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CHANGES OF ACIDITY AND CHEMICAL OXYGEN DEMAND AT THE RADIOLYSIS OF THE WATER SOLUTIONS OF FORMIC ACID

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Abstract: The dynamics of pH and COD changes and the concentration of hydrogen peroxide,CO_2 and changes at the optical absorption spectrum both before and after the irradiation of aqueous formic acid solution ($1x10^{-2}$M) by Co^{60} gamma rays at different irradiated dose was investigated. It has been established that, the values of pH goes up from 2,5 to 4.0 and Chemical Oxygen Demand decreases from 164 to 14 (mg O/L) with the absorbed dose but the optical absorbance initially grows within the range of 2 to 27kGy then goes down at the radiolysis of aerated aqueous solution of formic acid.

Keywords: Formic acid, γ- irradiation, spectrophotometer, xromatoqrapy, radiation-chemical yield.

1. Introduction

Formic acid is one of the intermediate products in the long row of phenol degradation into CO_2 under the ionizing irradiation of aqueous solution [1]. Radiolysis of aqueous solutions of formic acid was investigated [2], but they cover either the initial or late stages of formic acid degradation. However, practically, there is no systematic investigation covering wide range of absorbed irradiation dose, which makes it difficult for proper understanding the mechanism of irradiation induced degradation of aqueous formic acid solution and consequently the mechanism of complete phenol degradation into CO_2 and H_2O.

In the current study it has been investigated radiolysis of aerated aqueous solution of formic acid at the wide range absorbed gamma irradiation dose covering its initial conversion as well as the final stage of drastic oxidation.

2. Experimental

Aerated ($[O_2]=2,7x10^{-4}$M) aqueous formic acid solution ($1x10^{-2}$ M) was irradiated by Co^{60} gamma rays at the static condition in sealed glass vials at room temperature. The dose rate was 0.22Gy/sec which was determined by ferrous sulfate dosimeter, pH with pH meter PHS-25, chemical oxygen demand (COD) by the method [3], hydrogen peroxide by method [4], ultraviolet spectrum of products was taken by spectrophotometer Varian-Carry-50 at the wavelength (λ) range of 200-800nm.

3. Results and discussion

It has been investigated the dynamics of pH and COD changes, measured the concentration of hydrogen peroxide and CO_2 and changes at the optical absorption spectrum both before and after the irradiation of aqueous formic acid solution ($1x10^{-2}$M) by Co^{60} gamma rays at different irradiated dose.

The optical absorption spectra of aqueous formic acid solution both before and after the irradiation with different dose are presented in Fig. 1.

According to Fig.1 optical absorbance increases within the dose range 2 to 27kGy and then decreases at the higher doses. It is suggested that the increase of optical absorption is due to

the generation of oxalic acid which has higher extinction coefficient rather than formic acid. At the higher irradiation doses occurs the degradation of oxalic acid as well. Apart from that the beginning of the absorption band shifts toward the low wave zone (from 238nm to 226nm) as the irradiation dose increases. (Table 1)

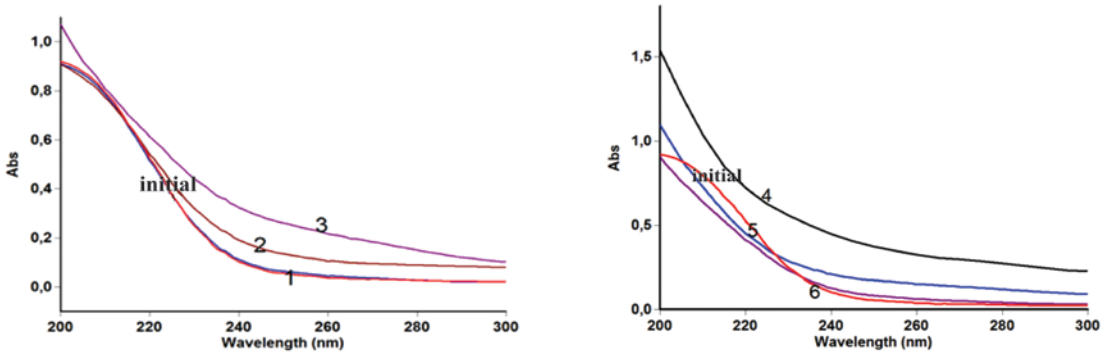

Fig.1 The optical absorption spectra of aqueous formic acid solution ($1x10^{-2}M$) both before and after the irradiation with different dose: 0-initial; 1-2kGy; 2-6kGy; 3-13kGy; 4- 27kGy, 5-40kGy; 6-80kGy.

Table 1. The shift of the beginning of the absorption as a function of irradiation dose

D (κGy)	2	6	13	27	40	80
λ_0(nm)	238	236	232	230	228	226

The gamma irradiation induced degradation of aerated formic acid solution leads to formation of CO_2 as well as increase pH and decrease COD. The results have shown in Fig.2.

