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**Aysun Qadirli**

Azerbaijan State Oil and Industry University  
magistrant  
aysun.qedirli2000@mail.ru

**Ulviya Guliyeva**

Institute of Radiation Problems of the Ministry of Science and Education  
ulviyegulieva13@gmail.com

**Salimkhan Aliyev**

Institute of Radiation Problems of the Ministry of Science and Education  
selimkhan.aliyev@gmail.com

## REGULATIONS OF THE RADIOLYSIS PROCESS OF AQUEOUS SOLUTIONS OF ORGANIC POLLUTANTS OF DIFFERENT CONCENTRATION

### Abstract

The radiolysis process of aqueous solutions of oxalate and formic acids at  $10^{-1}$ – $10^{-5}$  M concentration was studied in this study by gamma irradiation. Obtained results were explained by the physico-chemical and spectroscopic methods. Radiation-chemical yields was calculated for all systems. It varies between 0.03–0.25 molec/100 eV for oxalic acid and 0.04–0.5 molec/100 eV for formic acid. For the additional information about conversion products UV-spectroscopic studies were conducted. It was determined, that absorption (Abs) decreases in accordance with the decrease in concentration.

**Keywords:** *organic acids, radiation technology, water treatment, decomposition products*

**Aysun Qədirli**

Azərbaycan Dövlət Neft və Sənaye Universiteti  
magistrant  
aysun.qedirli2000@mail.ru

**Ülviyə Quliyeva**

Elm və Təhsil Nazirliyinin Radiasiya Problemləri İnstitutu  
ulviyegulieva13@gmail.com

**Səlimxan Əliyev**

Elm və Təhsil Nazirliyinin Radiasiya Problemləri İnstitutu  
selimkhan.aliyev@gmail.com

### Müxtəlif qatılıqlı üzvi çirkləndiricilərin suda məhlullarının radiolizi

#### Xülasə

Bu tədqiqatda qamma şüalarının təsiri altında  $10^{-1}$ – $10^{-5}$  M qatılıqda oksalat və qarışqa turşularının sulu məhlullarının radioliz prosesi öyrənilmişdir. Alınmış nəticələr fiziki-kimyəvi və spektroskopik üsullarla tədqiq edilmişdir. Bütün sistemlər üçün radiasiya-kimyəvi çıxımlar hesablanmışdır. Radiasiya-kimyəvi çıxım oksalat turşusu üçün 0,03–0,25 mol/100 eV, qarışqa turşusu üçün 0,04–0,5 mol/100 eV təşkil edir. Çevrilmə məhsulları haqqında əlavə məlumat üçün UB- spektroskopik tədqiqatlar aparılmışdır. Müəyyən edilmişdir ki, qatılığın azalmasına uyğun olaraq udulma (Abs) azalır.

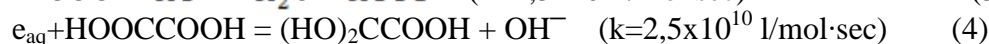
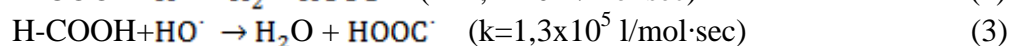
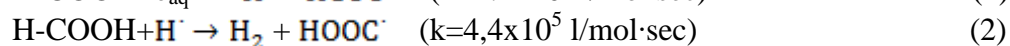
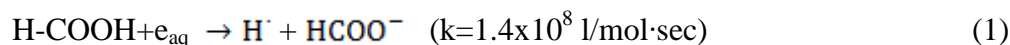
**Açar sözlər:** *üzvi turşular, radiasiya texnologiyası, water purification, parçalanma məhsulları*

## Introduction

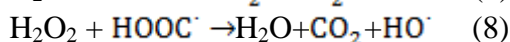
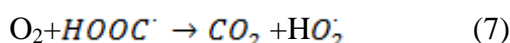
Water treatment from organic pollutants is very important for the water recycling in industry and drinking water treatment. Using modern oxidation methods (AOP`s) is possible to break down high molecular mass and toxic chemical compounds into less molecular mass and less harmful compounds. AOP`s include electrochemical, catalytic, photolytic, radiolytic and combined oxidation methods (Andreozzi, 1999: 51-59; Zhu, Zou, 2009: 47-54). It occurs due to oxygen-containing ions and radicals in the reactions occurring during the process, especially in the presence of OH radicals ( $E_0=2.7\text{eV}$ ). The conducted studies show that the reactions of OH radicals and organic molecules proceed faster at the value of the rate constant  $10^6\div 10^9\text{ M}^{-1}\text{s}^{-1}$  (Krystynik, 2021: 20).

