

Chemistry

STUDY OF INFLUENCE OF SOME ADDITIVES ON THE RATE
OF H₂O₂ DECOMPOSITION IN LIQUID PHASE.
II: INFLUENCE OF VITAMINS B_c, B₁ AND C

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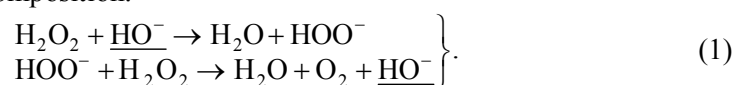
The influence of vitamins B_c (folic acid, FA), B₁ (thiamine, TA) and C (ascorbic acid, AA) on H₂O₂ (HP) decomposition rate in aqueous solutions was studied using gasometric method. In alkaline medium in the presence of FA the reactions are carried out at [H₂O₂]₀=[HOO⁻]=0.5 M. [FA]₀ is changed in the range 0–2.8·10⁻³ M. It is established that the reaction rate (*W*) decreases more than twofold. It is assumed that FA effectively reacts with HO[·] and HOO[·], which are chain carriers. So the reaction runs by radical-chain mechanism. In acidic medium (pH 3.5) catalyzed by Fe(II) cations HP decomposition occurs mainly by radical-chain mechanism. TA (0–2.5·10⁻⁴ M) also decreases *W* more than 4 times. At pH 3.5, [TA·HCl]₀ ≥ 1·10⁻⁴ M there is no O₂ evolution. The AA influence on the HP decomposition, *W* is studied at pH 3.5. In the presence of AA, [AA]₀ ≈ 1.25·10⁻³ M, *W* also decreases the radical-chain run catalyzed by Fe(II) cations HP decomposition.

Keywords: folic acid, thamine, ascorbic acid, radical-chain run catalyzed, reaction rate.

Introduction. The large applications which has H₂O₂ (HP) very briefly is presented in [1]. It is noted also that in alkaline medium HP is decomposed by two mechanisms: non-radical (~84%) and radical-chain (~16%) [2]. On the ground of obtained kinetic data it was shown that 2-cyano-3,4,4-trimethyl-2-butene-4-ol (unsaturated cyanolacton) and DMSO decrease the radical path of the cited reaction, but have positive action on the non-radical mechanism [1].

Vitamins B₁ (thiamine, TA) and B_c (folic acid, FA), which have natural origin, noticeably decrease the cumene autooxidation rate, which occurs by radical-chain mechanism [3]. It is interesting to answer the following question: do they influence also on the run of the nonradical reaction? To answer this question the influence of vitamins B₁, B_c and C (ascorbic acid, AA) on the reaction H₂O₂+HOO⁻ rate (*W*) is studied.

Experimental Part. It is well established that in alkaline medium HO⁻ anion catalyzes the HP decomposition:



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Considering the fact that the reaction product is O₂, the reaction rate is being determined using gasometric method [1].

The purity of used compounds is discussed in [1, 3, 4]. TEMPO was: 2,2',6,6'-tetramethylpiperidine-1-oxyl ("Sigma").

Results and Discussion.

1. The Influence of FA.

a) *In Alkaline Medium.* All reactions are carried out at 298.15 K and at [H₂O₂]₀=[HOO⁻]₀=0.5 M. The influence of [FA]₀ is studied. The obtained kinetic data are presented in the Table.

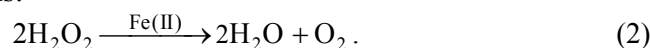
W_{O₂} dependence on [FA]₀

[FA] ₀ ·10 ³ , M	0	0.62	1.0	1.4	2.25	2.8
W _{O₂} ·10 ³ , mL/min	0.28	0.26	0.22	0.19	0.15	0.11

From the presented data it follows that even at FA low concentrations *W* noticeably decreases. It is assumed that FA suppresses the radical-chain run of the reaction.

b) *In Acidic Medium.* To verify the likelihood of the cited assumption the FA influence on the HP decomposition rate catalyzed by Fe(II) cations is studied. The mechanism of the noted reaction depends on [H₂O₂]₀/[Fe(II)]₀ = α. At α ≫ 1 the reaction occurs by radical-chain mechanism. The mechanism is known as Haber–Weiss mechanism [5]. The mechanism is discussed more detailed in [6 a, b]. In recent works Haber–Weiss mechanism is being used in general frame, but with some supplements [7].

The over-all reaction is:



At α ≪ 1 the reaction occurs by nonradical-chain mechanism (Bray–Gorin mechanism) [8].

