

The influence of moderate magnetic field on the generation of radicals by mixture of some choline derivative with hydroperoxides

N.V. Potapova, O.V. Kazakov, O.T. Kasaikina

N.N. SEMENOV FEDERAL RESEARCH CENTER FOR CHEMICAL PHYSICS
RUSSIAN ACADEMY OF SCIENCES, MOSCOW

email: pot.natalia2010@yandex.ru



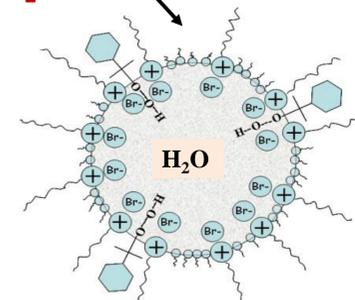
In this work, we studied the impact of endogenous substances containing (R_4N^+), namely choline (Ch) and L-carnitine (LCh) comparing to ACh on the radical generation via ROOH decomposition

- (a) in the bulk solution in organic media;
- (b) the effect of magnetic field of permanent magnets (0.61 T) on these processes;
- (c) effect of Ch, LCh and ACh adsorption on cellulose on their catalytic activities in ROOH decay.

Hydroperoxides form mixed aggregates with cationic surfactants



Choline derivatives, like cationic surfactants, contain R_4N^+ cation



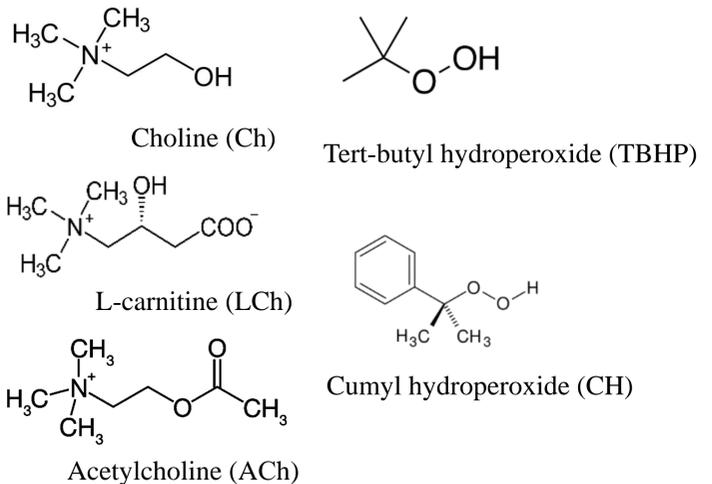
Activation energy for ROOH decomposition into free radicals

$$E_{\text{therm}} > 100 \text{ kJ/mol}$$

$$E_{\text{mic}} \sim 40 - 60 \text{ kJ/mol}$$

initiation rates were measured by the inhibitor method
radical scavenger – quercetin (Q)

Choline derivatives and hydroperoxides:



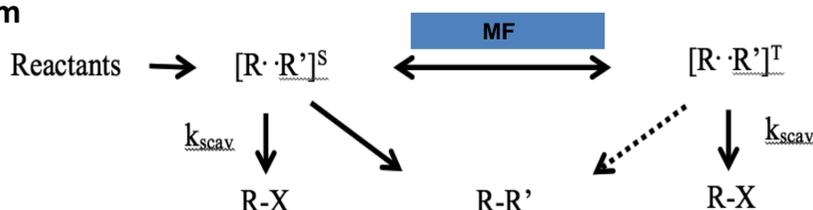
(a) in the bulk solution in organic media

Initiation rates W_i , M/s, in systems of choline derivatives (1 mM), and ROOH (20 mM), chlorobenzene, 22°C

System		Acetylcholine (ACh)	Choline (Ch)	L-carnitine (LCh)	without catalyst
$W_i \times 10^9$, M/s	1 mM (R_4N^+), 20 mM HC,	3.4±0.5	1.9±0.3	0.06±0.01	~ 0
	1 mM (R_4N^+), 20 mM TBHP,	1.4±0.2	0.13±0.02	0.05±0.01	~ 0

(b) the effect of magnetic field of permanent magnets (0.61 T) on these processes

Radical pair mechanism

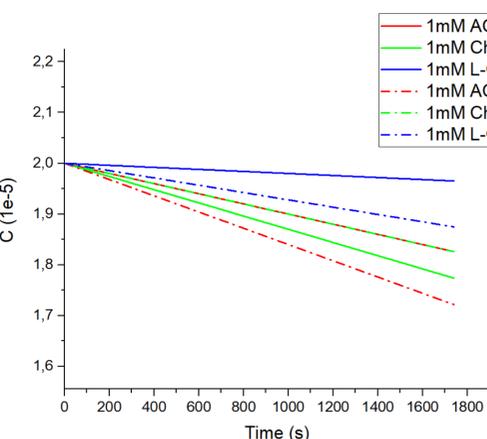


Reaction scheme for singlet-born radical pair.

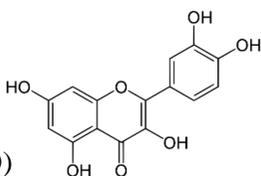
Fast S-T mixing increases the yield of R-X and decreases R-R'.

The relative yields are the opposite for a triplet born pair.

