RADIATION-CHEMICAL PROCESSES OF AQUEOUS SOLUTIONS OF LOW-MOLECULAR ORGANIC ACIDS UNDER THE IONIZING IRRADIATION

U.A. Gulieva, M.A. Gurbanov, S.M. Aliyev
ANAS Institute of Radiation Problems
ulviyegulieva13@gmail.com

Abstract: The aqueous solutions of oxalic acid and formic acid radiolysis under gamma rays was studied. The kinetics change of the hydrogen peroxide concentration, the COD and pH change, and the formation of gaseous products in their aqueous solutions depending on the absorbed dose were studied. In both solutions the acidity decreases, and this is due to the radiolytic decomposition of acids in the solution. From the initial part of kinetic curves, the radiation-chemical yields for CO_2 were calculated.

Key words: U-V and γ-irradiation, radiolysis, liquid radioactive waste, radiation-chemical yield

1. Introduction

Oxalic and formic acids are the main microcomponents of liquid radioactive wastes (LRW).The decomposition of these acids under the different radiation types (UV- and γ-irradiation) was studied in [1-4, 6-9], in order to clarify the possibility of applying radiation-chemical technologies for water purification from toxic components and to study mechanism of radiation-chemical transformations in liquid radioactive waste in which acids such as oxalic, formic and acetic are active reducing components.

Acids, depending on the amount of carboxyl groups (-COOH), have different reactive capacities for active water radiolysis particles, such as e_{aq}, OH, H, H_3O^+, etc. For example, the rate constant of hydrated electrons with oxalic acid molecules (k = $2.5x10^{10}$ l / mol· s [7]) is 2 orders of magnitude greater than with molecules of formic acid (k = $1.4x10^8$ l / mol · s [7]). Opposite, OH radicals weakly react with formic acid molecules (k = $1.3x10^5$ l / mol · s) than with oxalic acid molecules (k = $1.4x10^6$ l / mol·s [7]). These circumstances can create different features in the gases and liquid products formation process, during the radiolysis of aqueous solutions of formic and oxalic acids.

The aim of this work is a comparative study of the features of the kinetics of formic acid and oxalic acid oxidation and the formation of gaseous products in their aqueous solutions.

2. Experimental

Aerated ([O_2] =$2,7x10^{-4}$ M) aqueous solutions of formic and oxalic acid ($1x10^{-2}$ M) under the gamma irradiation by the ^{60}Co isotope in glass ampules (V = 20 ml) at static conditions at room temperature has been studied in this work. The dose rate was 0.2 Gy / s. In all cases, the volume of the solution was 10 ml, the volume of air above it was ~ 10 sm^3. Concentrations of hydrogen peroxide and COD were determined by the titrimetric method [12, 13], gaseous products were measured on a Gas Chromatograph 3101 (column-activated carbon AG-3, carrier gas-air), pH was measured in a pH meter PHS-25.

3. Results and discussion

The kinetics of brutto-reactions of organic acids, the COD and pH changes, formation of H_2, CO_2, H_2O_2 depending on the absorbed dose were studied.

The kinetics change of hydrogen concentration, forming during the oxalic and formic acid radiolysis is given in fig.1
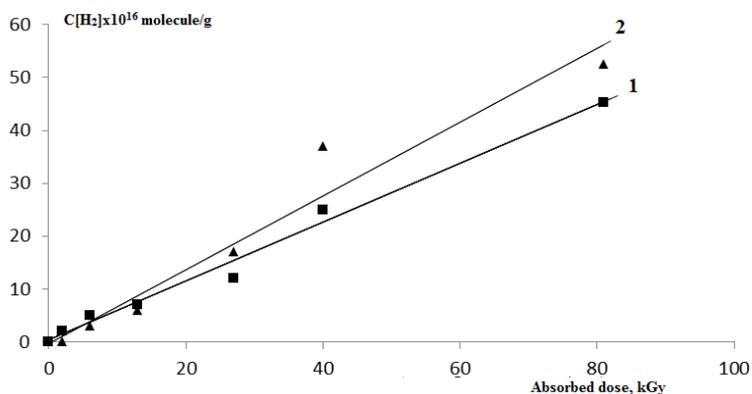

Fig.1. The kinetics of the hydrogen peroxide concentration on depending absorbed dose in radiolysis of oxalic (1) and formic acid aqueous solution (2). P = 0.2 Gy /sec, C=1x10⁻² M

As can be seen from fig. 1, with increasing absorbed dose, in both cases the hydrogen concentration increases linearly. The radiation-chemical yield of hydrogen for aqueous formic acid solution is 7×10^{-2} molecule/100 eV, and for oxalic acid is 5×10^{-2} molecule / 100 eV. These values are less than the yield of hydrogen in radiolysis of pure water (G ~ 0.45 molecule / 100 eV [8]. This is due to a decreasing hydrated electrons in acidic medium (at a pH of 0.5 that is G ~ 0) and with a sharp decreasing the reaction rate of $e^-_{aq} + e^-_{aq} \rightarrow H_2 + 2HO^-$, which is the channel for the formation of molecular hydrogen.