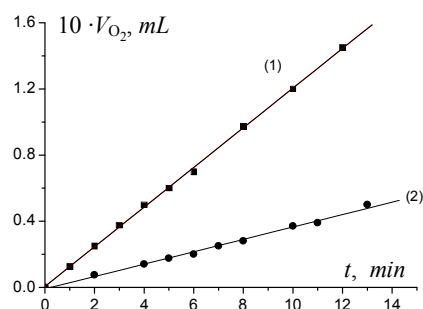
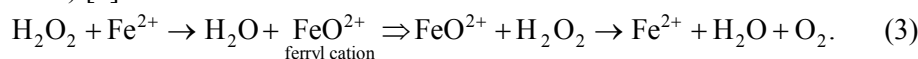


Fig. 1. The kinetic data at: pH 3.5; [H₂O₂] = 7·10⁻² M; [Fe(II)]₀ = 5·10⁻² M and T=298.15 K. [FA]₀=0 (1); 2.28·10⁻³ M (2).

Taking into consideration Haber–Weiss and Bray–Gorin mechanisms, FA's influence is studied at α ≫ 1 [9]. As was mentioned, at α ≫ 1 the reaction occurs mainly by radical-chain mechanism.

FA influence is studied in the following conditions: pH 3.5; [H₂O₂] = 7·10⁻² M; [Fe(II)]₀ = 5·10⁻⁴ M and T=298.15 K. The medium pH 3.5 is chosen taking into consideration the fact that *W* remains constant in the pH range 2 ≤ pH ≤ 4 [10]. The obtained kinetic data are presented

in Fig. 1. It follows that FA decreases H₂O₂+HOO⁻ reaction's rate reacting with free radicals, which are the radical-chain reaction carriers.

2. The Influence of TA.

a) *In Alkaline Medium.* The reaction conditions: all reactions are carried out at 303.15 K and at $[\text{H}_2\text{O}_2]_0 = [\text{HOO}^-]_0 = 0.5 \text{ M}$. $[\text{TA}]_0$ is changed in the range $0 - 2.5 \cdot 10^{-4} \text{ M}$. The obtained kinetic data are presented in Fig. 2.

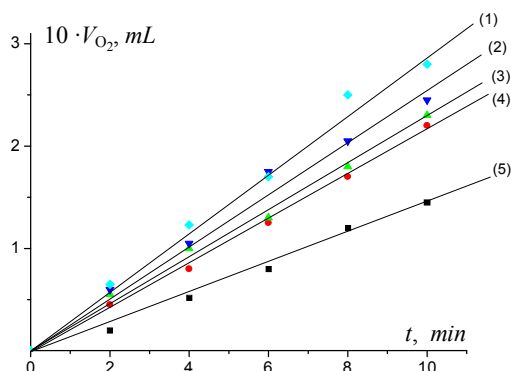


Fig. 2. $[\text{TA}]$ influence on kinetics of $\text{H}_2\text{O}_2 + \text{HOO}^-$ reaction, $T = 303.15 \text{ K}$. $[\text{TA}]_0 = 0$ (1); $0.25 \cdot 10^{-4}$ (2); $0.75 \cdot 10^{-4}$ (3); $1.25 \cdot 10^{-4}$ (4); $2.50 \cdot 10^{-4} \text{ M}$ (5).

Kinetic curves character shows that in the presence of even low concentrations of TA the reaction rate decreases. So, one can conclude, as in the case 1:

a) TA in a considerably degree decreases the radical-chain run of the reaction.

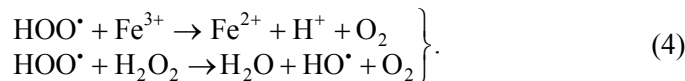
b) *In Acidic Medium.* In this case the reaction's conditions are: $[\text{H}_2\text{O}_2] = 7 \cdot 10^{-2} \text{ M}$; $[\text{Fe(II)}]_0 = 5 \cdot 10^{-3} \text{ M}$, pH 3.5, $T = 303.15 \text{ K}$. In acidic medium TA is present as hydrochloric salt ($\text{TA} \cdot \text{HCl}$).

It is established that at $[\text{TA} \cdot \text{HCl}]_0 \geq 1 \cdot 10^{-4} \text{ M}$ there is not O_2 evolution. Therefore, $\text{TA} \cdot \text{HCl}$ is an efficient inhibitor for radical-chain reactions [11].

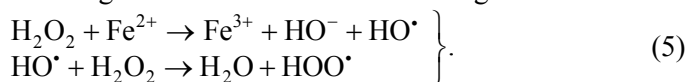
3. *The Influence of AA* [12]. AA contains unsaturated lacton ring. It may be easily oxidized with formation of dehydroascorbic acid (DHAA). It reveals antioxidant properties [13, 14].

The experiments are carried out in the following conditions: $[\text{H}_2\text{O}_2] = 7 \cdot 10^{-2} \text{ M}$; $[\text{Fe(II)}]_0 = 5 \cdot 10^{-3} \text{ M}$, pH 3.5, $T = 298.15 \text{ K}$.

