INFLUENCE OF THE MEDIUM ON THE ELEMENTARY STAGES OF THE INHIBITED OXIDATION OF LIPID MEMBRANES' MODELS

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Objective: Experimental research of the polar effects during inhibited and uninhibited oxidation of unsaturated compounds modeling lipid membranes' fragments.

Known mechanisms of vinyl compounds (left) and methyl linoleate (right) inhibited oxidation in solution:

	Vinyl compounds			Methyl linoleate	
(i)	$I \xrightarrow{O_2,\,M} M^\bullet$	k_i	(i)	$I \xrightarrow{O_2,\,LH} L^\bullet$	k_i
(1)	$M^\bullet + O_2 \rightarrow MO_2^\bullet$	k_1	(1)	$L^\bullet + O_2 \rightarrow LO_2^\bullet$	k_1
(2)	$MO_2^\bullet + M \rightarrow MOOM^\bullet (\equiv M^\bullet)$	k_2	(2)	$LO_2^\bullet + LH \rightarrow LOOH + L^\bullet$	k_2
(6)	$MO_2^\bullet + MO_2^\bullet \rightarrow$ molecular products	$2k_6$	(6)	$LOOH \rightarrow LO^\bullet + OH^\bullet$	$2k_6$
(7)	$MO_2^\bullet + InH \rightarrow In^\bullet + MOOH$	k_7	(7)	$LO_2^\bullet + InH \rightarrow In^\bullet + LOOH$	k_7
(8)	$MO_2^\bullet + In^\bullet \rightarrow$ molecular products	k_8	(8)	$LO_2^\bullet + In^\bullet \rightarrow$ molecular products	k_8

Chain initiation in α-olefins:

$$RH + O_2 \xrightarrow{k_{02}} R^\bullet + HO_2^\bullet$$
$$2RH + O_2 \xrightarrow{k_{03}} 2R^\bullet + H_2O_2$$

The Kirkwood-Onsager equation:

$$\lg k = \lg k_0 - \frac{1}{2{,}3k_BT}\cdot\frac{\varepsilon-1}{2\varepsilon+1}\left(\frac{\mu_1^2}{r_1^3}+\frac{\mu_2^2}{r_2^3}-\frac{\mu_\neq^2}{r_\neq^3}\right)$$

Oxidation substrates

methyl linoleate (LH)
$CH_3(CH_2)_3(CH_2CH{=}CH)_2(CH_2)_7COOCH_3$

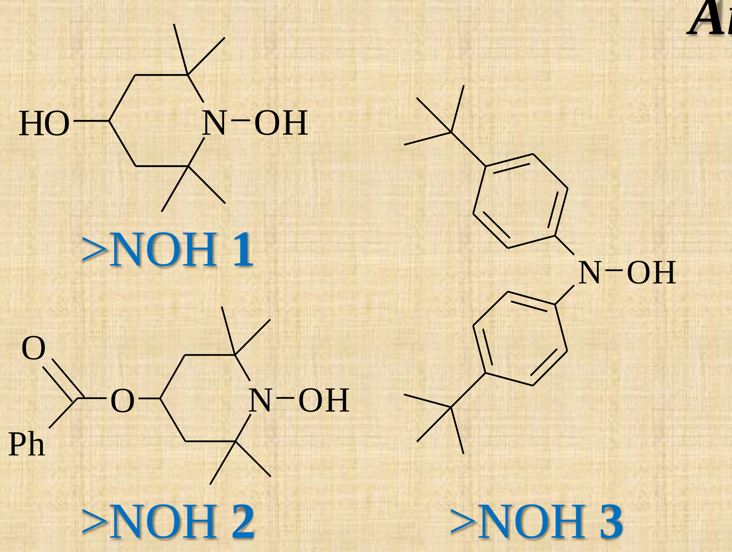
linoleic acid (LA)
$CH_3(CH_2)_3(CH_2CH{=}CH)_2(CH_2)_7COOH$

methyl methacrylate (MMA)
$CH_2=C(CH_3)-COO-CH_3$

styrene (St)
$CH_2=CH-Ph$

Solvents (S)

chlorobenzene (CB)
acetonitrile (AcN)
benzonitrile (BN)
nitrobenzene (NB)
dimethyl sulfoxide (DMSO)

