

UDC 544.54

Radiation chemistry**THE SIMILARITIES IN THE PHOTOLYTIC AND RADIOLYTIC TRANSFORMATIONS OF MYCOTOXINS AND PHENOL IN WATER SOLUTIONS****Academician of ANAS A.A.Garibov, Kh.F.Mamedov**

The comparative analysis of kinetic regularities of photolytic and radiolytic transformations of phenol and mycotoxins in their water solutions, thermodynamic parameters of elementary reactions of these processes had been carried out. The mechanisms explaining photolytic and radiolytic transformations of phenol and mycotoxins in their oxygen-containing and oxygen-free water solutions had been offered.

Keywords: *UF-radiation, radiolytic transformations, mycotoxins, phenol*

The polycyclic mycotoxins produced by microscopic fungi in plant foods besides poisonous properties have also cancerogenic, teratogenic and mutagen effects [1-7]. Studies radiolytic and photolytic transformations of mycotoxins in water solutions as well as the development of mechanisms that explain these transformations is of great importance in solving the problem of food security.

In wastewater from oil refineries along with hydrocarbons, phenols which are found fatally affect the microorganisms involved in the processes of water purification in the aeration tanks. Due to the fact that the information on radiolytic and photolytic processes in water solutions of phenol [8-12] are not systematic, there is an urgent need for systematic study of the radiolytic and photolytic reactions and the development of appropriate mechanisms, which describe the transformation.

Photolytic and radiolytic transformations occurring in oxygen-free and oxygen-containing water solutions in recent publications are presented in detail [4-8]. The article compares the kinetic regularities of radiolytic and photolytic transformations in these systems and established the chain character of these reactions in water solutions with the participation of molecular oxygen.

Methodology

Analysis of reagents, organic compounds used in the experiments conducted in the liquid chromatograph Shimadzu LC-10AVP, chromatography-mass spectrometry GCMS-QP 2010, gas chromatograph GC-2010, enzyme-linked immunosorbent assay systems (ELISA) manufac-

tured by R-Biopharm and TEKNOPOL [3- 7] .

Irradiation of solutions was carried out by UF-light DRK-120 lamp (absorption dose $3,2 \cdot 10^{15}$ eV/q·s), in the Stationary radiation research installation K-25 ^{60}Co (absorbed dose of $0,33, 0,71$ Gy/s $2,06 \cdot 10^{15}, 4,43 \cdot 10^{15}$ eV/q·s) [4,7].

Results and discussion

Kinetic regularities of transformations in the water solutions of phenol and mycotoxins under UV- light ionizing radiation ^{60}Co , widely described in the recent scientific studies of the authors [4-8, 13].

Fig. 1 shows the kinetic curves of phenol (monooksibenzol) which are derivative of aromatic benzene, as well as kinetic curves of phenol transformations irradiated UV light in water solutions of various concentrations with oxygen and without, being a typical example of the radiolytic and photolytic transformations in aqueous solutions of most mycotoxins having cyclic group associated with benzene ring.

As a typical example had been presented through a comparative analysis of the photolytic process in the water solutions of phenol and mycotoxins enriched with oxygen. The system of probable all elementary reactions and set of their thermodynamic constants having place at the radiolysis of the saturated with oxygen and chlorophenol's water solutions and saturated with oxygen mycotoxin's water solutions in recent publications are presented in detail [4,5,8].

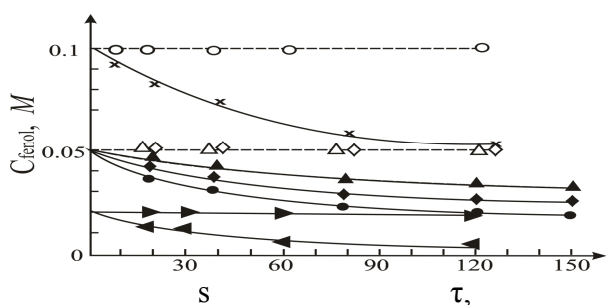


Fig. 1. Kinetics of reducing the concentration of phenol in the water solution by irradiation with UV light

