Radiation-Chemical Degradation of Oxalic Acid in Water Solutions

Muslim Gurbanov, Ulviyye Guliyeva, Sahib Mammadov* and Hokman Mahmudov

Institute of Radiation Problems, Azerbaijan National Academy of Sciences, Baku Az1143, Azerbaijan

Abstract: Co⁶⁰ gamma ray radiolysis of aqueous oxalic acid solution (1×10^{-2} M) was investigated within the dose range up to 80 kGy. The value of pH increases from 2.0 to 4.0 and approximately 90% of oxalic acid and its derivatives are degraded at the dose of 80 kGy. Dissolved O₂ affects to the degradation of oxalic acid at the initial stage due to total consumption of O₂ at the dose of 2 kGy. Formation of CO₂ occurs at a higher rate at the initial stage until the dissolved O₂ is fully consumed. The kinetic model of oxalic acid degradation in aqueous solution under the gamma irradiation was tested. The suggested mechanism complies with the experimental data both of our own and of that reported earlier.

Key words: Oxalic acid, γ -irradiation, kinetic model, radiation-chemical yield.

1. Introduction

Oxalic acid is one of the proposed intermediate products in the multistage phenol degradation into CO₂ under the ionizing irradiation of aqueous solution [1]. On the other hand, radiation-chemical conversion of liquid radioactive waste significantly predefines their safe storage. Consequently, detailed knowledge of the processes interlining the radiolysis of oxalic acid which is one of the components of liquid radioactive waste remains still of interest. Radiation chemical degradation of oxalic acid produces long row of organic acids and gaseous products like CO₂ and H₂ [2]. Radiolysis of aqueous solutions of oxalic acid has been previously investigated [2-4], but they cover either the initial or late stages of oxalic acid degradation. However, there is no systematic investigation covering wide range of absorbed irradiation dose, which makes it difficult for proper understanding the mechanism of radiolysis of aqueous oxalic acid solution and consequently the mechanism of complete phenol degradation into CO₂ and H₂O as well as utilization and safe storage of

liquid radioactive waste.

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

2. Experimental Sections

Aerated ($[O_2] = 2.7 \times 10^{-4}$ M) aqueous oxalic acid solution (1×10^{-2} M) was irradiated by Co⁶⁰ gamma rays at the static condition in sealed glass vials at room temperature. The dose rate was 0.22 Gy/s which was determined by ferrous sulfate dosimeter, pH with pH meter PHS-25, KMnO₄ (potassium permanganate) was used for measuring COD (chemical oxygen demand). CO₂ was analyzed by a gas chromatography.

3. Results and Discussion

To create the model of oxalic acid radiolysis, the authors applied the schema of the reactions fully describing the radiolysis of water [5]. The following preconditions were taken into account at the computer modelling of radiolysis applied to the aerated aqueous oxalic acid solution: Oxalic acid concentration = $1 \times$

*Corresponding author: Sahib Mammadov, Ph.D., research filed: radiation chemistry. E-mail: mammadov_sahib@yahoo.com.

10^{-2} M and concentration of dissolved $O_2 = 2.7 \times 10^{-4}$ M. The dose rate 0.22 Gy/s; pH = 1-4, radiation-chemical yield of water radiolysis products as in Table 1.

The following list of reactions (Table 2) was

selected as the most appropriate to describe the experimental data both of our own and of that reported earlier.

The results of calculations demonstrated in Figs. 1 and 2, and compared with the experimental data.

Table 1 The radiation chemical yields (G) of water radiolysis products.

Intermediate products	H^+	OH	e_{aq}	H	H_2	H_2O_2
G (molec/100ev)	3.45	2.49	3.05	0.6	0.425	0.8

Table 2 The list of reactions considered at the modelling of aqueous oxalic acid solution radiolysis.

