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KINETIC REGULARITIES OF RADIOLYTIC DEGRADATION OF CHLOROFORM IN WATER SOLUTIONS

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Abstract: The regularities of removing chloroform ($CHCl_3$) from its water solutions under the influence of ionizing radiation were studied. It is shown that the decrease of the concentration of chloroform with increasing absorbed dose occurs. The degree of decomposition of chloroform is about 95% at 6kGy.

Keywords: Water solution of chloroform, γ-radiation, chromatography analysis, radiolytic decomposition.

1. Introduction

Chlorinated hydrocarbons are forming during the chlorination of water in the water disinfection process. A number of chlorinated compounds are formed in the process, but the main of them are trichloromethane.

Traditional methods are used for the purification of potable water from the chlorinated compounds, as well innovative methods based on the use of UV and ionizing radiation.

In [1], the process of removing of *trichloroethylene and tetrachloroethylene* from water solutions under the influence of electron beam was studied. Kinetic modeling based on the reaction of intermediate particles of water radiolysis with doped chlorinated molecules was carried out for the clarification of dechlorination mechanism.

In [2], the reaction of hydroxyl radicals and hydrogen atoms with chloroacetone (1.1 dichloroacetone and 1,1,1 -trichloro*acetone*) was studied by pulse radiolysis method. Appropriate constant of reaction rate constants of e_q, OH and H radicals with above mentioned molecules were defined.

In [3], constants of radical reaction rate and electrons, forming in the radiolysis of water with molecules of 4-chlorophenol were defined by pulse radiolysis method.

In [4], the process of cleaning waste and drinking water from methanehalogen ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$) was studied.

It was shown that, the degree of transformation of chloroform increases with an increase of absorbed dose and reaches to 95% at 6kGy dose. Similar results were obtained for the process of radiolytic transformation of other halogenmethanes.

The aim of this work is the study of kinetic regularities of radiolytic degradation of chloroform in water solution at various initial concentration of chloroform.

2. Experimental technique

Water solutions of chloroform (0.03%, 0.5%, 0.7%, 1.0%) were irradiated with γ-radiation from ^{60}Co isotope under static conditions in glass ampules at room temperature. Dose rate is determined by ferrosulfate dosimeter, pH indicators according to standard methods and CO_2-chromatography. In the experiments, chloroform solutions with content 0.03%, 0.5%, 0.7%, 1.0% were used. The samples were irradiated in the range of absorbed dose (4,3-43kGy).

Fig. 1 shows the kinetic curves of changes of the concentration of chloroform depending on the absorbed dose.

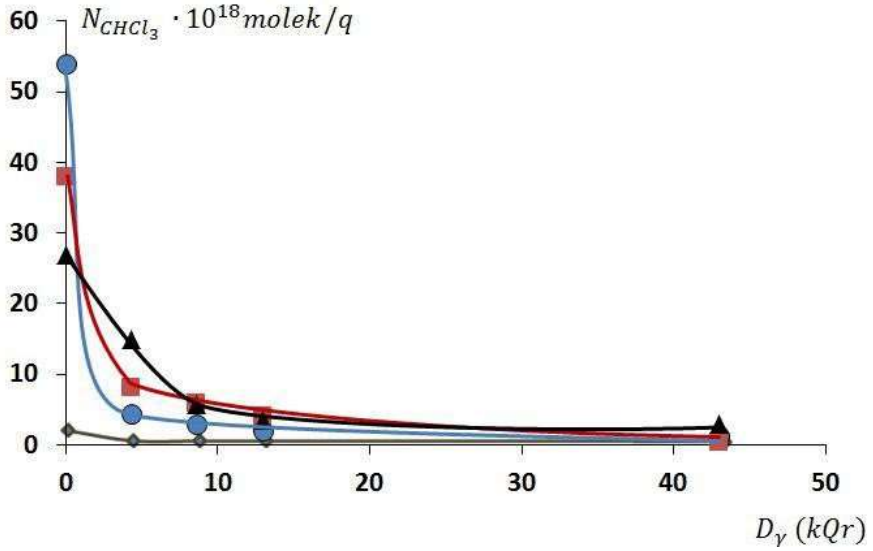

Fig.1. Dependence of the concentration of the chloroform on absorbed dose at its different content: ● 1 % - $CHCl_3$, ■ 0,7 % - $CHCl_3$, ◆ 0,5 % - $CHCl_3$, ▲ 0,03 % - $CHCl_3$

As it is seen from Fig. 1. the concentration of chloroform decreases with the increase of absorbed dose. The rate of transformation of chloroform depends on its initial content and increases up to (6-130) molec. / 100ev with increasing of last radio-chemical yield. Calculated radio-chemical yields are shown in Table 1.

