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RADIOLYTIC DECOMPOSITION OF TCDD IN WATER SOLUTIONS AND IN DAMP PLANT PRODUCTS

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Are studied the kinetic of the decomposition of 2, 3, 7, 8-tetrachlorodibenzoparadioxin (TCDD) in water solution and in damp plant products under the action of ionizing radiation of ^{60}Co. The values of the radiation-chemical yield of the decomposition of TCDD in the solutions are $(0.3…1.5)\cdot10^{-5}$mol./100 eV (for solutions with concentrations of TCDD 0.2…2 μg/l in open reaction cell) and in the air-bubbled solution $2.4\cdot10^{-5}$ mol./100 eV (for a solution with a concentration of TCDD 2 μg/l). The absorbed dose of ionizing radiation equal to 25 kGy, in the presence of molecular oxygen leads to a decrease in the studied quantities of TCDD practically to zero.

Dioxine is polycyclic substances, possessing strong mutagen, immunodepressantny, cancerogenic, teratogenny and embriotoksikogenny properties. The lethal dose of dioxine (on each kg of organism is 10^{-6} g) is one thousand times less than a lethal dose of military toxic agents. Having got into receptors, dioxine weakens the vital functions [6, 7]. Hundreds types of dioxine, with two internal cycles formed by connection of two benzene rings with one or two C-O-C bonds, and sometimes only with one linear C-C bond, are known. They are the accompanying components of plastic, pesticides, papers, defoliant production. Pollution by dioxine meet in waste of plants on burning of garbage, pulp and paper industry and processing of a tree. Dioxine is capable to accumulate in the biosphere, water, products. In a gastrointestinal tract dioxine practically doesn't decay. The contents in children's food, in milk and water is inadmissible. The Maximum-permissible Concentration (MPC) in foodstuff makes 0.000001...0.000003 mg/kg. The probability of finding of dioxine in plants and their roots is great, there is a danger of emergence in meat and dairy products [1–7].

The purpose of this research is to study the possibility of decomposition of TCDD in dilute water solutions, in damp plant products, in extracts of TCDD from plant products under the influence of ionizing radiation.

Extraction of TCDD from contaminated maize roots was carried out according to the scheme: extraction by chloroform - cleaning chloroform extract - removal of chloroform by evaporation - alkaline hydrolysis by solution of KOH in water-alcohol mixture – concentration of the solution. Water solution of 2 μg/l TCDD was prepared for comparative analysis (10 ml of a water solution containing 500 mg/l TCDD was diluted 500 fold with distilled water, 10 ml of the resulting solution was again diluted 500 fold with distilled water). The qualitative and quantitative identification of components in irradiated solutions and analysis of extracts analyzed products was performed using HPLC, GC and LC-MS (LCsolution, GC-2010, GCMS-QP 2010 systems from Shimadzu). For HPLC analysis was used fluorescence detector RF-10AXL and photodiode array detector SPD-M10AVP, "Supelco" column, mobile phase water – acetonitrile [8–11]. The dose rate from the source of ^{60}Co of radiation-chemical installation was 0.33 Gy/s [9–11]. The radiolytic decomposition of TCDD almost has not been studied. Irradiation of solutions was carried out in an open glass reaction cell with an open tap. In the reaction solution with an open cell tap was dissolved 0.0003 M atmospheric oxygen. The loss of O_2 in the oxidation of TCDD replenished by absorption from the air. Bubbling by air (600 ml/min) was performed directly in the reaction solution in the irradiated cell. In addition to HPLC analysis the changes in the infrared spectrum of the irradiated solution were studied ("Specord-IR", Carl-Zeiss). The hydrogen peroxide content in the solutions was determined by the photo colorimetric method using color intensity of hydrogen peroxide with $Ti(SO_4)_2$ [12, 13].

In order to explore the possibility of radiolytic transformation of TCDD, the irradiation of dilute aqueous TCDD (2 μg/l) and extract from contaminated maize roots (0.2 μg/l) by absorbed doses of ionizing radiation ^{60}Co source, equal to 1, 2.5, 10 and 25 kGy were performed.