Reactions	K, L/M·s
1. $HOCCOOH = H^+ + HOCCOO^-$	5.6×10^8
2. $H^+ + HOCCOO^- = HOCCOOH$	1×10^{10}
3. $HOCCOO^- = H^+ + ^-OCCOO^-$	5.4×10^5
4. $H^+ + ^-OCCOO^- = HOCCOO^-$	1×10^{10}
5. $e + HOCCOOH = (HO)_2CCOOH + OH^-$	2.5×10^{10}
6. $e + HOCCOO^- = (HO)_2CCOOH + 2OH^-$	3.2×10^9
7. $e + ^-OCCOO^- = (HO)_2CCOOH + 3OH^-$	4.6×10^7
8. $H + HOCCOOH = (HO)_2CCOOH$	3.3×10^5
9. $H + HOCCOO^- = (HO)_2CCOOH + OH^-$	1.6×10^4
10. $H + ^-OCCOO^- = (HO)_2CCOOH + 2OH^-$	1×10^4
11. $OH + HOCCOOH = H_2O + CO_2 + ^*COO^- + H^+$	1.4×10^6
12. $OH + HOCCOO^- = H_2O + CO_2 + ^*COO^-$	1.9×10^7
13. $OH + ^-OCCOO^- = OH^- + CO_2 + ^*COO^-$	9.7×10^5
14. $HCOOH = H^+ + HCOO^-$	1.8×10^6
15. $H^+ + HCOO^- = HCOOH$	1×10^{10}
16. $^*COOH = ^*COO^- + H^+$	4×10^8
17. $^*COO^- + H^+ = ^*COOH$	1×10^{10}
18. $OH + HCOOH = H_2O + COOH$	1.3×10^8
19. $OH + HCOO^- = ^*COO^- + H_2O$	1.4×10^8
20. $e + HCOOH = H + HCOO^-$	1.4×10^8
21. $H + HCOOH = H_2 + COOH$	4.4×10^5
22. $2 ^*COO^- = ^-OCCOO^-$	1×10^8
23. $O_2 + ^*COOH = HO_2 + CO_2$	2×10^9
24. $H_2O_2 + ^*COOH = OH + H_2O + CO_2$	5×10^7
25. $2 ^*COOH = HOCCOOH$	4×10^8
26. $2 ^*COOH = HCOOH + CO_2$	5×10^8
27. $O_2 + ^*COO^- = O_2 + CO_2$	2×10^9
28. $2(HO)_2CCOOH = GA + HOCCOOH$ glyoxylic acid GA = $OCHCOOH$	1×10^8
29. $2(HO)_2CCOOH = DA$ dihydroxycitartaric acid DA = $(C(OH)_2COOH)_2$	1×10^8
30. $2(HO)_2CCOOH = HOCCOOH + 2HCOOH$	1×10^9
31. $(HO)_2CCOOH + COOH = HA$ Dihydroxymalonic acid = HA	1×10^9
32. $H_2O_2 + (HO)_2CCOOH = OH + H_2O + HOCCOOH$	1×10^5

*- indicates for radical products.

Fig. 1 Kinetics of pH with the irradiation dose in the radiolysis of aerated oxalic acid solution (1×10^{-2} M); dose rate = 0.22 kGy/s.

Fig. 2 Kinetics of changes of TOC (●), and concentration of CO₂ (■) and H₂ (♦) with the irradiation dose. Dose rate = 0.22 Gy/s; dots are experimental; lines calculated.

The irradiation induced degradation of aerated formic acid solution leads to formation of CO₂ as well as increases pH and decreases COD. The results of pH changes both experimental and calculated are shown in Fig. 1.

As seen from the Fig. 1 with the increasing of irradiation dose the value of pH goes up from 2.0 to

4.0. The increased value of pH, most probably, is the result of significant degradation of oxalic acid and its derivatives as well as formation of carbonic acid. It is reported that formation of carbonic acid increases at the pH ≥ 4.0 [6]. The considered model enables to compute the concentration of H⁺ ions i.e. the pH of the solution against to irradiation dose.

Computed value of pH was compared with the experimental data in Fig. 1 and they are in a good agreement with each other.

Fig. 2 demonstrates results of experimentally defined changes in TOC (total organic carbon), concentration of CO₂ and H₂ accumulated during the irradiation. Experimental data are compared with the computed values.

As seen from the Fig. 2, total amount of organic carbon decreases with the irradiation dose. In contrast, the accumulation of CO₂ and H₂ increases. The kinetics of CO₂ formation is characterized induction period of up to dose of approximately 10 kGy. H₂ accumulation is in a linear dependence with the irradiation dose. 90% of organic carbon out of 1×10^{-2} M oxalic acid degrades at the 80 kGy. Accumulation of gaseous products raises the safe storage risk of liquid radioactive wastes. But the solubility of CO₂ increases with the raising of partial CO₂ pressure and at pH ≥ 4 most of CO₂ captures with the water solution due to shifting equilibrium to the right.

4. Conclusions

Approximately 90% oxalic acid and its derivatives

are degraded at the dose of 80 kGy.

Significant increase in pH under gamma irradiation occurs until 40 kGy and reaches the maximum value of 4.

References

- [1] Sato, K., Takmito, K., and Tsuda, S. 1978. "Degradation of Aqueous Phenol Solution by Gamma Irradiation." *Environmental Science and Technology* 12 (9): 1043-6.
- [2] Gordeev, A. V., Ershov, B. Q., and Kosareva, I. M. 2005. "Diffusion-Kinetic Model of Radiation Chemical Conversion of Oxalic Acid and Oxalate Ions in Water Solutions." *High Energy Chemistry* 39 (4): 250-4.
- [3] Jestkova, T. P., Jukova, T. N., and Makarov, I. E. 2011. "The Specifics of Radiolytic Degradation of Oxalic Acid in the Aerated Water Solutions." *High Energy Chemistry* 45 (2): 115-8.
- [4] Kartashova, L. I., Chulkov, V. N., Didenko, O. E., and Pikayev, A. K. 2000. "Hydrogen Peroxide Yields in the Radiolysis of Aerated Aqueous Solutions of Formic Acid." *High Energy Chemistry* 34 (6): 467-9.
- [5] Buxton, A. W. 1988. "Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen Atoms and Hydroxyl Radicals in Aqueous Solutions." *Phys. Chem. Ref. Data* 17 (2): 513.
- [6] Carrol, J. J., and Mather, A. E. 1992. "The System Carbon Dioxide-Water." *Journal of Solution Chemistry* 21: 607-62.