X - solution (0,1M) phenol - H₂O (60°C) at the bubbling air flow .;

● - solution (0,05M) phenol - H₂O (60° C) at the air barbotage;

▲ - solution (0,05M) phenol - (0,025M) - CaOCl₂-H₂O (60°C) at the air barbotage;

◆ - solution (0,05M) phenol - (0,012M) CaOCl₂ - H₂O (60°C) at the air barbotage;

► - solution (0,02M) phenol - H₂O (60° C) without oxygen;

◄ - solution (0,02M) phenol - 0,0003M O₂ - H₂O (60°C)* in the quartz reactor with the open valve;

○, Δ, ◇- kinetics of the change in the concentration of phenol heated to 60°C without irradiation.

* - Atmospheric oxygen (0,0003M) dissolved in 10 ml of the solution in the quartz reactor with the open valve or in an ampoule, in accordance with the oxidation of the phenol, oxygen is consumed and reduced to the same concentration as a result of absorption from the atmosphere

On the value of the dose of UV light radiation ($3,2 \cdot 10^{15}$ eV/q.s) by reaction (1) had been identified the initial decomposition rate of phenol and mycotoxins respectively equal to 10^{-8} M/s and 10^{-11} – 10^{-13} M/s, by reaction (2) (reaction of hydrogen atoms with phenol and mycotoxins) respectively 1 M/s və 10^{-8} – 10^{-11} M/s. Based on the rate constants of elementary reactions, and the initial concentration of the primary and intermediate products had been evaluated ratio (W_i / W_2) of each elementary reaction rate to the rate of the reaction (2).

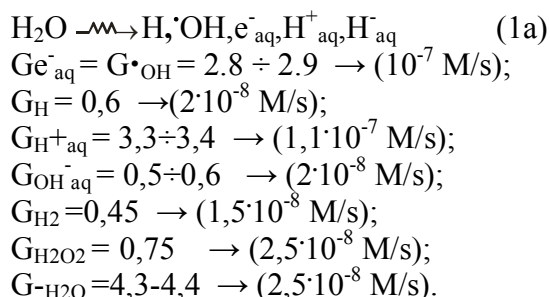
As shown in the basic circuit necessary elementary reaction to obtain the final product during the irradiation with UV radiation containing oxygen aqueous phenol solution are reactions (1), (2), (11), (12), (5), (8), (7) and (18a). The ratio of the reaction rate of said elementary reactions to reaction rate (2), by irradiating oxygen containing aqueous phenol solution shows that the reaction rate to form new

organic product (7) and (18a) respectively in relation to the rate competitive reactions (9) and (19) , at least 10^4 , and 10^{15} times more.

This indicates that at the irradiation of the oxygen containing aqueous phenol solution as the final product, phenol dimers, telomers and oligomers are formed by higher speed.

Similarly, on the value of absorbed dose ($0,33$ Gy/s və ya $2,06 \cdot 10^{15}$ eV/q.s) from the source ^{60}Co ionizing radioactive gamma radiation have been identified, the rate of preliminary decomposition of phenol according to the reaction (1) $1,7 \cdot 10^{-9}$ M/s, the rate of preliminary decomposition of 10-1000 mkq / l mycotoxins respectively $3 \cdot 10^{-13}$ və $3 \cdot 10^{-15}$ M/s, the rate of reaction (2) (reaction of hydrogen atoms with the phenol and mycotoxin) respectively 1,8 M/s və $5 \cdot (10^{-6}$ – $10^{-7})$ M/s. Based on the reaction rate constant of elementary reactions, and the initial concentration of the primary and intermediate products had been evaluated ratio of each elementary reaction rate (W_i / W_2) to the rate of reaction (2).

