PACS: 82.50.Rx

STUDY OF GAMMA RADIOLYSIS OF AQUEOUS FORMIC AND OXALIC ACID SOLUTIONS BY UV- SPECTROSCOPY

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Abstract: In this study the radiolytic conversion of formic and oxalic acids depending on their initial concentration and ratio in aqueous solutions were investigated by UV spectroscopy. The change in UV absorption spectra found out that the solution of formic acid is the most radiation-resistant, depending on absorbed dose. It is established that the most effective conversion is observed in the solution of oxalic acid in water during the combined radiolysis of oxalic and formic acids.

Keywords: gamma radiolysis, oxalic acid, formic acid, absorption bands

1. Introduction

Radiolysis of aqueous solutions of low-molecular organic acids has been studied in many works [3,7-9] with the aim of elucidating the possibilities of radiation-chemical technology for wastewater treatment of industrial enterprises. In addition, these acids are part of the liquid radioactive waste, so it is of interest to study the radiolytic transformations of acids from the point of view of the formation of gaseous products, like hydrogen and carbon oxides [1, 2, 4, 8].

In these studies, the kinetic regularities of radiolytic transformations in aqueous solutions of these acids were mainly studied by chemical and chromatographic methods, as a result, it has been monitored the change in pH indicator, chemical consumption of oxygen, concentration of the initial components and gaseous products of the transformation depending on the absorption dose.

There are also several papers [5,6,8] devoted to the use of spectrometric methods for studying the processes of radiolytic transformations in aqueous solutions of low molecular organic acids, in particular formic and oxalic acids. But, there is no detailed study of the processes taking place with the use of UV - spectroscopy.

The purpose of this work is to study the radiolytic transformations of formic and oxalic acids depending on their initial concentrations and ratios in aqueous solutions by UV spectroscopy.

2. Experiment

The solutions were irradiated with γ - radiation from the ^{60}Co isotope under static conditions, in glass ampoules at room temperature. The dose rate was determined by ferrosulfate dosimetry and was 0.2-0.16 Gy/s. Spectrophotometric measurements were performed in a VARIAN SCAN-50 spectrophotometer in the range of λ = 200-800 nm.

3. Results and Discussion

We carried out 3 series of experiments, in which the absorption spectra of irradiated solutions were studied:

1. At different absorption doses (2-80 kGy) and a fixed initial concentration of acids ($1 \cdot 10^{-2}$ M.)
2. At different initial concentrations of these acids ($1 \cdot 10^{-5}$ M- $1 \cdot 10^{-1}$ M) and at a fixed dose (13 kGy)

3. At a concentration of formic and oxalic acids ($1\cdot10^{-2}$ M) and at different ratios in solution - 1:7 [5 ml of formic ($1.25 \cdot 10^{-3}$ M) + 35 ml of oxalic acid ($9\cdot10^{-3}$M)]; 1:1 [20 ml of formic ($5\cdot10^{-3}$ M) + 20 ml of oxalic acid ($5\cdot10^{-3}$ M)], 7:1 [35 ml of formic ($9\cdot10^{-3}$ M) + 5 ml oxalic acid ($1.25\cdot10^{-3}$ M)].