The study by applying radiation technology to the studied system is related to some reasons. So with this method, it is possible to reduce the amount (solidity) of harmful compounds to the minimum level and convert them into 1:53-56 lower molecular mass compounds. The process begins with the formation of carbon-bonded (carbon-centered) radicals as a result of reactions of OH radicals with organic molecules. In the presence of dissolved oxygen in the system, carbon-centered radicals are converted to peroxy radicals, which in turn are converted to lower molecular mass products.

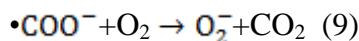
Oxalic and formic acids are decomposition products of complex organic acids (Belov, Naumchik, 2013: 46-49). Formic acid is a radiolytically unstable organic compound. Both acids are currently widely used as organic pollutants. Despite the extensive study of radiolytic decay under the influence of gamma rays (Pirogova, Zhestkova, Voronin, 2002: 287-289; Gordeev, Ershov, Kosareva, 2005: 207-211), mechanistic issues at larger doses have been less studied. Formic acid reacts with  $e_{\text{aq}}$ , H, OH as follows (Gurbanov, Guliyeva, Mammadov, Mahmudov, 2015: 353-356):



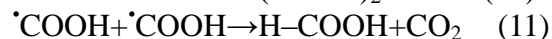
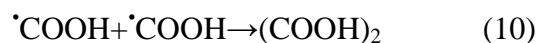
$\text{HOOC}^\cdot$  radicals formed during reactions (2) and (3) can easily react with  $\text{O}_2$  and  $\text{H}_2\text{O}_2$  and be oxidized:



Along with  $\text{HOOC}^\cdot$  (formyl) radicals in the solution, anionic radicals of carbon dioxide also react with molecular oxygen.



The formed formyl radicals can polymerize and disproportionate:



Reaction (6) is more likely to occur. Thus, ~4% of formic acid is in the dissociated form in the solution.

$$K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = 1.8 \cdot 10^{-4} \quad (12)$$

The decomposition products of formic acid are oxalic acid, H<sub>2</sub>O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O (Gulieva, Gurbanov, Abdullayev, Kerimov, 2017: 32-36). Formic acid with a concentration of 0.01 mol/l at a dose of 60 kGy is converted to oxalic acid.

The radiolysis process of aqueous solutions of oxalate and formic acids at 10<sup>-1</sup>÷10<sup>-5</sup> M concentration was studied in this study. All samples were irradiated with the same dose (D=13 kGy).

The aim of the work is to study the kinetic and spectroscopic regularities of the processes occurring during the radiolysis of aqueous solutions of oxalic and formic acids of different concentrations irradiated with the same dose.

### Methodology.

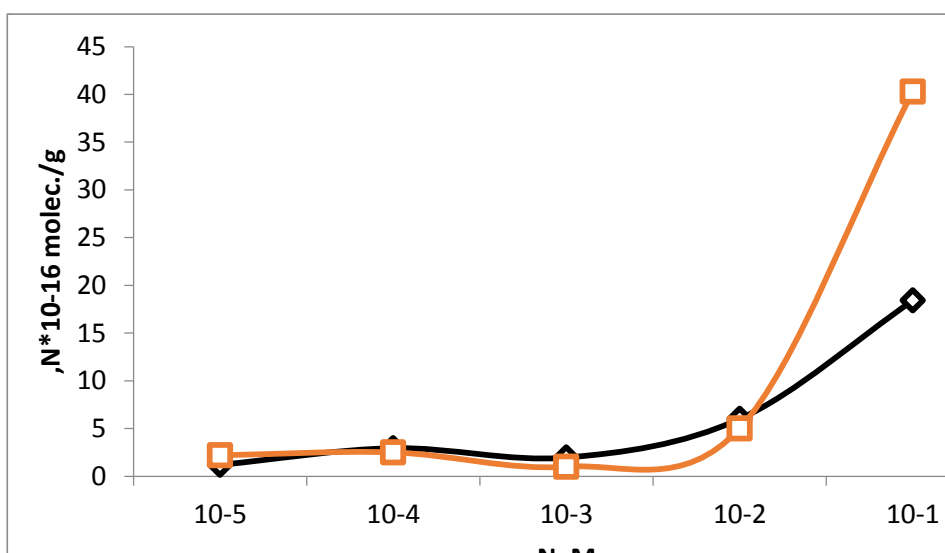
Solutions of formic and oxalic acids in water with a concentration of 10<sup>-1</sup>÷10<sup>-5</sup> M were prepared. The total volume of ampoules was V<sub>um</sub>=12 ml, the analyzed volume was V<sub>um</sub>=5 ml. All ampoules are sealed in weather conditions. Irradiation was carried out at room temperature, in static conditions and in a <sup>60</sup>Co isotope device. During the irradiation, the power of the device was 0.16 Gy/sec (Zhestkova, Zhukova, 2001: 635-637).