The formation of hydrogen peroxide on depending absorbed dose during the radiolysis of aqueous solutions of formic and oxalic acid is shown in fig.2.
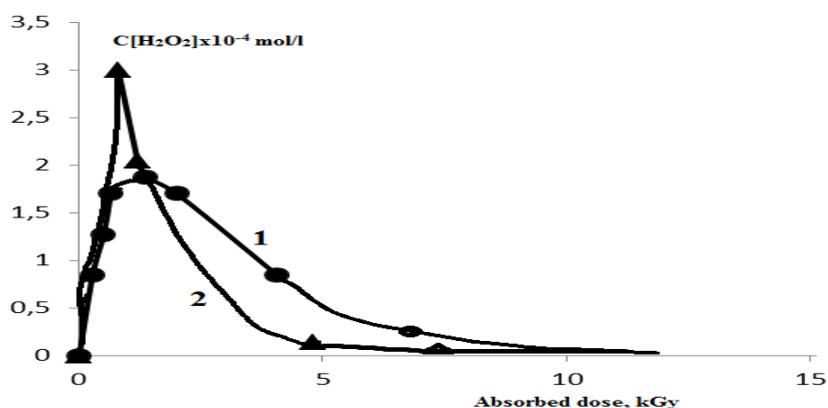

Fig. 2. The kinetics of the the concentration of hydrogen peroxide on depending adsorbed dose in radiolysis of formic acid (1) oxalic (2) and aqueous solution. P = 0.2 Gy/sec, C=1x10⁻² M

As can be seen from fig. 2, with increasing absorbed dose, the concentration of hydrogen peroxide increases with the radiolysis of aqueous solution of formic acid and at a dose of ~ 1.8 kGy passes through a maximum. A further increase of the absorbed dose leads to a decrease of

the hydrogen peroxide concentration. For oxalic acid, the concentration of hydrogen peroxide, depending on the absorbed dose, also initially increases, at 2 kGy passes through a maximum corresponding to a concentration of 2.7×10^{-4} mol/l. The radiation-chemical yield calculated from the initial part of the kinetic curve is equal to 3.1 molecule / 100 eV for the formic acid and 3.2 mol/100 eV for oxalic acid. These values are greater than the values hydrogen peroxides yield forming during the pure water radiolysis(0.7-0.8 molecule / 100 eV) [8]. This shows, that in the aqueous solution of these acids there are additional channels for the formation of hydrogen peroxide [3]. The close values of the initial yields of H_2O_2 formation in solutions of formic and oxalic acid indicate a similar mechanism of the formation of H_2O_2, which includes the disproportionation of peroxide radicals formed in the reaction of oxygen with hydrated electrons, H atoms, and organic radicals arising from the interaction of OH radicals with acid molecules.

The pH value change on depending absorbed dose during radiolysis of aqueous solutions of formic and oxalic acid is shown in fig.3. As can be seen from the figure, in both solutions the acidity decreases. In the radiolysis of aqueous formic acid solution, the pH increases from 2.6 up to 4, and in the radiolysis of aqueous oxalic acid solution, from 2.1 up to 4.2, which is due to the accumulation of a carboxylic acid in the solution.
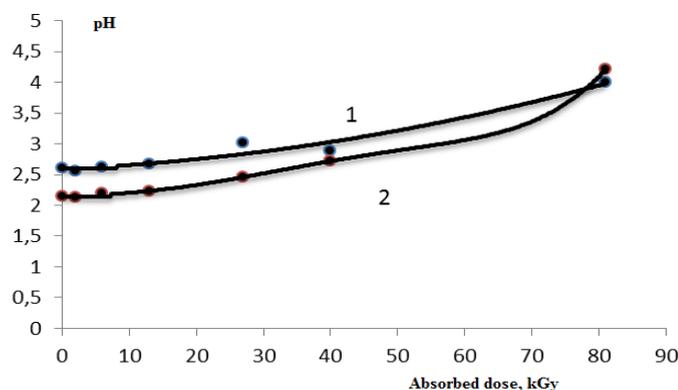

Fig.3. pH value change on depending absorbed dose during radiolysis of aqueous solutions of formic (1) and oxalic (2) acids. 1×10^{-2} M, P = 0.2 Gy / s

Fig. 4 shows the kinetic curves of the formation of carbon dioxide, depending on the absorbed dose in the radiolysis of aqueous solutions of formic and oxalic acids.
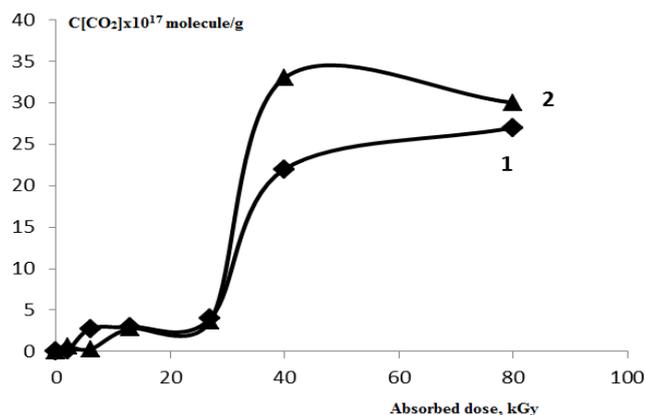