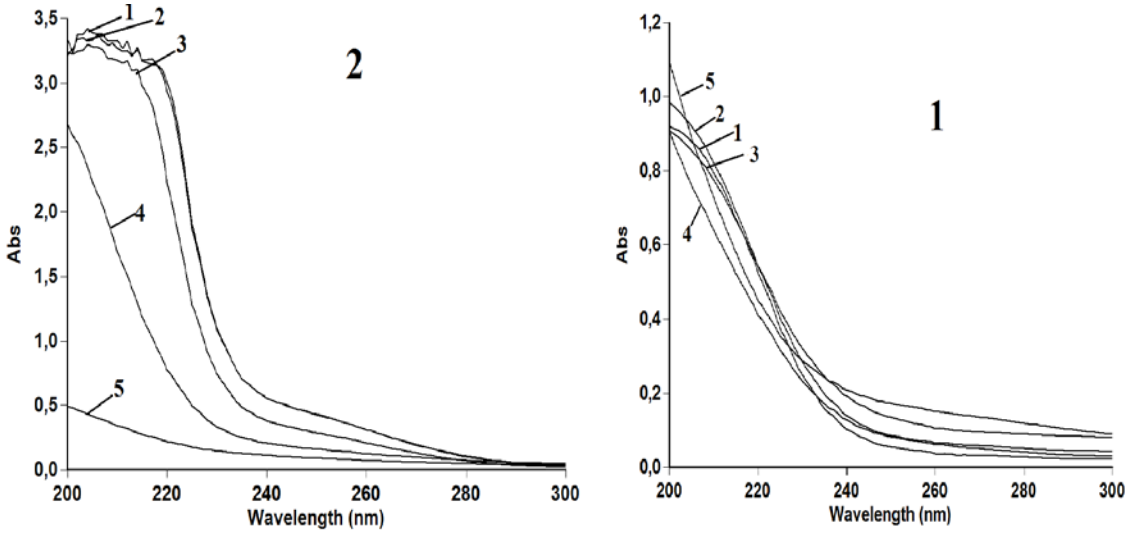

Fig.1. Spectra of UV absorption of aqueous solutions of formic (1) and oxalic (2) acids with a concentration of $1x10^{-2}$ M at absorption doses: initial (1); 2 kGy (2); 13 kGy (3); 40 kGy (4); 80 kGy (5), (P = 0.2 Gy/s)

As it can be seen from Fig. 1, the absorbance of corresponding absorption bands decreases slightly up to 40 kGy in the radiolysis of aqueous solutions of formic acid.Further growth of the absorption dose leads to an increase in the absorbanceup to 1.1.

The absorbancedecreases with an increase in the dose up to 80 kGy in the radiolysis of aqueous solutions of oxalic acid,. In the region of 200-220 nm, new absorption regions appear corresponding to the products of oxalic acid conversion under the influence of radiation. The absorbance (Abs) is about 0.5at a dose of 80 kGy.

In the Fig.2 it has been presented the absorption spectra of aqueous solutions of formic (1) and oxalic (2) acids with different initial concentrations at a fixed dose (13 kGy).

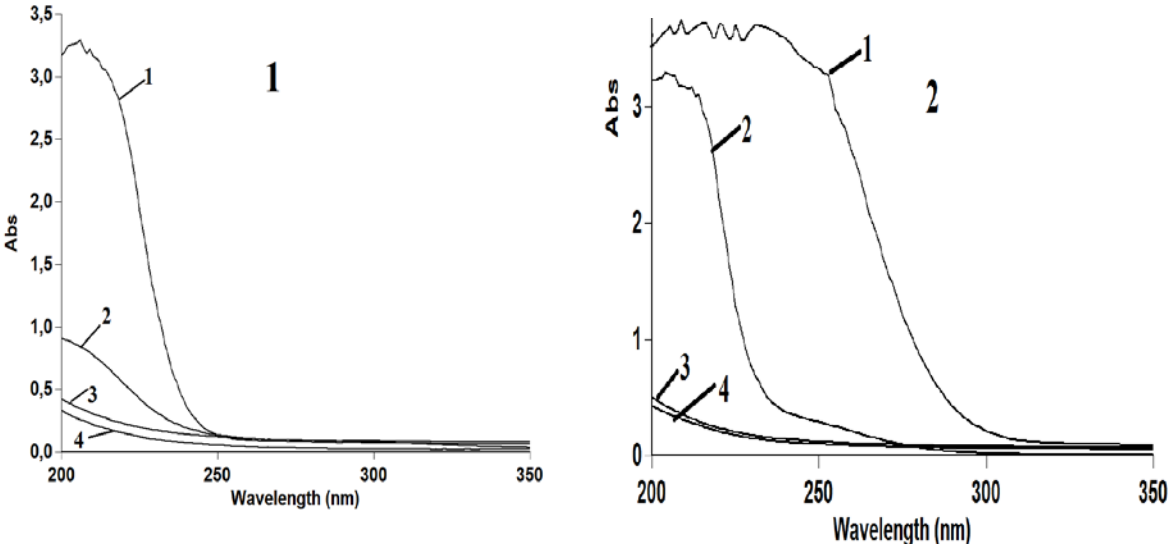

Fig.2. Spectra of UV absorption of aqueous solutions of formic (1) and oxalic (2) acids with different concentrations: $1x\ 10^{-1}$ M (1);$1x10^{-2}$ M (2); $1x10^{-4}$ M (3); $1x10^{-5}$ M (4) (P=0,16 Gy/s, D=13 kGy)

As it can be seen from Fig. 2, the effectiveness of radiolytic conversion increases with increasing initial concentration in the radiolysis of aqueous solutions of formic acid. Absorption bands of products, in particular oxalic acid, are observed at a concentration of $1\cdot10^{-1}$ M. In addition, shift of the absorption bands toward the short-wavelength region is observed with an increase in

the initial concentration of formic acid.