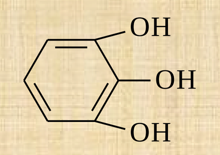


>NOH 1
>NOH 2
>NOH 3

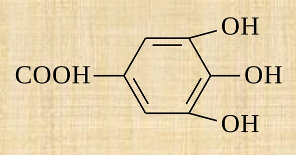
Hydroxylamines

Antioxidants

pyrogallol (PG)

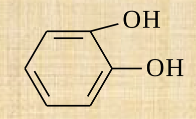


gallic acid (GA)



4-methoxyphenol (MP)
$CH_3-O-Ph-OH$

pyrocatechol (PC)

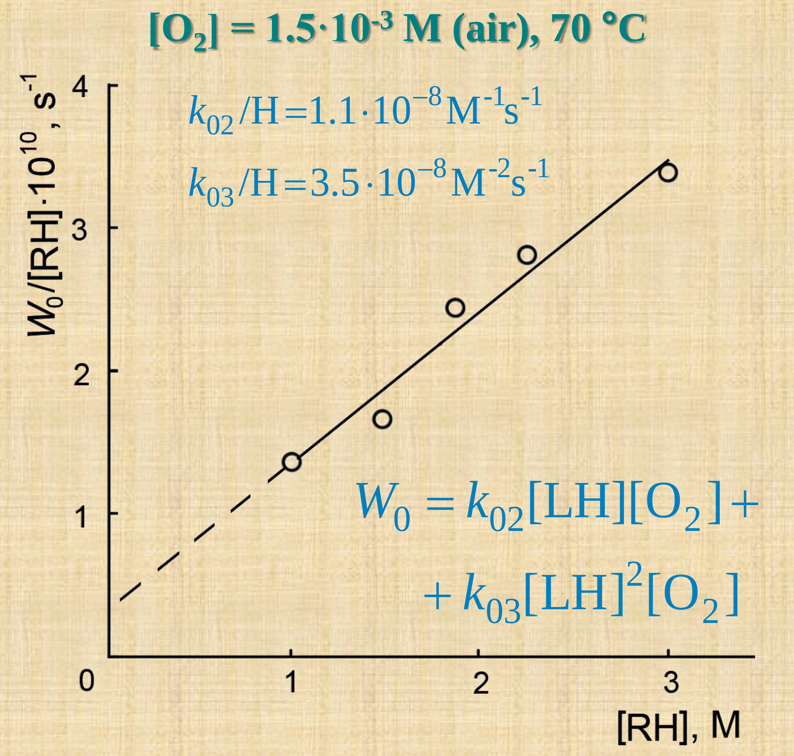


diphenylamine (DPA)
$Ph-NH-Ph$

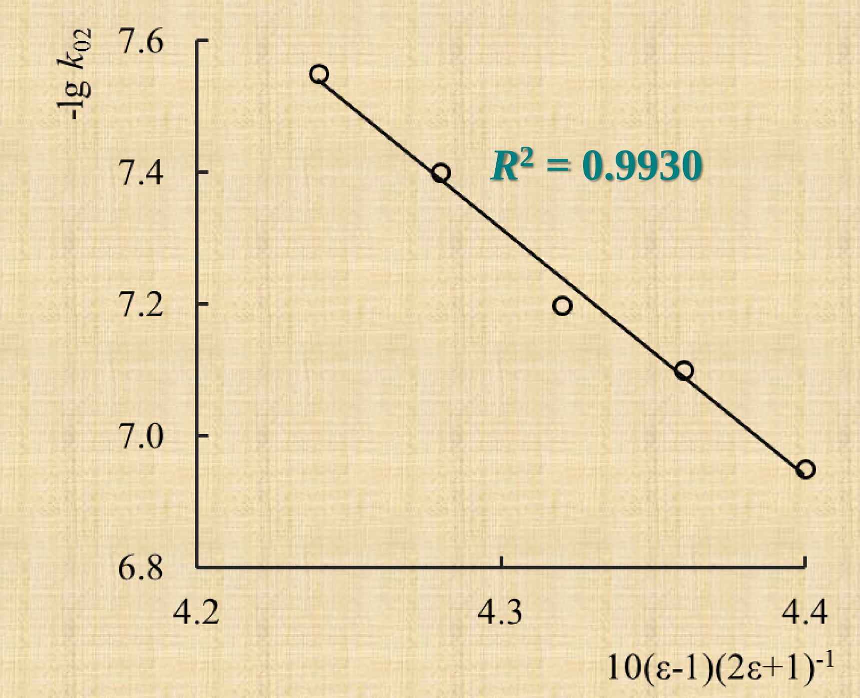
di-1-naphthylamine (DNA)
$Np-NH-Np$

Chain initiation

Dependence of W_0 during the auto-oxidation of LH on its concentration in chlorobenzene; $[O_2] = 1.5\cdot10^{-3}$ M (air), 70 °C