Table 1.The radiation-chemical yields of degradation of chloroform at various initial content of chloroform.

$CHCl_3$, % (weight.)	G (molec./100ev)
0,03	6,4
0,5	46
0,7	80
1	129

The obtained data indicates that reaction of consumption has chain character at the concentration of chloroform in the water solutions at ≥ 0.5%.

There occur changes of pH-indicator as a result of chemical transformations in water solution of chloroform (Fig. 2).

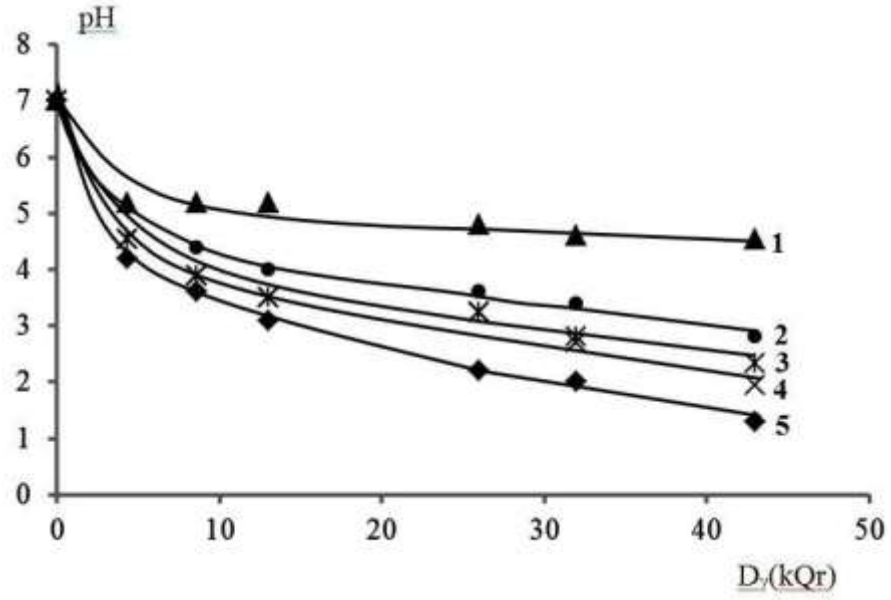

Fig. 2. Change of pH depending on absorbed dose at different initial content of chloroform: 1 – 0,03 % $CHCl_3$, 2 – 0,2 % $CHCl_3$, 3 – 0,5 % $CHCl_3$, 4 – 0,7 % $CHCl_3$, 5 – 1,0 % $CHCl_3$

As it is seen, the increase of the absorbed dose leads to decreasing of pH, indicating the formation of acidic products. These products may be formed as a result of hydrolysis of some products. For example, in the reaction of hydrolysis CCl_3OOH and phosgene.

$$CCl_3OOH + H_2O \rightarrow 2HCl + HClO + CO_2 \; (3H^+ + ClO^- + 2Cl^- + CO_2)$$

$$COCl_2 + H_2O \rightarrow 2HCl + CO_2 \; (2H^+ + 2Cl^- + CO_2)$$

The following prospective processes take place in the radiolysis of water solutions of chloroform:

a) Direct water radiolysis

$H_2O \rightarrow e^-, OH, H, O, H_2, H_2O_2, H^+, OH^-$

b) Reaction with chloroform molecules:

$OH + CHCl_3 \rightarrow H_2O + CCl_3$

$H + CHCl_3 \rightarrow H_2 + CCl_3$

$e + CHCl_3 \rightarrow CHCl_2 + Cl^-$

c) Competitive reaction:

$OH + OH \rightarrow H_2O_2$

$H + OH \rightarrow H_2O$

$H + H \rightarrow H_2$

$H + O_2 \rightarrow HO_2$

$e^- + O_2 \rightarrow O_2^-$

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

$HO_2 + O_2^- + H_2O \rightarrow H_2O_2 + O_2 + OH_{aq}^-$

$HO_2 + OH \rightarrow H_2O + O_2$

$HO_2 \rightleftarrows H^+_{aq} + O_2^-$

$HO_2 + H^+_{aq} \rightleftarrows H_2O_2^+$

d) Transformation of CCl_3 radicals:

$CCl_3 + O_2 \rightarrow CCl_3O_2$

$CCl_3 + CCl_3 \rightarrow C_2Cl_6$

$CCl_3 + HO_2 \rightarrow CCl_3OOH$

e) Transformation of $CHCl_2$ radicals:

$CHCl_2 + CHCl_3 \rightarrow CHCl_2 + CCl_3$

$CHCl_2 + CCl_3 \rightarrow C_2HCl_5$

$CHCl_2 + CHCl_2 \rightarrow C_2H_2Cl_4$

f) The impact of oxygen:

$CCl_3 + O_2 \rightarrow CCl_3O_2$

$CCl_3O_2 + CHCl_3 \rightarrow CCl_3OOH + CCl_3$

$CHCl_2 + O_2 \rightarrow CHCl_2OO^{\cdot}$ (HOCl + COCl)

$COCl + CHCl_3 \rightarrow COCl_2 + CHCl_2$

$CHCl_2O_2 + CHCl_3 \rightarrow C_2H_2Cl_2 + CCl_3 + O_2$

g) Hydrolysis reactions

$COCl_2 + H_2O \rightarrow 2HCl + CO_2$ $(2H^+ + 2Cl^- + CO^2)$

$CCl_3OOH + H_2O \rightarrow 2HCl + HClO + CO_2$ $(3H^= + ClO^- + 2Cl^- + CO_2)$

h) $CCl_3O_2 + CCl_3O_2 \rightarrow C_2Cl_6 + 2O_2$

$CHCl_2O_2 + CHCl_2O_2 \rightarrow C_2H_2Cl_4 + 2O_2$

i) Reaction of secondary products.

$C_2H_2Cl_4$ and CH_2Cl_6 were identified as products of transformation of chloroform, so the secondary reactions of these molecules with the primary particles while discussing the mechanism of the process:

$OH + C_2H_2Cl_4 \rightarrow CCl_3CHCl + H_2O$

$H + C_2H_2Cl_4 \rightarrow H_2 + C_2HCl_4$

$e^- + C_2H_2Cl_4 \rightarrow C_2H_2Cl_3 + Cl^-$

$OH + CH_2Cl_2 \rightarrow H_2O + CHCl_2$

$H + CH_2Cl_2 \rightarrow HCl + CH_2Cl + CHCl_2 + H_2$

$e^- + CH_2Cl_2 \rightarrow CH_2Cl + Cl^-$

At high doses end-products can also react with hydrogen peroxide:

$$C_2HCl_4 + H_2O_2 \rightarrow \text{products}$$

$$CHCl_2 + H_2O_2 \rightarrow \text{products}$$

Simplified diagram of chain transformation of chloroform can be presented by the following reactions

1. $CCl_3 + O_2 \rightarrow CCl_3O_2$
2. $CCl_3O_2 + CHCl_3 \rightarrow CCl_3OOH + CCl_3$
3. $CCl_3 + CCl_3 \rightarrow C_2Cl_6$
4. $CCl_3 + CCl_3O_2 \rightarrow C_2Cl_6 + O_2$
5. $CCl_3O_2 + CCl_3O_2 \rightarrow C_2Cl_6 + 2O_2$

For nonramified chain reaction we can write

$$W_1 = W_2 \quad (1)$$

$$W_{init.} = W_{recom.} \quad (2)$$

For radiation-chemical yield of radiolytic decomposition of chloroform solution, we obtain

$$G(-CHCl_3) = k_1[O_2]\sqrt{\frac{k\ k\ [O}{G \cdot 10^2}\ \frac{k\ [O\ ]}{k_3 + \frac{1\ 4\ \ 2]}{k_2[CHCl_3]} + k_5\left(\frac{1\ \ 2}{k_2[CHCl_3]}\right)^2}} \cdot \frac{1}{\sqrt{P}}$$

As it is seen from the equation, radiation-chemical yield of radiolytic decomposition of chloroform depends on concentration of dissolved oxygen, oxygen chloroform ratio and square root of absorbed dose rate.

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КИНЕТИЧЕСКИЕ ЗАКОНОМЕРНОСТИ РАДИОЛИТИЧЕСКОЙ ДЕГРАДАЦИИ ХЛОРОФОРМА В ВОДНЫХ РАСТВОРАХ

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Резюме: Исследованы закономерности удаления хлороформа ($CHCl_3$) из его водных растворов под действием ионизирующего излучения. Показано, что происходит уменьшение концентрации хлороформа с ростом поглощенной дозы. Степень разложения хлороформа составляет 95% при 6 кГр.

Ключевые слова: Водные растворы хлороформа, γ-излучение, хроматоргафический анализ, радиолитическое разложение.

XLOROFORMUN SUDA MƏHLULLARININ RADİOLİTİK DEQRADASİYA PROSESİNİN KİNETİK QANUNAUYĞUNLUQLARININ TƏTQİQİ

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Xülasə: İonlaşdırıcı şüaların təsiri ilə xloroformun radiolitik parçalanma prosesinin qanunauyğunluqları öyrənilmişdir. Udulan dozalardan asılı olaraq xloroformun qatılığı azalır. 6 kQr dozada xloroformun 95%-i parçalanır.

Açar sözlər: Xloroformun suda məhlulları, γ-şüalar, xromatoqrafik analiz, radiolitik parçalanma.