Fig 4. Kinetics of the carbon dioxide concentration change on depending absorbed dose during the radiolysis of aqueous solution of formic (1) and oxalic (2) acid is irradiated.

$$C = 1 \times 10^{-2}, P = 0.2 \text{ Gy/s}$$

As can be seen from fig. 4, the formation of carbon dioxide during the radiolysis of aqueous solution of formic acid and oxalic acid is observed with an induction period. Up to ~ 30 kGy, the formation of carbon dioxide occurs at a low rate. The carbon dioxide concentration increases rapidly reaching a stationary value corresponding to pH = 4.2, from 40 kGy with increasing absorbed dose. In this case, becomes the equilibrium of dissociation between the solution of formic acid and carbon dioxide in closed system.

From the induction period of the kinetic curves, the radiation-chemical yields of CO_2 are calculated for both acids, that are approximately 0.1 molecule / 100 eV.

As can be seen from fig. 5, the COD decreases with increasing absorbed dose. In ~ 80 kGy dose, the oxidation of organic matter occurs during the radiolysis of aqueous solutions of both acids.
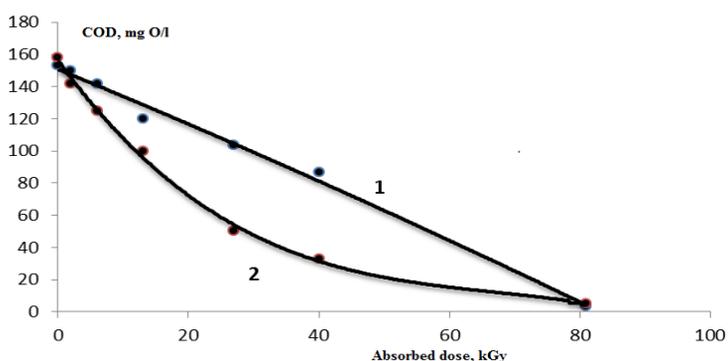

Fig. 5. Kinetics of COD change on depending adsorbed dose of aqueous solution of formic (1) and oxalic (2) acids. $C=1 \times 10^{-2}$ M, P = 0.2 Gy / s

The accumulation of gaseous products causes a risk for the secure storage of liquid radioactive waste. But with increasing partial pressure of carbon dioxide, its solubility rises in water and when the pH≥4, the carbon dioxide is in equilibrium with carbonic acid in the solution [11, 12]

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РАДИАЦИОННО-ХИМИЧЕСКИЕ ПРОЦЕССЫ ВОДНЫХ РАСТВОРАХ НИЗКОМОЛЕКУЛЯРНЫХ ОРГАНИЧЕСКИХ КИСЛОТ ПОД ДЕЙСТВИЕМ ИОНИЗУРУЮШЕГО ИЗЛУЧЕНИЯ

У.А. Кулиева, М.А. Курбанов, С. М. Алиев

Резюме: Исследован радиолиз водных растворов щавелевой и муравьиной кислоты под действием гамма лучей. Изучалась кинетика изменения концентрации перекиси водорода, изменение ХПК и рН, образования газообразных продуктов радиолиза их водных растворов. Зависимости от поглощенной дозы в обоих растворах кислотность уменьшается, и это связано с накоплением карбоновой кислоты в растворе. Из начальных частей кинетических кривых вычислены радиационно-химические выходы для CO_2.

Ключевые слова: *УФ- и γ-излучения, радиолиз, жидкие радиоактивные отходы, радиационно-химический выход*

IONLAŞDIRICI ŞÜALARIN TƏSIRI ALTINDA KİÇİK MOLEKULLU ÜZVİ TURŞULARIN SUDA MƏHLULLARININ RADİASİYA-KİMYƏVİ PROSESLƏRİ

Ü.A. Quliyeva, M.Ə. Qurbanov, S.M. Əliyev

Xülasə: Oksalat və qarışqa turşularının suda məhlullarının qamma şüalarının təsiri altında radioliz proesesi tədqiq edilmişdir.Hidrogen peroksidin qatılığının dəyişmə kinetikası, OKT və pH-ın dəyişməsi, radioliz zamanı əmələ gələn qaz məhsulları öyrənilmişdir. Udulan dozadan asılı olaraq hər iki məhlulda turşuluq azalır. Bu da məhlulda turşuların toplanması ilə izah edilir.CO_2 üçün kinetik əyrilərin başlanğıc hissəsindən radiasiya-kimyəvi çıxım hesablanmışdır.

*Açar sözlər:*UB- və γ-şüalanma, maye radioaktiv tullantılar,radiasiya-kimyəvi çıxım.