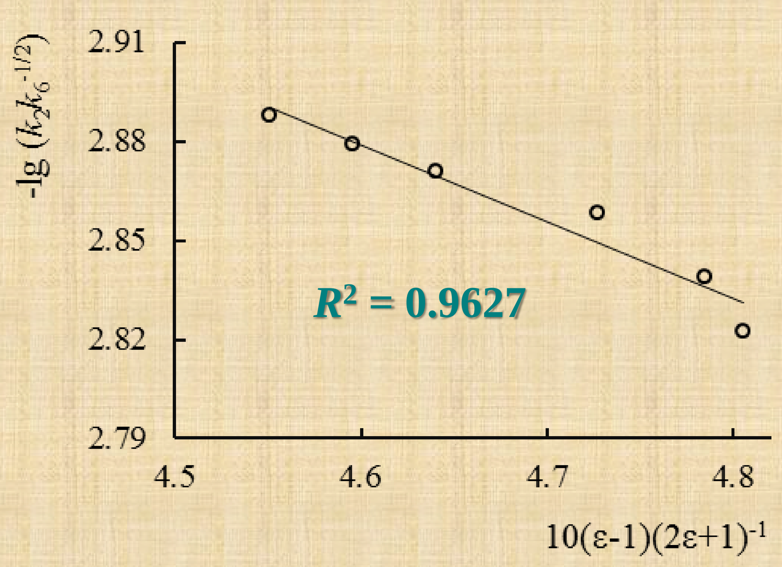


Dependence of lg k_{02} on (ε-1)(2ε+1)$^{-1}$ upon the autooxidation of LH in the mixture of bezonitrile and chlorobenzene, [LH] = 1.5 M, 70 °C

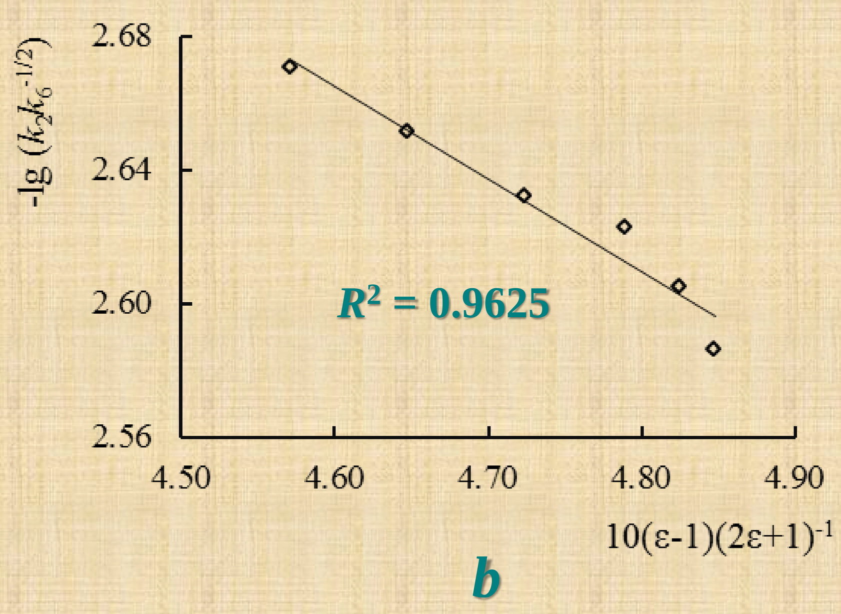


Chain propagation

Dependences of lg ($k_2k_6^{-1/2}$) on (ε-1)(2ε+1)$^{-1}$ upon the oxidation of MMA in the medium of acetonitrile (*a*) and dimethyl sulfoxide (*b*), 50 °C