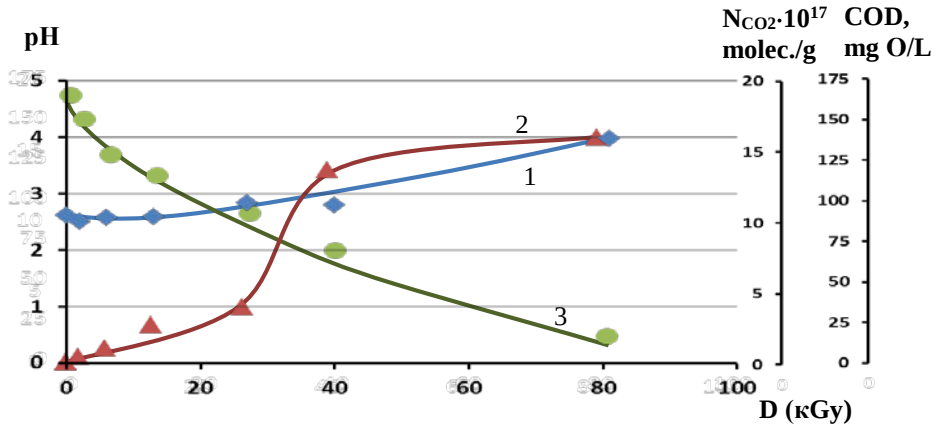

Fig. 2 Variation of pH (1), COD (2) and formation of CO_2 (3) with the irradiation dose in the radiolysis of aerated formic acid solution ($1x10^{-2}M$)

As seen from the Fig.2 with the increasing of irradiation dose the value of pH goes up from 2,5 to 4,0. The flat value of pH=4, most probably, is due to formation of carbonic acid. It is reported that, carbonic acid degrades into CO_2 and water at the pH less than 4, 0 [5]. At the same figure (Fig.2) it has been presented the variation of COD with the irradiated dose which shows the decrease the COD from ~150 to 12 (mg O/L) at 80 kGy. Accordingly, irradiation of aerated formic acid solution leads to decreasing of total organic acids (formic acid and its derivatives).

Formation of CO_2 occurs from the beginning of the irradiation and goes up linearly with the irradiation dose indicating that formation of CO_2 is due to both the decomposition of formic acid as well as its derivatives.

Fig. 3 presents the formation of H_2O_2 in the radiolysis of aerated formic acid solution. Accordingly the concentration of H_2O_2 goes up to the maximum value of $2x10^{-4}$ M with the irradiation dose then goes down.

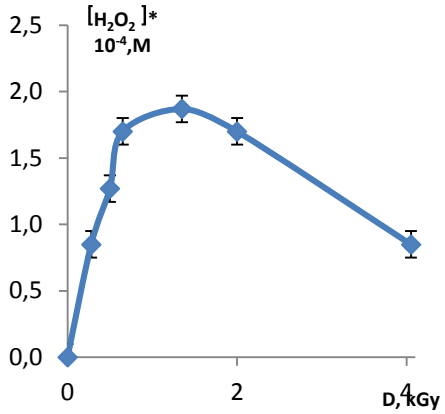

Fig. 3. Formation of H_2O_2 with the irradiation dose in the radiolysis of aerated formic acid solution ($1x10^{-2}M$)

The radiation yield of H_2O_2 calculated at the initial stage of its formation is equal to 3,1molec/100ev. This value is higher than the yield of H_2O_2 in the radiolysis of pure water (0,7-0,8), indicating that there is an additional channel for the formation of H_2O_2 in the radiolysis of aerated formic acid solution.

The formation of glyoxalic, hydroxytartronic and dihydroxytartronic acids in the radiolysis of aerated formic acid solution has been proposed [6] have not been identified due to their very low concentration.

4. Conclusion

1. It has been established that, the values of pH goes up from 2,5 to 4.0 and optical absorbance from 164 to 14 (mg O/L) with the absorbed dose but the optical absorbance initially grows within the range of 2 to 27kGy then goes down at the radiolysis of aerated aqueous solution of formic acid.
2. The initial radiation chemical yield of H_2O_2 is equal to 3,1molec/100ev.

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ИЗМЕНЕНИЯ КИСЛОТНОСТИ И ХИМИЧЕСКОГО ПОТРЕБЛЕНИЯ КИСЛОРОДА ПРИ РАДИОЛИЗЕ ВОДНОГО РАСТВОРА МУРАВЬИНОЙ КИСЛОТЫ

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Резюме: Исследована динамика изменения pH и ХПК и концентрации пероксида водорода, CO_2 и оптический спектр поглощений до и после облучения водного раствора муравьиной кислоты ($1x10^{-2}$M) по Co^{60} гамма-лучей при различных поглощенных дозах. Установлено, что при увеличении дозы pH увеличивается от 2,5 до 4.0, Химическое Потребления Кислорода уменьшается от 164 до 14 (мг О /л), а оптическая плотность в начале увеличивается с ростом дозы, а дальнейшее увеличение дозы приводит к уменьшению её значения.

Ключевые слова: Муравьиная кислота, γ- облучение, спектрофотометр, хроматография, радиационно-химический выход.

QARIŞQA TURŞUSUNUN SULU MƏHLULUNUN RADİOLİZİ PROSESİNDƏ TURŞULUĞUN VƏ OKSİGENƏ KİMYƏVİ TƏLƏBATIN DƏYİŞMƏ KİNETİKASI

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Xülasə: Qarişqa turşusunun sulu məhlulunun radiolizi prosesində turşuluğun və oksigenə kimyəvi tələbatin dəyişmə kinetikası, H_2O_2 və CO_2-nin qatılığının dəyişməsi, müxtəlif dozalarda şüalandırılmış məhlulun şüalanmadan əvvəlki və sonrakı optiki udulma spektrləri öyrənilmişdir. Müəyyən edilmişdir ki, doza artıqca pH 2.5-dən 4,0-ə kimi artır, Oksigenə Kimyəvi Tələbat 164 -dən14-ə (mq O /l) kimi azalır, optik udulma isə ilkin olaraq doza artıqca artır və dozalnın sonrakı artımı optiki udulmanın azalmasına gətirir.

Açar sözlər: Qarışqa turşusu, γ- şüalanma, spektrofotometr, xromatoqrafiya, radiasiya-kimyəvi çıxış.