It is established that in AA absence, $W = 0.10 \text{ M}^{-1} \text{ min}^{-1}$. In its presence ($[\text{AA}]_0 = 1.25 \cdot 10^{-3} \text{ M}$) $W = 0.033 \text{ M}^{-1} \text{ min}^{-1}$. W decrease in AA presence shows that it reacts with free HO^\bullet radicals. It means that it decreases the radical-chain run of the reaction, because O_2 is being formed as the result of the following reaction:

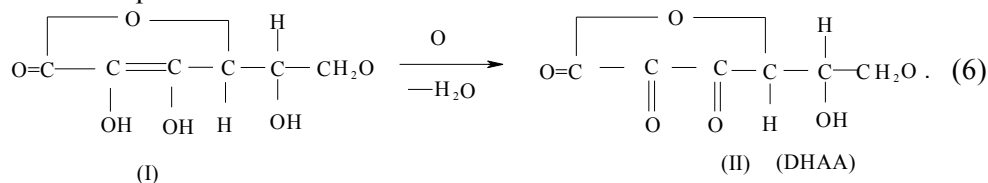


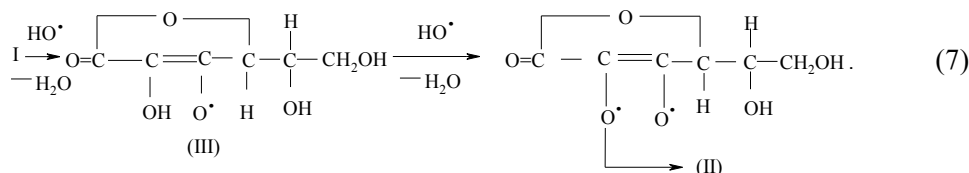
In its turn HOO^\bullet free radical is being formed as result of the following reactions:



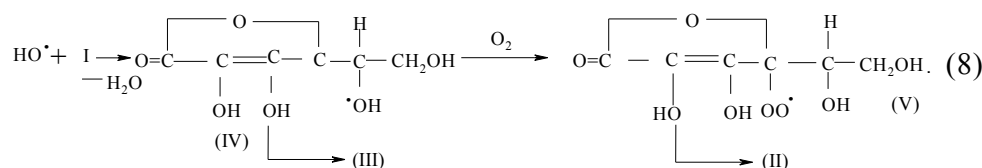
It is evident that AA reacting with HO^\bullet will suppress the O_2 formation.

The product of AA oxidation is DHAA:





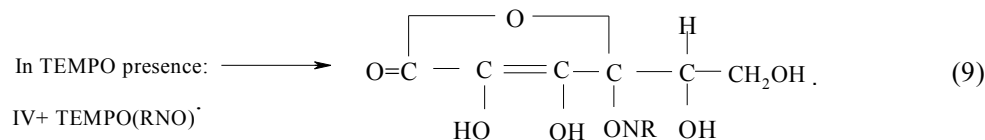
We assume that the following reactions can also be carried out:



This reaction results of W decrease, because a part of evolved O_2 will react with IV. This conclusion is confirmed studying TEMPO's influence on the $\text{H}_2\text{O}_2 + \text{Fe}^{2+}$ rate in the presence of AA.

It is well established that TEMPO reacts directly with free radicals, in which the free valence is on C atom $-\text{C}^\bullet$. [15] as it is in IV.

In following initial conditions: $[\text{H}_2\text{O}_2]=7 \cdot 10^{-2} \text{ M}$; $[\text{Fe(II)}]_0=5 \cdot 10^{-4} \text{ M}$, pH 3.5, $[\text{AA}]_0=1.25 \cdot 10^{-3} \text{ M}$, $T=298.15 \text{ K}$ and $[\text{TEMPO}]_0=1 \cdot 10^{-4} \text{ M}$, $W=0.040 \text{ M}^1 \text{ min}^{-1}$, which is less than W at $[\text{AA}]_0=0$ and $[\text{TEMPO}]_0=0$, but more than



Therefore, a part of the evolved O_2 will not be consumed in the reaction (8), if TEMPO is present.

This conclusion may be confirmed quantitatively using the values of the rate constants of the reactions: $\text{RNO}^\bullet + \text{C}^\bullet - (10^9 \text{ M}^{-1} \text{ s}^{-1})$; $\text{O}_2 + \text{C}^\bullet - (10^8 - 10^9 \text{ M}^{-1} \text{ s}^{-1})$ [16].

It must be considered that $[\text{RNO}^\bullet]_0 / [\text{O}_2]_{\text{solub}} \gg 1$ (see also the Discussion in [1]).