The radiation-chemical yields of water radiolysis intermediates are shown below:



The reaction rates of radical formation from phenol and mycotoxins equal respectively $1,7 \cdot 10^{-9}$ m/s ($W_i/W_2 = 10^{-9}$) and $3 \cdot (10^{-13}$ – $10^{-15})$ M/s ($W_i/W_2 = 10^{-8}$), the reaction rate of hydrogen atoms with phenol and mycotoxins which are equal to $W_2 = 1,8 \text{ M/s}$ ($W_2 / W_2 = 1$) and $W_2 = 5 \cdot (10^{-6}$ – $10^{-7}) \text{ M/s}$ ($W_2/W_2 = 1$) shows that the value of the ratio 0,05M solution of phenol for reactions (1a), (7) and (9) equal $W_{1a}/W_2 = 10^{-7}$, $W_7/W_2 = 3 \cdot 10^{-10}$, $W_9/W_2 = 2 \cdot 10^{-6}$. Consequently, for the phenol solution with a concentration of 0.05 M channel oxidation (reaction 9) compared with recombination channel (reaction 7) 10^4 times, and the solutions to the concentration of mycotoxins 10–1000 mq / kq 10^{10} faster.

Table

Principle circuit of photolysis of the aqueous solutions of phenol and mycotoxins