Gas analysis was performed in a GAZOCHROM-3101 gas chromatograph (column - activated charcoal AG-3, carrier gas - air). The amount of hydrogen peroxide was determined according to the standard methodology. Since the amount of KMnO<sub>4</sub> used for titration is solid, 25 ml of 0.005 N solution was prepared and 25 ml of distilled water was added. KMnO<sub>4</sub> solution with a concentration of 0.0025 N was used in the titration (Tisa, Abdul Raman, Wan Daud, 2014: 260-275).

Spectroscopic studies were determined in a VARIAN SCAN-50 (UV-Visible Spectrophotometer) spectrophotometer at a wavelength of λ=200-800 nm. The volume of the cuvette used during the analysis is 4 ml, and its thickness is 10 mm.

Because oxalic and formic acids were observed to decompose at doses of 10-20 kGy in previous studies, an absorption dose of 13 kGy was chosen for the study. At the initial stage of radiolysis, the process proceeds with the formation of radicals as a result of the interaction of •OH radicals with oxalate and formate ions, and the subsequent stage with the transformation of radicals.

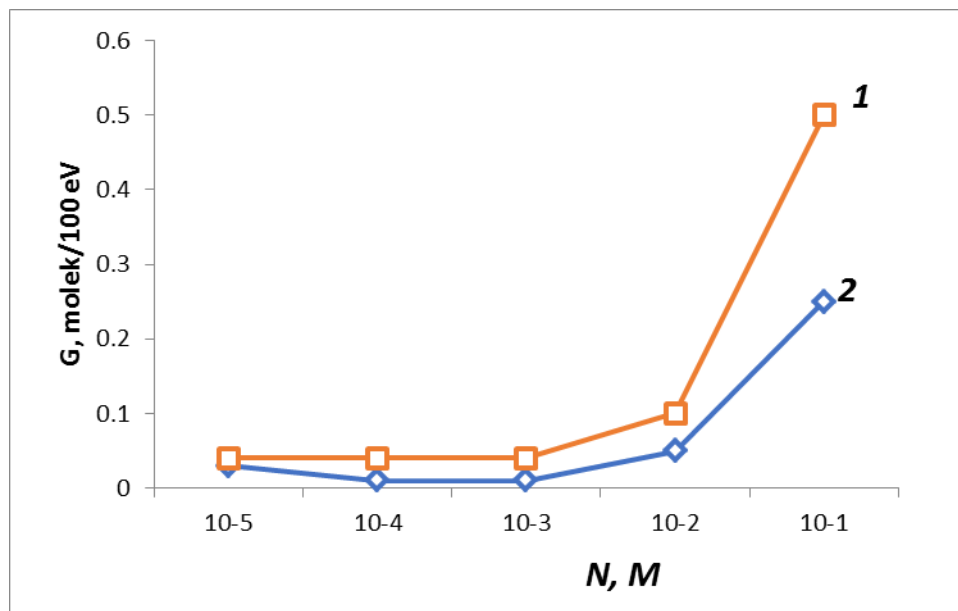
Fig. 1 shows the graph of the concentration dependence of hydrogen produced as a function of concentration for both acids (Gordeyev, Yershov, Kosareva, 2005: 250-254).



**Fig. 1.** Kinetics of changes in the concentration of hydrogen formed during the radiolysis of oxalic and formic acids aqueous solutions depending on total solution concentration.  
 1-formic acid, 2-oxalic acid (D=13 kGy, P=0.16 Gy/sec)

As can be seen from fig. 1, the amount of hydrogen gas produced during the radiolysis of oxalate and formic acids of different concentrations decreases with the decrease in density, or vice versa. At  $10^{-1}$  concentrations of hardness for both acids, the hardness changes sharply and takes a large value. Thus, intense gas formation at the absorption dose of 10-20 kGy is related to the decomposition of oxalate and formic acids themselves (Pirogova, Zhestkova, Voronin, 2002: 287-289).