In the radiolysis of aqueous solutions of oxalic acid there is observed a stronger change in the composition of the products with an increase in its initial concentration. At $1 \cdot 10^{-1}$ M, the absorbance reaches ~5.8. Analogously with formic acid, the absorption bands also shift towards the short-wavelength region with an increase in its initial concentration in the radiolysis of aqueous solutions of oxalic acid, At low concentrations (10^{-4}-10^{-5}), similar absorption bands are observed in the radiolysis of aqueous solutions of oxalic and formic acids (the absorbance is approximately 0.3-0.4 at 200 nm).

The obtained results agree with the data on the kinetics of the conversion of formic and oxalic acids [5],in which their effective constants of gross oxidation reactions are determined, equal to $5 \cdot 10^{-6}$ s^{-1} and $7 \cdot 10^{-6} s^{-1}$, indicating more efficient oxidation of oxalic acid than the formic acid.

Dihydroxyvinna, dihydroxytartaronic, hydroxytartaronic, glyoxalic, tartaric acid are formed at radiolytic conversion of aqueous solutions of formic and oxalic acid. The likely reactions of these products are given below [1]:

$2\ HOOC - C(OH)_2 = HOOC - [C(OH)_2]_2 - COOH$

Dihydroxyvinna acid

$HOOC - [C(OH)_2]_2 - COOH + OH = C(OH)_2\ (COOH)_2 + CO_2$

Dihydroxytartaronic acid

$C(OH)_2\ (COOH)_2 + OH = HOOC - C(OH)_2 + CO_2$

Glyoxalic acid

$C(OH)_2\ (COOH)_2 + H = HOOC - CHO + COOH$

$HOOC - CHO + OH = HOOC - C(OH)_2$

$HOOC - CHO + H = HOOC - CHOH$

Tartaric acid

As usual, in wastewater there is observed a mixture of low molecular organic acids, of which the main components are formic and oxalic acid. Therefore, it is of interest to study the radiolysis of aqueous solutions of mixtures of these acids.

Figure 3 shows the absorption spectra of aqueous solutions of mixtures of formic and oxalic acids and at their different ratios in a solution - 5ml formic + 35ml oxalic acid; 20ml formic + 20ml oxalic acid, 35ml formic + 5ml oxalic acid at different doses (2-80 kGy).