N:	Reaction	W_i/W_2	Reaction	W_i/W_2
(1)	$\text{PhOH} \xrightarrow{-h\nu} \text{PhO}^\bullet + \text{H}^\bullet$	10^{-8}	$\text{ArH} \xrightarrow{-h\nu} \text{H}^\bullet + \text{Ar}^\bullet$	$10^{-2} - 10^{-3}$
(2)	$\text{H}^\bullet + \text{PhOH} \rightarrow \text{PhO}^\bullet + \text{H}_2$	1	$\text{H}^\bullet + \text{ArH} \leftrightarrow \text{Ar}^\bullet + \text{H}_2$	1
(2a)			$\text{H}^\bullet + \text{ArH} \leftrightarrow \text{H}^\bullet \text{ArH}$	1
(3)	$\text{H}^\bullet + \text{PhO}^\bullet \rightarrow \text{PhOH}$	10^{-6}	$\text{H}^\bullet + \text{Ar}^\bullet \rightarrow \text{ArH}$	$10^{-4} - 10^{-5}$
(4)	$\text{H}^\bullet + \text{H}^\bullet \rightarrow \text{H}_2$	10^{-6}	$\text{H}^\bullet + \text{H}^\bullet \rightarrow \text{H}_2$	$10^{-4} - 10^{-5}$
(5)	$\text{H}^\bullet + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}_2$	$5,6 \cdot 10^{-6}$	$\text{H}^\bullet + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}_2$	0,5-5,5
(6)	$\text{PhO}^\bullet + \text{PhOH} \rightleftharpoons \text{PhOH} + \text{PhO}^\bullet$	$10^{-7} - 10^{-9}$	$\text{Ar}^\bullet + \text{ArH} \rightarrow \text{products}$	$10^{-9} - 10^{-11}$
(6a)			$\text{Ar}^\bullet + \text{H}^\bullet \text{ArH} \rightarrow \text{products}$	$10^{-11} - 10^{-13}$
(7)	$\text{PhO}^\bullet + \text{PhO}^\bullet \rightarrow \text{telomers}$	10^{-7}	$\text{Ar}^\bullet + \text{Ar}^\bullet \rightarrow \text{products}$	$10^{-5} - 10^{-6}$
(8)	$\cdot\text{OH} + \text{PhOH} \rightarrow \text{PhO}^\bullet + \text{H}_2\text{O}$	10^{-5}	$\cdot\text{OH} + \text{ArH} \rightarrow \text{Ar}^\bullet + \text{H}_2\text{O}$	1
(9)	$\cdot\text{OH} + \text{PhO}^\bullet \rightarrow \text{HOPhOH}$	$10^{-11} - 10^{-12}$	$\cdot\text{OH} + \text{Ar}^\bullet (\text{ArH}) \rightarrow \text{HOArH}$	$10^{-4} - 10^{-5}$
(10)	$\text{H}^\bullet + \cdot\text{OH} \rightarrow \text{H}_2\text{O}$	$10^{-11} - 10^{-12}$	$\text{H}^\bullet + \text{OH}^\bullet \rightarrow \text{H}_2\text{O}$	10^{-4}
(11)	$\text{H}^\bullet + \text{O}_2 \rightarrow \text{HO}_2^\bullet$	0,2-3	$\text{H}^\bullet + \text{O}_2 \rightarrow \text{HO}_2^\bullet$	$10^{-4} - 10^{-5}$
(12)	$\text{PhOH} + \text{HO}_2^\bullet \rightarrow \text{PhO}^\bullet + \text{H}_2\text{O}_2$	$10^{-6} - 10^{-7}$	$\text{ArH} + \text{HO}_2^\bullet \rightarrow \text{Ar}^\bullet + \text{H}_2\text{O}_2$	$10^{-7} - 10^{-8}$
(13)	$2\text{HO}_2^\bullet \rightarrow 2\cdot\text{OH} + \text{O}_2 (\text{H}_2\text{O}_2 + \text{O}_2)$	10^{-10}	$2\text{HO}_2^\bullet \rightarrow 2\cdot\text{OH} + \text{O}_2 (\text{H}_2\text{O}_2 + \text{O}_2)$	$10^{-8} - 10^{-9}$
(14)	$\text{H}_2\text{O}_2 \xrightarrow{-h\nu} 2\cdot\text{OH}$	$10^{-14} - 10^{-15}$	$\text{H}_2\text{O}_2 \xrightarrow{-h\nu} 2\cdot\text{OH}$	$10^{-15} - 10^{-17}$
(15)	$\text{PhO}^\bullet + \text{HO}_2^\bullet \rightarrow \text{H}_2\text{O}_2 + \text{xinon} (\text{HO}_2\text{PhO}^\bullet)$	$10^{-7} - 10^{-8}$	$\text{Ar}^\bullet + \text{HO}_2^\bullet \rightarrow \text{HOAr} (\text{O}_2 + \text{ArH})$	10^{-6}
(16)	$\text{H}_2\text{O}_2 + \text{PhOH} \rightarrow \text{PhO}^\bullet + \cdot\text{OH} + \text{H}_2\text{O}$	$10^{-17} - 10^{-19}$	$\text{H}_2\text{O}_2 + \text{ArH} \rightarrow \text{Ar}^\bullet + \cdot\text{OH} + \text{H}_2\text{O}$	$10^{-18} - 10^{-20}$
(17)	$\text{PhOH} + \text{O}_2 \rightarrow \text{PhO}^\bullet + \text{HO}_2^\bullet$	$10^{-15} - 10^{-17}$	$\text{ArH} + \text{O}_2 \rightarrow \text{PhO}^\bullet + \text{HO}_2^\bullet$	$10^{-12} - 10^{-14}$
(18a)	$2\text{PhO}^\bullet + \text{O}_2 \rightarrow \text{sim} - \text{QP}$	$10^{-6} - 10^{-7}$	$\text{Ar}^\bullet + \text{O}_2 \rightarrow \text{ArO}_2^\bullet$	100
(18b)			$\text{ArH} + \text{ArO}_2^\bullet \rightarrow \text{Ar}^\bullet + \text{ArOOH}$	$10^{-3} - 10^{-5}$
(18c)			$\text{Ar}^\bullet + \text{ArO}_2^\bullet \rightarrow \text{ArOOAr}$	$10^{-4} - 10^{-6}$
(18e)			$\text{ArO}_2^\bullet + \text{ArO}_2^\bullet \rightarrow \text{products}$	10^{-9}
(18f)			$\text{ArO}_2^\bullet + \text{HO}_2^\bullet \rightarrow \text{ArOOH} + \text{O}_2$	10^{-6}
(19)	$\text{PhO}^\bullet + \text{H}_2\text{O}_2 \rightarrow \text{HOPhO}^\bullet + \cdot\text{OH}$	$10^{-21} - 10^{-23}$	$\text{H}_2\text{O}_2 + \text{Ar}^\bullet \rightarrow \text{ArH} + \text{HO}_2^\bullet$	$10^{-17} - 10^{-19}$
(20)	$\text{H}^\bullet + \text{HO}_2^\bullet \rightarrow \text{H}_2\text{O}_2 (2\cdot\text{OH})$	10^{-6}	$\text{H}^\bullet + \text{HO}_2^\bullet \rightarrow \text{H}_2\text{O}_2 (2\cdot\text{OH})$	$10^{-4} - 10^{-5}$
(21)	$\text{H}^\bullet + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{H}_2\text{O}$	$10^{-14} - 10^{-15}$	$\text{H}^\bullet + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{H}_2\text{O}$	$10^{-10} - 10^{-11}$
(22)	$\cdot\text{OH} + \text{HO}_2^\bullet \rightarrow \text{H}_2\text{O} + \text{O}_2$	10^{-12}	$\cdot\text{OH} + \text{HO}_2^\bullet \rightarrow \text{H}_2\text{O} + \text{O}_2$	$10^{-4} - 10^{-5}$
(23)	$\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2$	10^{-18}	$\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2$	$10^{-3} - 10^{-5}$
(24)	$\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^\bullet + \text{H}_2\text{O}$	10^{-21}	$\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^\bullet + \text{H}_2\text{O}$	10^{-12}
	$W_2 = 1 \text{ M/s}, W_1 = 10^{-8} \text{ M/s}$		$W_2 = 10^{-8} - 10^{-11}, W_1 = 10^{-11} - 10^{-13} (\text{M/s})$	

