^\bullet$ → products (k_{L5})	$THO_2^\bullet$ + $PhO^\bullet$ → products (k_{T5})
$THO_2^\bullet$ + LH_2 → $LH^\bullet$ + THO_2H (k_{TL2}) $LHO_2^\bullet$ + TH_2 → $TH^\bullet$ + LHO_2H (k_{LT2}) $LHO_2^\bullet$ + $THO_2^\bullet$ → O_2 + products (k_{LT3})	

Fig. 1



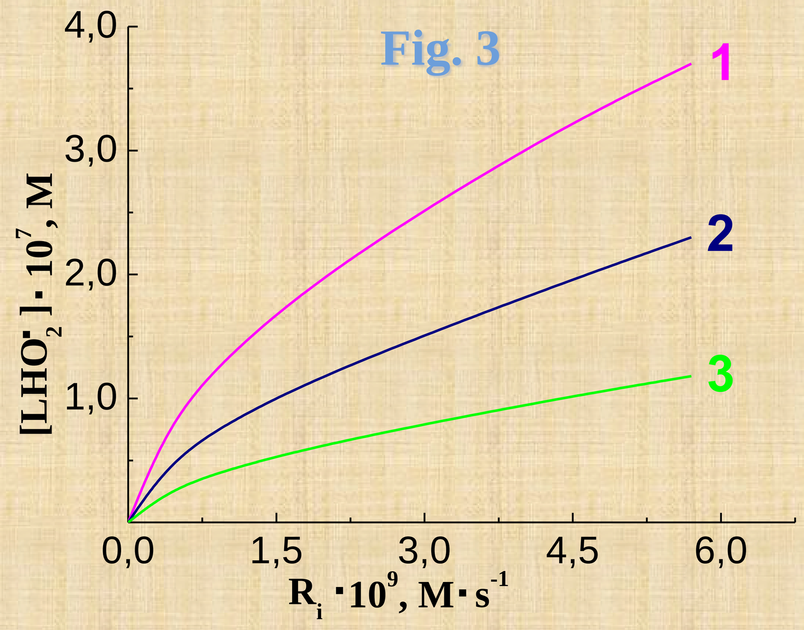
Kinetics of oxygen uptake during the oxidation of Triton X-100 inhibited by Trolox.
[AAPH] = $4.0\cdot10^{-3}$ M; $[TH_2]$ = 0,1 M;
[Trolox], M: 1 – 0; 2 – $2.0\cdot10^{-6}$; $2.7\cdot10^{-6}$.

Fig. 2



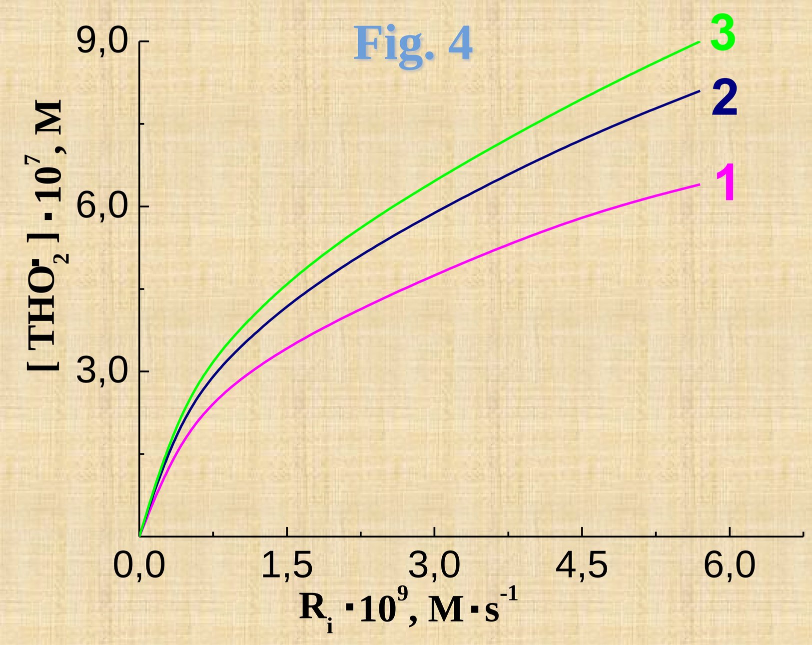
Dependence of Triton X-100 and LH_2 oxidation rate on R_i.
$[TH_2]$, M: 1 – 0.05, 2 – 0.1, 3 – 0.15; $[LH_2]$ = 0.02 M.

Fig. 3



Simulated dependences of $[LHO_2^\bullet]$ on R_i
$[TH_2]$, M: 1 – 0.05, 2 – 0.1, 3 – 0.15; $[LH_2]$ = 0,02 M.

Fig. 4



Simulated dependences of $[THO_2^\bullet]$ on R_i
$[TH_2]$, M: 1 – 0.05, 2 – 0.1, 3 – 0.15; $[LH_2]$ = 0.02 M.

Basic regularities

The joint oxidation scheme explains the "inhibitory" effect of Triton X-100, which is mainly associated to substitution of more active $LHO_2^\bullet$-radicals by less active $THO_2^\bullet$-radicals.

The effect of phenolic antioxidants on the oxidation of Triton X-100 is similar to their effect on any hydrocarbons that are oxidized by a free radical mechanism. Therefore, the evaluation values of the termination constants obtained by the inhibitors method are correct.

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