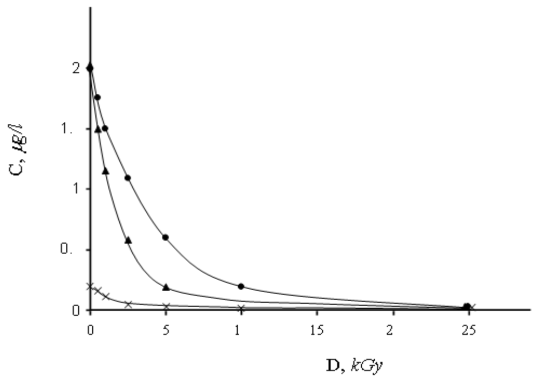
In Fig. 1 shows the concentration decrease of TCDD depending on the value of the absorbed dose.

Apparently, increase of speed of TCDD decomposition (approximately by 1.5 times) is observed by at bubbling of solutions by air. Are given the values of radiochemical yields of TCDD decomposition in irradiated water solutions below:

– the absorbed dose of ionizing radiation equal to 1.0 kGy is equivalent $6.24\cdot10^{21}$ eV/kg;

– during absorption of this dose (3000 s) concentration of TCDD decreases on 0.5 μg/l (at irradiation of solution with concentration of TCDD 2 μg/l in open cells) that corresponds to decomposition $9.3\cdot10^{14}$ molecules of THDD in 1 liter of water solution (the relative molecular mass of TCDD is equal to 322 g/mol);

– it is possible to receive from the above results the values of a radiochemical yield of TCDD molecule's decomposition at absorption by solutions the energy 100 eV.



Dependence of concentration decrease of TCDD in water solutions and in contaminated damp maize roots on absorbed dose:
●, ▲ – irradiation of the TCDD water solution (2 μg/l) in open cell and at bubbling by air;
× – irradiation of the THDD (0.2μg/l) in water solution (in open reaction cell) and In damp maize roots

These values are equal, respectively $1.5 \cdot 10^{-5}$ and $2.4 \cdot 10^{-5}$mol./100 eV for solution with concentration of TCDD 2 μg/l in open cell and at bubbling by air solution, $3 \cdot 10^{-6}$ mol./100 эВ for solution with concentration of TCDD 0.2 μg/l in open cell.

Estimated by weighting on electronic scales of the dried-up filter paper, after the filtration of the irradiated solution, the mass of the formed polymers approximately corresponds to decrease in concentration of TCDD.

All free radical products of water's radiolysis can take part (e^-_{aq}, H, OH, O, H^+_{aq}, OH^-_{aq}) in the course of decomposition of TCDD.

The mechanism of radiolytic transformation of the halogenated aromatic substances and radiochemical yields of the formed products (H_2, Cl_2, HCl, C_6H_6, $C_6H_4Cl_2$, $C_6H_5C_6H_5$, $C_6H_5C_6H_4Cl$, etc. multimers) are in detail stated in work [14].

Unlike the stated mechanism for the galogenated aromatic substances, in our experiments is carried out the radiolysis of oxygen-containing water solutions of microquantities of organic xenobiotics (TCDD).

Consideration the constants of speeds of the main elementary reactions and studying of transformation of TCDD and formation of polymeric products we offered the following mechanism of radiolytic decomposition of TCDD in the diluted water solutions. Primary concentration of free radical products are considered for assessment of the role of elementary reactions. TCDD in the scheme is designated for brevity by a formula Ar_xH_yCl:

$$Ar_xH_yCl \rightsquigarrow {}^{\bullet}Ar_xH_y + Cl^{\bullet}, \qquad (0)$$

$$H_2O \rightsquigarrow H, {}^{\bullet}OH, e^-_{aq}, H^+_{aq}, OH^-_{aq}, \qquad (0')$$