Thus, when irradiated by ionizing radiation phenol solutions, despite of the branched chain nature of the process, formed from phenol polyoxibenzene (hydroquinone, pyrocatechol, resorcinol, hydroxyhydroquinone ftorog-lutsin) possess toxic properties, that shows unprofitability and an inefficiency of this process for water purification from phenols and phenol derivatives.

Due to the fact that in contrast to ionizing radiation, while applying UV irradiation end products of the process are telomers and oligomers and in

oxygenated water solutions, this process acquires chain character, photolytic process of purification of phenol-containing water solutions can be characterized as efficient and cost-effective process.

Due to the fact that in most cases the mycotoxins are a benzene ring linked to the cyclic groups, after photochemical and radiation-chemical conversion it to other polycyclic compounds their physico-chemical properties specific for mycotoxins are changed. The result is that they do not adversely impact living organisms and no urgent need to process the natural decontamination easily deduced [13].

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SULU MƏHLULLARDA MİKOTOKSİNLƏRİN VƏ FENOLUN RADİOLİTİK VƏ FOTOLİTİK ÇEVİRİLMƏLƏRİNDƏ UYGUNLUQLAR

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Sulu məhlullarda fenolun və mikotoksinlərin fotolitik və radiolitik çevrilmələrinin kinetik qanunauyğunluqlarının və bu proseslərin elementar reaksiyalarının termodinamik parametrlərinin müqayisəli analizi aparılmışdır. Fenolun və mikotoksinlərin oksigensiz və oksigenli sulu məhlullarda fotolitik və radiolitik çevrilmələrini izah edən mexanizmlər təklif edilmişdir.

Açar sözlər: UB-şüalanma, radiolitik çevrilmələr, mikotoksinlər, fenol

СХОДСТВО РАДИОЛИТИЧЕСКИХ И ФОТОЛИТИЧЕСКИХ ПРЕВРАЩЕНИЙ В ВОДНЫХ РАСТВОРАХ ФЕНОЛА И МИКОТОКСИНОВ

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Проведен сравнительный анализ кинетических закономерностей фотолитических и радиолитических превращений фенола и микотоксинов в их водных растворах, термодинамических параметров элементарных реакций этих процессов. Предложены механизмы, объясняющие фотолитические и радиолитические превращения фенола и микотоксинов в их кислородсодержащих и бескислородных водных растворах.

Ключевые слова: УФ-излучение, радиолитические превращения, микотоксины, фенол