Conclusion.

1. The Influence of FA, TA is studied on the H_2O_2 decomposition rate in water solutions.

2. In alkaline medium FA and TA decrease the $\text{H}_2\text{O}_2 + \text{HOO}^-$ reaction's rate as the result of their reactions with HO^\bullet free radicals, which are being formed in the run of the cited reaction via radical-chain path.

3. In acidic medium FA and AA very effectively decrease catalyzed by Fe(II) cations H_2O_2 decomposition rate.

4. Studying the influence of the mixture AA+TEMPO it is confirmed that AA oxidation may be initiated also as a result of free radical action on C-H bond of 4th C atom.

REFERENCES

1. **Beylerian N.M., Minasyan P.G.** Study of the Influence of Some Additions on the Rate of H₂O₂ Decomposition in Liquid Phase. I: Influence of Unsaturated Cyanolacton and DMSO. // Proceedings of the YSU. Chemistry and Biology, 2016, № 3, p. 14–18.
2. **Beylerian N.M., Asaturyan M.Z.** On the Mechanism of H₂O₂ Decomposition in Alkaline Medium. // Oxidation Communications, 2004, v. 27, № 2, p. 263.
3. **Beylerian N.M., Minasyan P.G., Saroukhanyan E.R.** Study of the Influence of Some Additions on the Rate of Cumene Autoxidation. I: The Influence of Vitamins B₆ and B₁. // Oxidation Communications, 2014, v. 37, № 3, p. 657–661.
4. **Beylerian N.M., Minasyan P.G.** Study of Influence of Some Additives on the Rate of Cumene Autoxidation. II. Influence of Unsaturated Cyano-Lacton and Dimethyl Sulfoxide. // Proceedings of the YSU. Chemistry and Biology, 2016, № 2, p. 17–22.
5. **Haber F., Weiss J.** The Catalytic Decomposition of H₂O₂ by *Ip* Iron Salts. // Proc. of the Royal Soc., 1934, A147, p. 332.
6. **Dolgoplosk B.A., Tiniakova E.I.** (a) Oxidation-Reduction Systems as Free-Radical Sources. M., 1978, Chap. 3, p. 73; (b) Generation of Free-Radicals and Their Reactions. M., 1982, Chap. 3, p. 174 (in Russian).
7. **Tachiev G., Roth J.A., Bowen A.R.** Kinetics of HP Decomposition with Complexed and “Free” Iron Catalysts. // Inter. J. Chem. Kinetics, 2000, v. 32, p. 24.
8. **Bray W.C., Gorin M.N.** Ferryl Ion, a Compound of Tetravalent Iron. // J. Am. Chem. Soc., 1932, v. 54, p. 2124.
9. **Beylerian N.M., Asaturyan M.Z., Minasyan P.G.** The Influence of Folic Acid on the Rate of H₂O₂ Decomposition in Alkaline and Acidic Aqueous Solutions. // Proceedings of the YSU. Chemistry and Biology, 2011, № 2, p. 8–12 (in Russian).
10. **Beylerian N.M., Asaturyan M.Z.** Vitamin C Influence on HP Decomposition Rate Catalyzed by Fe(II), *ibid*, 2007, № 3, p. 7.
11. **Beylerian N.M., Minasyan P.G., Saroukhanyan E.R., Asaturyan M.Z.** Thiamine Impact on the Rates of H₂O₂ Decomposition in Aqueous Solution and Cumene Initiated Autooxidation in Emulsions. // Proceedings of the YSU. Chemistry and Biology, 2012, № 3, p. 8–12.
12. **Kolotova A.I., Gloushankova E.R.** Vitamins (Chemistry, Biochemistry and Physiological Role). L., 1976, p. 155–178 (in Russian).
13. **Nandi D., Patra C.A., Swarup D.** Effect of Cysteine, Methionine, Ascorbic Acid and Thiamine on Arsenic Induced Oxidative Stress and Biochemical Alterations in Rats. // Toxicology, 2005, v. 211, p. 26.
14. **Burguières E., McCue P., Kwon In.Y., Shetty K.** Effect of Vitamin C and Folic Acid on Seed Vigour Response and Phenolic-linked Antioxidant Activity. // Bioresource Technology, 2007, v. 98, p. 1393.
15. **Khlopliankina M.S., Bouchachenko A.L., Neiman M.B., Vasilieva A.G.** On the Mechanism of Kinetic Chains Rupture in Oxidation Reactions by Radical Stabilizers. // Kinetika i Kataliz, 1965, v. 6, p. 397 (in Russian).
16. **Denisov E.T.** In Book: Reaction Constants of Homolytic Liquid Phase Reactions. M.: Nauka, 1971, pp. 176–178, 217 (in Russian).