$$H_2O \rightsquigarrow H_2O^+ + e^-_{aq}, \qquad (0'a)$$

G_H = 0.6 atom/100 eV or $2 \cdot 10^{-8}$ M/s, $G_{\bullet OH}$ = 2.8...2.9 or 10^{-7} M/s,
G_{H2} = 0.45 or $1.5 \cdot 10^{-8}$ M/s, G_{H2O2} = 0.75 or $2.5 \cdot 10^{-8}$ M/s,
Ge^-_{aq} = 2.8...2.9 or 10^{-7} M/s, G_{H^+aq} = 3.3...3.4 or $1.1 \cdot 10^{-7}$ M/s,
G_{OH^-aq} = 0.5...0.6 or $2 \cdot 10^{-8}$ M/s, G_{-H2O} = 4.3...4.4 or $2.5 \cdot 10^{-8}$ M/s.

$H_2O^+ + H_2O \rightarrow H_3O^+ (H^+_{aq}) + {}^{\bullet}OH$	(1)	$k_1 = 1.2 \cdot 10^{10}\ M^{-1}s^{-1}$,	[14]
$H + Ar_xH_yCl \rightarrow {}^{\bullet}Ar_xH_y + HCl\ (H^{\bullet}Ar_xH_yCl)$	(2)		
$H + Ar_xH_yCl \rightarrow {}^{\bullet}Ar_xH_{y-1}Cl + H_2$	(2a)	$k_{2a} = 10^8...10^9\ M^{-1}s^{-1}$,	[14, 15]
${}^{\bullet}OH + Ar_xH_yCl \rightarrow {}^{\bullet}Ar_xH_{y-1}Cl + H_2O$	(3)	$k_3 = 10^9...10^{10}\ M^{-1}s^{-1}$,	[14, 15]
$H + O_2 \rightarrow HO^{\bullet}$	(4)	$k_4 = 2 \cdot 10^{10}\ M^{-1}s^{-1}$,	[14]
$HO^{\bullet}_2 + Ar_xH_yCl \rightarrow {}^{\bullet}Ar_xH_{y-1}Cl + H_2O_2$	(5)	$k_5 = 10^{0,15}...10^{2,2}\ M^{-1}s^{-1}$,	[15]
$HO^{\bullet}_2 + {}^{\bullet}Ar_xH_y \rightarrow Ar_xH_{y-1} + H_2O_2 (HO_2Ar_xH_y)$	(6)	$k_6 = 10^8...10^9\ M^{-1}s^{-1}$,	[16]
${}^{\bullet}OH + {}^{\bullet}Ar_xH_y \rightarrow HOAr_xH_y$	(7)	$k_7 = 10^9...10^{10}\ M^{-1}s^{-1}$,	[15, 16]
$H + Ar_xH_{y-1} \rightarrow {}^{\bullet}Ar_xH_y$	(8)	$k_8 = 10^8...10^9\ M^{-1}s^{-1}$,	[14, 15]
${}^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}$	(9)	$k_9 = 4.5 \cdot 10^7\ M^{-1}s^{-1}$,	[14]
$e^-_{aq} + H_2O_2 \rightarrow {}^{\bullet}OH + {}^{\bullet}OH$	(10)	$k_{10} = 1.3 \cdot 10^{10}\ M^{-1}s^{-1}$,	[14]

$2\,{}^{\bullet}Ar_xH_y \rightarrow H_yAr_xAr_xH_y$ (11) $2k_{11} = 10^2...10^9\ M^{-1}s^{-1}$, [15, 16]

${}^{\bullet}Ar_xH_y + O_2 \rightarrow H_yAr_xO^{\bullet}_2$ (12) $k_{12} = 10^7...10^8\ M^{-1}s^{-1}$, [15, 16]

$H_yAr_xO^{\bullet}_2 + {}^{\bullet}Ar_xH_y \rightarrow H_yAr_xOOH_yAr_x$ (13) $k_{13} = 10^8...10^9\ M^{-1}s^{-1}$, [15, 16]

Supervision at all experiments only of trace amounts of hydrogen peroxide is explained by existence of the competing reactions (2), (2a), (3), (4), (5).