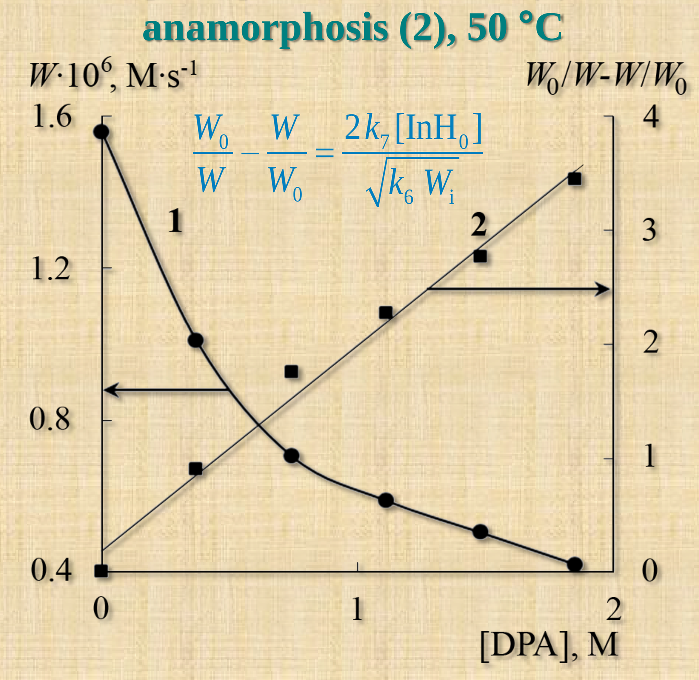
a



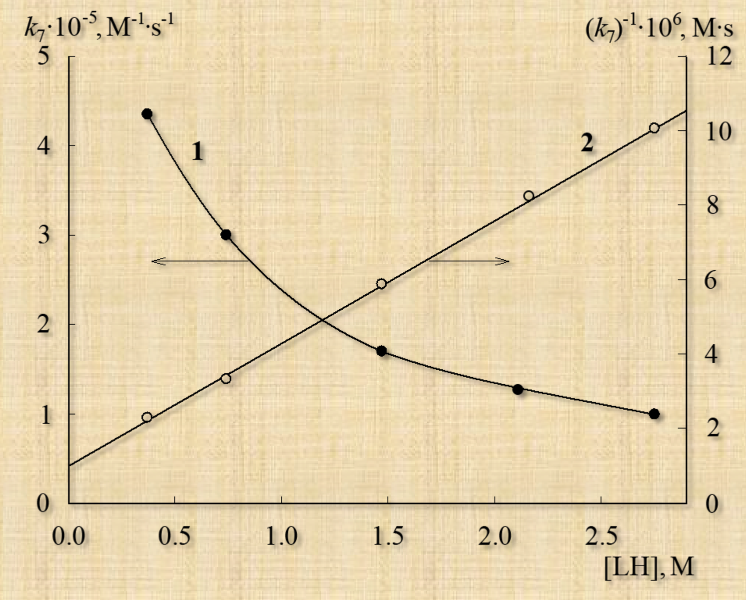
b

Linear chain termination (inhibited oxidation)

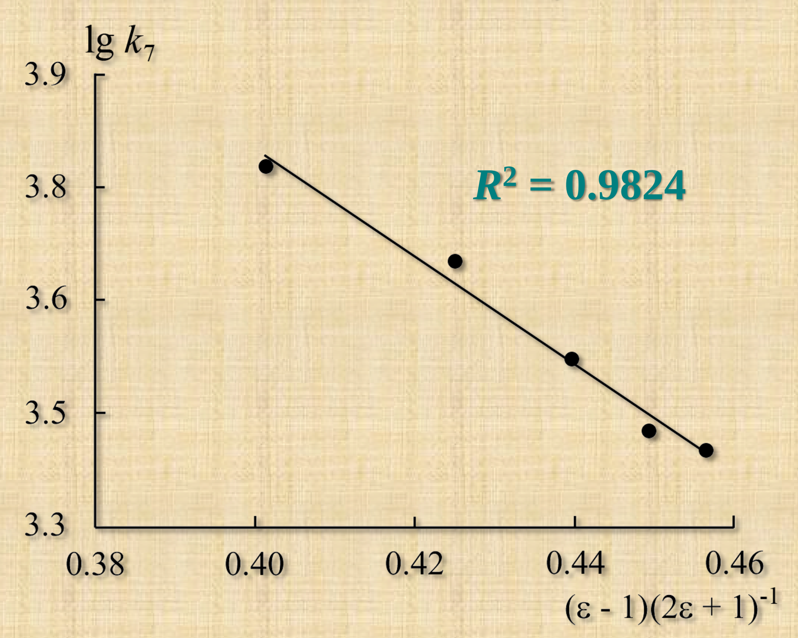
Dependence of MMA inhibited oxidation rate on [DPA] in benzonitrile (1) and its anamorphosis (2), 50 °C