Kinetic curves of Q consumption in TBHP systems (20 mM) - 1 mM choline derivative in chlorobenzene at 22 °C



Quercetin (Q)



initiation rates were measured by the inhibitor method

$$\lambda_Q = 374 \text{ nm}, \quad \epsilon = 2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$$

Initiation rates in TBHP systems (20mM) - 1 mM choline derivative, quercetin acceptor in chlorobenzene, 22°C

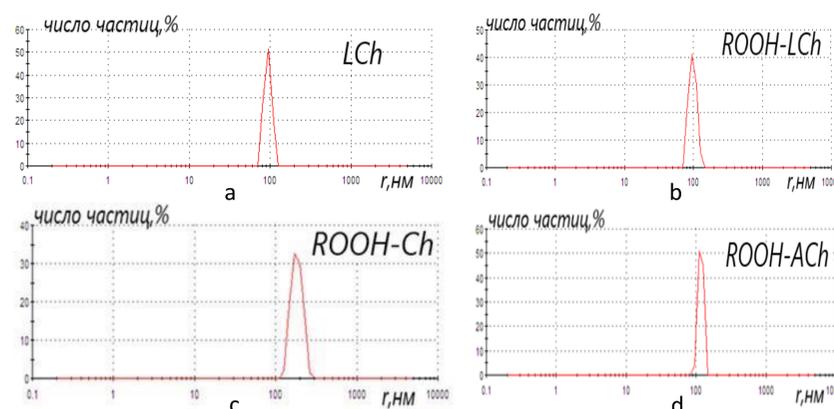
Choline derivatives	in magnetic field	without magnetic field	ME
ACh	1.0±0.1	1.6±0.2	-0.375
Ch	1.3±0.1	1.0±0.2	+0.3
LCh	0.2±0.02	0.72±0.08	-0.72

Conclusions:

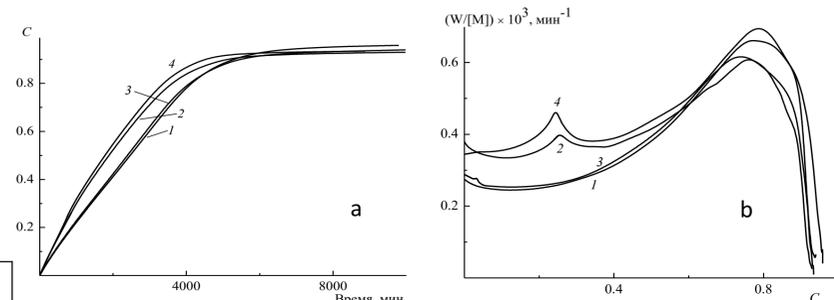
- (a) Measurement of the rates of generation of radicals (W_i) by the method of inhibitors showed that in mixtures of ACh and Ch with tert-butyl and cumyl hydroperoxides in chlorobenzene medium, accelerated decomposition of hydroperoxides into radicals takes place. The activity of LCh in generating radicals under the same conditions is much lower. By dynamic light scattering, ACh and Ch were found to disperse in organic media only in the presence of ROOH whereas LCh formed nanoaggregates both itself and together with ROOH of the same size of 100 nm. Ch, similar to ACh, caused the catalytic decomposition of ROOH into radicals in mixed aggregates with ROOH.
- (b) In magnetic field (0.61 T), the decrease in the rate of radical initiation was observed only in the cases of ACh and Ch. The rate of radical initiation by system LCh-ROOH was not affected by this magnetic field.
- (c) Adsorbed on microcrystalline cellulose ACh and Ch retain the ability to catalyze the radical decay of ROOH and initiate radicals whereas adsorbed LCh does not affect the ROOH decay. It is obvious that radical decomposition is accelerated only in microaggregates such as reverse micelles, and carnitine, unlike other choline derivatives, is an internal salt, which makes it difficult to include peroxide and its decomposition is more difficult. It is possible that the magnetic field influences the properties of the double electric layer and the orientation of the peroxide bond in microaggregates, the homolysis of which determines the decomposition rate of the hydroperoxide into radicals.

This study is partly supported by the Russian Foundation for Basic Research grant No. 20-03-00753.

Size distribution of particles formed upon dispersion of 1 mM choline derivative in chlorobenzene (a – LCh) and in 20 mM CH solution: b – LCh, c – Ch, d – ACh.



(c) effect of Ch, LCh and ACh adsorption on cellulose on their catalytic activities in ROOH decay



Dependence of conversion C (a) on time and the reduced rate of polymerization ($W/[M]$) on conversion (b) in the course of styrene polymerization initiated by 0.05 M cumyl hydroperoxide with additives of 4 wt % of heterogeneous catalysts: 1 – without catalyst; 2 - ACh/Cel; 3 - LCh/Cel; 4 - Ch/Cel. T = 60°C.

The equation for the rate of radical polymerization at low conversions is:

$$W = a \cdot [M] \cdot W_i^{0.5}$$

where W_i is the rate of initiation, $a = k_p / (2k_t)^{0.5}$ is the ratio of the rate constants of growth (k_p) and termination (k_t) of the chain, which is determined by the activity of the monomer (M) and the macroradical leading the chain reaction;

For styrene at 60°C $a = 0.021 \text{ (l mol}^{-1} \text{ s}^{-1})^{0.5}$, and the initiation rate can be calculated from the equation:

$$W_i = (W / ([M] \cdot a))^2$$

Adsorption value (Γ) of choline derivatives on the surface of microcrystalline cellulose, as well as experimental polymerization rates (W)* of styrene and calculated chain initiation rates (W_i) in the presence of catalysts.

Catalysts	ACh	Ch	LCh	without catalyst
Adsorption, $\Gamma \times 10^4$, mol/g	7.9	20.8	19.4	-
$(W/[M_0]) \times 10^6$, s ⁻¹	5.7	5.65	4.4	4.3
$W_i \times 10^8$, mol l ⁻¹ s ⁻¹	7.3	7.2	4.4	4.1

* The error in determining the rate of polymerization did not exceed 15%.