KINETICS OF METHYL LINOLEATE OXIDATION IN NANO-HETEROGENEOUS SYSTEM

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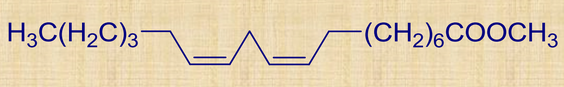
Objective: to research the kinetics of methyl linoleate oxidation in micelles

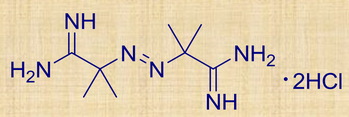
Experimental conditions

LH (0.01; 0.02; 0.04 M) in Triton X100 (0.04–0.1 M) micelles; air saturation; pH = 7.4; T = 310 K;
$W_i = 4.28 \times 10^{-10} - 4.28 \times 10^{-9}$ M×s^{-1}

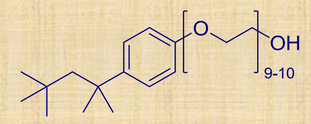
Materials



Methyl linoleate (LH). oxidation substrate

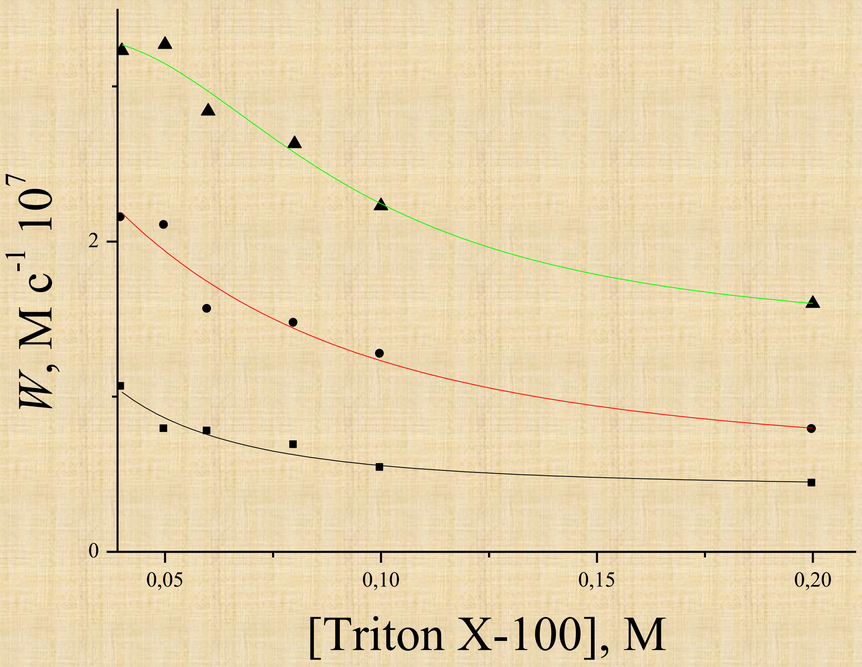


AAPH. initiator



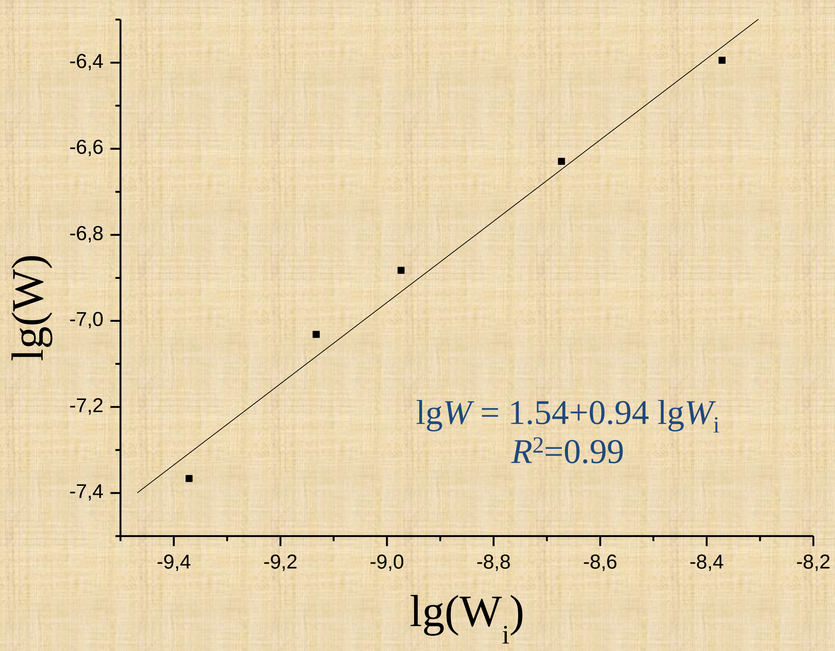
Triton X-100. detergent

Dependence of the methyl linoleate oxidation rate on the [Triton X100]



$W_i = 2.14 \times 10^{-9}$. M×s^{-1}, green – [LH] = 0.04 M, red – [LH] = 0.02 M, black – [LH]= 0.02 M