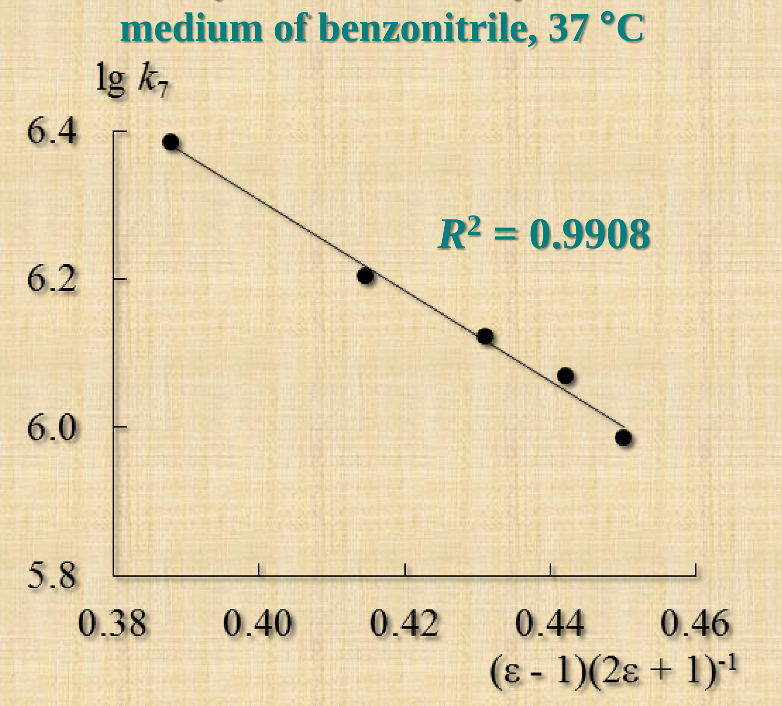
Dependence of k_7 on [LH] upon its oxidation in the medium of chlorobenzene in the presence of PC (1) and anamorphosis of this curve (2); 50 °C



Dependences of lg k_7 on (ε-1)(2ε+1)$^{-1}$ upon the oxidation of MMA inhibited by DPA in the medium of benzonitrile, 50 °C



Dependences of lg k_7 on (ε-1)(2ε+1)$^{-1}$ upon the oxidation of styrene inhibited by >NOH 2 in the medium of benzonitrile, 37 °C



Complexing equilibrium scheme

$$InH + S \overset{K}{\rightleftarrows} InH\cdots S$$

$$k_7 = \frac{k_{7(0)}}{1+K[S]}$$

where **S** is polar solvent, ***K*** is equilibrium constant of complexing

Values of $k_{7(0)}\cdot10^{-6}$ (M^{-1}·s^{-1}) upon the oxidation of styrene inhibited by hydroxylamines (>NOH) in the medium of polar solvents

Polar solvent	>NOH 1	>NOH 2	>NOH 3
AcN	3.11	–	2.03
BN	4.21	3.40	2.52
DMSO	0.91	0.82	0.71

Comparison of the values of $k_{7(0)}$ and K for MMA and aromatic amines calculated from kinetic dependences and IR-spectroscopy data

InH	S	K, M^{-1}		$k_{7(0)}\cdot10^{-4}$, M^{-1}·s^{-1}	
		Kinetics, 50 °C	IR, 25 °C	Kinetics, 50 °C	IR, 25 °C
DPA	AcN	0.30	0.35	0.92	1.04
	NB	0.21	0.13	0.99	0.85
	BN	0.56	0.41	0.92	0.78
DNA	AcN	0.22	0.29	1.08	1.28
	NB	0.12	0.10	1.05	1.01
	BN	0.49	0.38	1.19	1.04

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