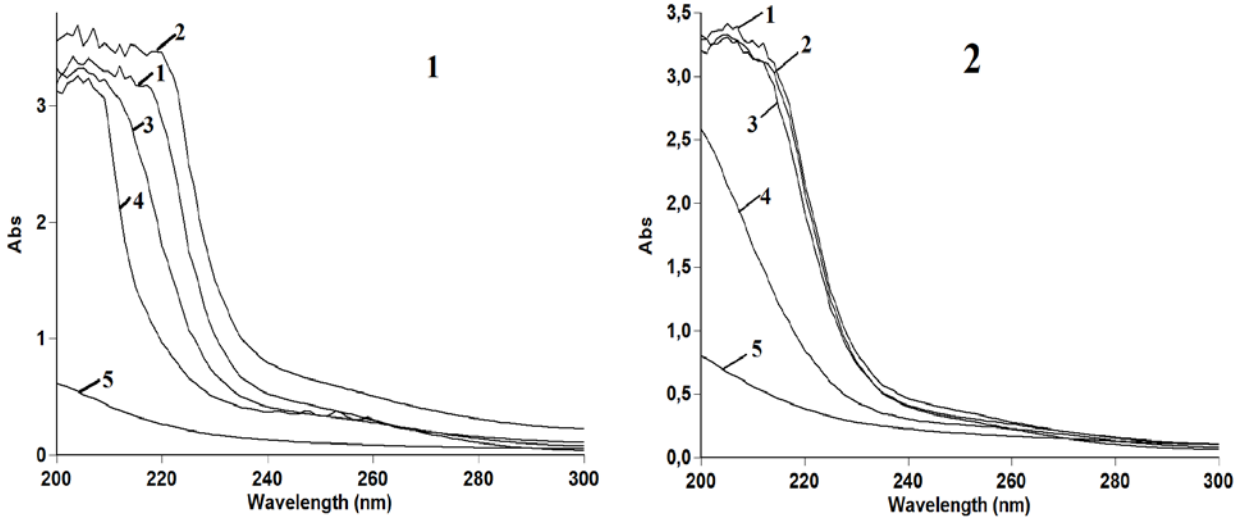

Figure 3. UV-absorption spectra of aqueous solution of the mixtures of formic and oxalic acids at the concentration of formic and oxalic acids ($1 \cdot 10^{-2}$M) and at their different ratios in the solution – 5ml formic + 35ml oxalic acid (1); 20ml formic+20ml oxalic acid (2); 35ml formic+5ml oxalic acid (3) at different doses (2-80kGy). Initial (1); 2kGy (2); 13kGy (3); 40 kGy (4);80kGy (5). P=0.16 Gy/s

It can be seen from Fig. 3 that, there is observed more effective conversion of oxalic acid in the joint radiolysis of aqueous solution of oxalic and formic acids, which agrees with the data on radiolysis of aqueous solution of individual acid given above.

Irradiation of mixtures of oxalic and formic acid is accompanied by a mixture of absorption spectra.

Hypsochromic effect occurs with increasing absorbed dose. Irradiation of mixtures of oxalic and formic acids is accompanied by the mixture of absorption spectra. At doses of 2 kGy, there is a shift toward the long-wave region, and at high doses toward the short-wave region ($\Delta\lambda$ = 10-16 nm).). At 80 kGy, the observed absorption spectrum is characteristic for the formic acid.

Comparison of the absorption spectra of the radiolysis products depending on absorbed dose shows that formic acid is more radiation resistant in radiolysis of aqueous solutions of mixtures of oxalic acid and formic acid. The primary reactions of the decomposition of these acids occur in reactions with e_{solv}, H and OH radicals. Although the molecules of these acids react weakly with hydrogen atoms and OH radicals ($\sim 10^5$- 10^6 $l \cdot mol^{-1} \cdot s^{-1}$) [8], but solvated electrons react very effectively with molecules of these acids ($\sim 10^8$-10^{10} $l \cdot mol^{-1} \cdot s^{-1}$), and a higher value of the rate constant is characteristic for the oxalic acid molecule (2.5 $l \cdot mol^{-1} \cdot s^{-1}$).

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ИССЛЕДОВАНИЕ ГАММА РАДИОЛИЗА ВОДНЫХ РАСТВОРОВ МУРАВЬИНОЙ И ЩАВЕЛЕВОЙ КИСЛОТ МЕТОДОМ УФ- СПЕКТРОСКОПИИ

М.А. Курбанов, У.А. Кулиева

Резюме: В данной работе исследовано радиолитическое превращение муравьиной и щавелевой кислот в зависимости от их начальных концентраций и соотношения в водных растворах методом УФ-спектроскопии. На основе дозовой зависимости изменения УФ-спектров поглощения выявлено, что наиболее радиационно-стойким является раствор муравьиной кислоты. Устоновлено, что при совместном радиолизе смесей водных растворов щавелевой и муравьиной кислот более эффективное превращение наблюдается в растворе щавелевой кислоты.

Ключевые слова: гамма радиолиз, щавелевая кислота, муравьиная кислота, полос поглощение

QARIŞQA VƏ OKSALAT TURŞULARININ SUDA MƏHLULLARININ QAMMA RADİOLİZİNİN UB- SPEKTROSKOPİYA METODU İLƏ TƏDİQİ

M.Ə. Qurbanov, Ü.A. Quliyeva

Xülasə: Baxılan işdə UB-spektroskopiya metodu ilə qarışqa və oksalat turşularının ilkin qatılıqdan və nisbətdən asılı olaraq suda məhlullarının radiolizi öyrənilmişdir. Udma spektrlərinin udulan dozadan asılı olaraq müqayisəsindən görünürki, qarışqa turşusu radiasiya cəhətdən daha davamlı turşudur. Müəyyən edilmişdirki, qarışqa və oksalat turşularının birgə radiolizi zamanı ən effektiv çevrilmə oksalat turşusunun suda məhlulunda gedir.

Açar sözlər: qamma radioliz, oksalat turşusu, qarışqa turşusu,udma zolağı