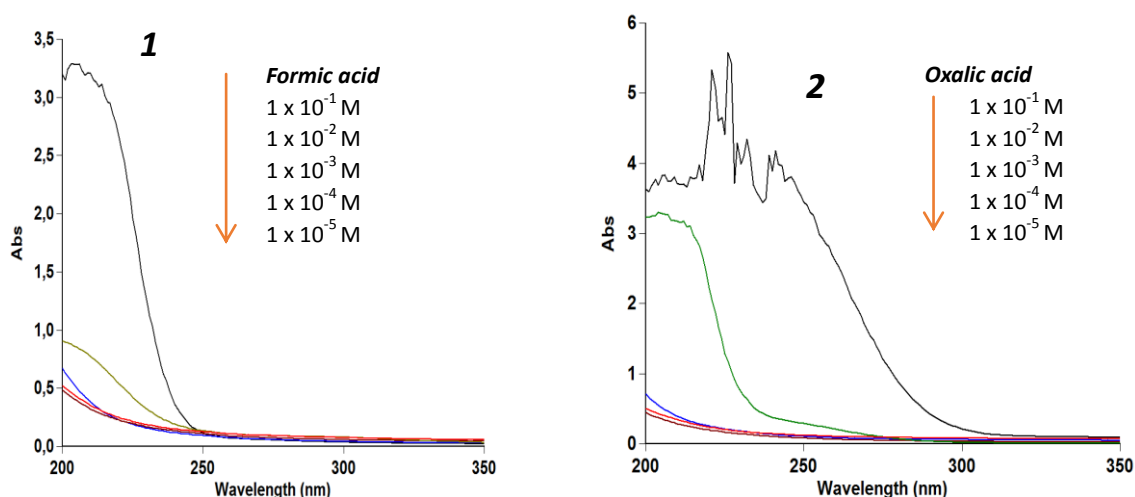
Fig. 2 shows the variation of radiation-chemical yield for both acids depending on the concentration.



**Fig. 2.** Kinetics of radiation-chemical output during radiolysis of aqueous solutions of oxalic and formic acids at different concentrations  
1- formic acid, 2-oxalic acid (D=13 kGy, P=0.16 Gy/sec)

As can be seen from Fig. 2, during the radiolysis of aqueous solutions of formic and oxalic acids irradiated with the same dose (D=13 kGy), the radiation-chemical output also decreases in accordance with the decrease in density. It varies between  $0.03 \div 0.25$  molek/100 eV for oxalic acid and  $0.04 \div 0.5$  molek/100 eV for formic acid (Gurbanov, Guliyeva, 2018: 46-50).

In order to get additional information and to identify products formed during the conversion process UV-spectroscopic studies were conducted. Fig. 3 shows the results of the UV-spectroscopic study of radiolysis of aqueous solutions of oxalic and formic acids of different concentrations.



**Fig. 3.** UV-absorption spectra of radiolysis of various aqueous solutions of oxalate (1) and formic acid (2) ( $\lambda=250-350$  nm,  $D=13$  kGy,  $P=0.16$  Gy/sec)

As can be seen from fig. 3, from a comparison of the UV absorption spectra obtained by radiolysis of an aqueous solution of both acids, it can be seen that with decreasing concentration the absorbance (Abs) value also decreases. In both cases, a decrease in the direction of  $10^{-1} \rightarrow 10^{-2} \rightarrow 10^{-3} \rightarrow 10^{-4} \rightarrow 10^{-5}$  M is observed. It was determined, that the number and density of products formed in large concentrations is greater. During the radiolysis of aqueous formic acid solution at  $1 \cdot 10^{-1}$  mol/l concentration were observed decomposition products at  $\lambda=200-230$  nm. At  $1 \cdot 10^{-1}$  mol/l and  $1 \cdot 10^{-2}$  mol/l concentration during the radiolysis of aqueous oxalic acid solution decomposition products are observed at  $\lambda =200-260$  nm. Absorption is not observed in the absorption spectrum of the aqueous solution of oxalic acid in the wavelength region  $\geq 300$  nm, so it is classified as a simple aliphatic compound (Belov, Naumchik, 2013: 46-49). The products obtained from the decomposition of formic acid include dihydroxy tartaric acid, hydroxytartaric acid, and glyoxal acids. The processed glyoxal acid is later converted to oxalic acid. The extinction coefficient of formic acid ( $\epsilon=451$  l·mol<sup>-1</sup>·sec) is many times smaller than the decomposition products formed and the extinction coefficient of oxalic acid ( $\epsilon=1800$  l·mol<sup>-1</sup>·sec). The complex content of transformation products is related to oxidation processes due to atomic oxygen and hydroxyl radicals in the system, as well as reduction reactions due to atomic oxygen and hydrated electrons.

### Conclusions

1. From the comparison of the UV-absorption spectra obtained from the radiolysis of the water solution of both acids, it can be seen that Abs decreases in accordance with the decrease in concentration.

2. It was determined, that intense gas formation at the absorption dose of 10-20 kGy is related to the decomposition of oxalate and formic acids themselves. The radiation-chemical output also decreases in accordance with the decrease in density.

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