There may be other reactions of formed macroradicals of polymer organic matrix of plant product (R_XH) with free-radical products of water radiolysis and TCDD at irradiation of damp plant products:

$R_xH - \gamma \rightarrow H + R_x^{\bullet}$

$H + O_2 \rightarrow HO^{\bullet}_2$ (4) $k_4 = 2\cdot10^{10}\ M^{-1}s^{-1}$

$HO_2^{\bullet} + R_xH \rightarrow H_2O_2 + R_x^{\bullet}$ (14) $k_{14}\ (44^oS) = 0{,}003\ M^{-1}s^{-1}$

$R_x^{\bullet} + O_2 \rightarrow R_xO_2^{\bullet}$ (15) $k_{15} = 10^7...10^8\ M^{-1}s^{-1}$

$Ar_xH_yCl + R_xO_2^{\bullet} \rightarrow$ products (16) $k_{16} = 10^4...10^6\ M^{-1}s^{-1}$

${}^{\bullet}Ar_xH_y + R_xO_2^{\bullet} \rightarrow$ products (17) $k_{17} = 10^8...10^9\ M^{-1}s^{-1}$

$H_yAr_xO^{\bullet}_2 + R_xO_2^{\bullet} \rightarrow$ products (18) $k_{18} = 10^2...10^9\ M^{-1}s^{-1}$.

The formed radicals of TCDD under the influence of ionizing radiation and with the participation of free radical products of a radiolysis of water and molecular oxygen besides oxidation are exposed to a mutual recombination, to a recombination with macroradicals of organic matrix of plant product and to recombination via oxygen bridges, forming heavier (polymeric) products. Toxicity and cancerogenic properties of formed polymeric products depending on degree of polymerization are more below toxicity of TCDD [2, 5, 6, 9–11]. The absorbed dose of ionizing radiation equal to 25 kGy leads to decrease the studied concentration of TCDD practically to zero.

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РАДИОЛИТИЧЕСКОЕ РАЗЛОЖЕНИЕ ТХДД В ВОДНЫХ РАСТВОРАХ И ВО ВЛАЖНЫХ РАСТИТЕЛЬНЫХ ПРОДУКТАХ

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Изучена кинетика разложения 2, 3, 7, 8-тетрахлордибензопарадиоксина (ТХДД) в разбавленных водных растворах и во влажных растительных продуктах под действием ионизирующего излучения ^{60}Co. Значения радиационно-химического выхода разложения ТХДД в исследуемых растворах равны (0,3…1,5)·10^{-5}мол./100 эВ (для растворов с концентрациями ТХДД 0,2…2 мкг/л в открытых реакционных ячейках) и 2,4·10^{-5} мол./100 эВ в барботируемом воздухом растворе (для раствора с концентрацией ТХДД 2 мкг/л). Поглощенная доза ионизирующего излучения, равная 25 кГр, в присутствии молекулярного кислорода приводит к снижению исследуемых количеств ТХДД практически до нуля.

РАДІОЛІТИЧНЕ РОЗКЛАДАННЯ ТХДД У ВОДНИХ РОЗЧИНАХ ТА У ВОЛОГИХ РОСЛИННИХ ПРОДУКТАХ

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Вивчена кінетика розкладання 2, 3, 7, 8-тетрахлордибензопарадіоксину (ТХДД) у розведених водних розчинах та у вологих рослинних продуктах під дією іонізуючого випромінювання ^{60}Co. Значення радіаційно-хімічного виходу розкладання ТХДД у досліджуваних розчинах складають (0,3...1,5)·10^{-5}мол./100 еВ (для розчинів з концентраціями ТХДД 0,2...2 мкг/л у відкритих реакційних клітинках) і 2,4·10^{-5} мол./100 еВ у барботованому повітрям розчині (для розчину з концентрацією ТХДД 2 мкг/л). Поглинута доза іонізуючого випромінювання, що дорівнює 25 кГр, у присутності молекулярного кисню призводить до зниження досліджуваних кількостей ТХДД практично до нуля.