The reaction order with respect to the initiator



Estimated number of methyl linoleate molecules in micelle

$$N = N_{agr}\frac{[LH]}{[Triton]}$$

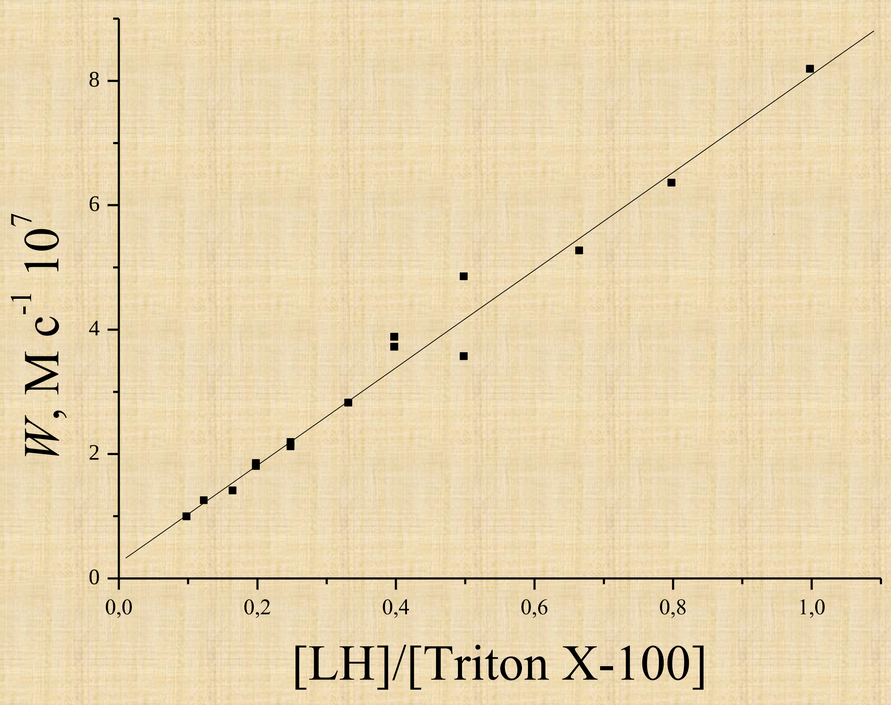
Estimated number of O_2 molecules in micelle

$$N(O_2) = \frac{[O_{2\ \text{lipid phase}}]}{[LH]_{max} \times N}$$

$[LH]_{max}$= 3 M
$[O_{2\ \text{lipid phase}}] = 1.5 \times 10^{-3}$ M

$N(O_2)$=N/2000

Dependence of the oxidation rate on the [LH]/[Triton X100]



Probable causes of linear termination:

- In order to quadratic termination is occur in the given system, two radicals should appear all at once inside the same micelle, which is unlikely.
- The reaction sequence (L3) → (D3) → (W1) is leading to the $O_2^{\bullet-}$ low active radical formation.
- The reaction $2HO_{2\ (\text{water phase})}^{\bullet} \rightarrow H_2O_2 + O_2$ (W2) is leading to the quadratic chain termination. However the rate (W2) is low due to the week $[HO_{2\ (\text{water phase})}^{\bullet}]$.

Other kinetic features

- The oxidation rate depends on the number of molecules in micelle.
- The oxidation rate does not depend on [micelles].
- Reaction (D2) is rate-limiting step during the oxidation in micelle since one O_2 molecule is accounted for ~10-200 micelles.
- Chain length exceeds the number of LH molecules in micelle, which indicates intermicellar chain termination.

Estimated methyllinoleate oxidation mechanism in micelles

Water phase

$AAPH \rightarrow RO_{2\ (\text{water phase})}^{\bullet}$ (W_i); $k_{Wi} \approx 1.07 \times 10^{-6}$

$HO_{2\ (\text{water phase})}^{\bullet} \leftrightarrow O_2^{\bullet-} + H^+$ (W1) K=1/400

Diffusion

$RO_{2\ (\text{water phase})}^{\bullet} \rightarrow RO_{2\ (\text{lipid phase})}^{\bullet}$ (D1)

$O_{2\ (\text{water phase})} \leftrightarrow O_{2\ (\text{lipid phase})}$ (D2)

$HO_{2\ (\text{lipid phase})}^{\bullet} \leftrightarrow HO_{2\ (\text{water phase})}^{\bullet}$ (D3)

Lipid phase

$LH + RO_{2\ (\text{lipid phase})}^{\bullet}\ (HO_{2\ (\text{lipid phase})}^{\bullet}) \rightarrow L^{\bullet} + ROOH\ (H_2O_2)$ (L0); $k_{L0(HO2)} = 1.18 \pm 0.2 \times 10^3$ (linoleic acid)

$L^{\bullet} + O_{2\ (\text{lipid phase})} \rightarrow LO_2^{\bullet}$ (L1); $k_{L1} = 10^9$

$LO_2^{\bullet} + LH \rightarrow L^{\bullet} + LOOH$ (L2); k_{L2}=60-70

$LO_2^{\bullet} \rightarrow \text{product} + HO_{2\ (\text{lipid phase})}^{\bullet}$ (L3)

$2LO_2^{\bullet} \rightarrow \text{product}$ (L4) $k_{L1} = 4.4 \times 10^6$

Rate limiting step in micelle – (L2); Diffusion limiting step – (D2).

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