Chemistry

STUDY OF INFLUENCE OF SOME ADDITIVES ON THE RATE OF H_2O_2 DECOMPOSITION IN LIQUID PHASE. II: INFLUENCE OF VITAMINS B_c, B_1 AND C

P. G. MINASYAN [*], N. M. BEYLERIAN [**]
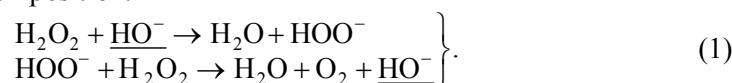
Chair of Organic Chemistry YSU, Armenia

The influence of vitamins B_c (folic acid, FA), B_1 (thiamine, TA) and C (ascorbic acid, AA) on H_2O_2 (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 $[H_2O_2]_0=[HOO^-]=0.5$ *M*. $[FA]_0$ is changed in the range $0–2.8\cdot10^{-3}$ *M*. It is established that the reaction rate (*W*) decreases more than twofold. It is assumed that FA effectively reacts with $HO^{\bullet}$ and $HOO^{\bullet}$, 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 $(0–2.5\cdot10^{-4}$ *M*) also decreases *W* more than 4 times. At pH 3.5, $[TA\cdot HCl]_0 \geq 1\cdot10^{-4}M$ there is no O_2 evolution. The AA influence on the HP decomposition, *W* is studied at pH 3.5. In the presence of AA, $[AA]_0 \approx 1.25\cdot10^{-3}M$, *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 H_2O_2 (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-olyd (unsaturated cyanolacton) and DMSO decrease the radical path of the cited reaction, but have positive action on the non-radical mechanism [1].

Vitamins B_1 (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 B_1, B_c and C (ascorbic acid, AA) on the reaction $H_2O_2+HOO^-$ rate (*W*) is studied.

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

$$\left. \begin{array}{l} H_2O_2 + \underline{HO^-} \rightarrow H_2O + HOO^- \\ HOO^- + H_2O_2 \rightarrow H_2O + O_2 + \underline{HO^-} \end{array} \right\}. \tag{1}$$

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[*] E-mail: parandzemminasyan@mail.ru   [**] E-mail: bnorayr@mail.ru

Considering the fact that the reaction product is O_2, 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 $[H_2O_2]_0=[HOO^-]_0=0.5$ *M*. The influence of $[FA]_0$ is studied. The obtained kinetic data are presented in the Table.

W_{O_2} dependence on [FA]$_0$

$[FA]_0 \cdot 10^3$, *M*	0	0.62	1.0	1.4	2.25	2.8
$W_{O_2} \cdot 10^3$, *mL/min*	0.28	0.26	0.22	0.19	0.15	0.11

From the presented date 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 $[H_2O_2]_0/[Fe(II)]_0 = \alpha$. At $\alpha \gg 1$ 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:

$$2H_2O_2 \xrightarrow{\text{Fe(II)}} 2H_2O + O_2 . \tag{2}$$
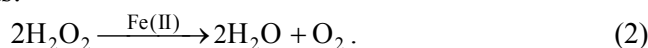
At $\alpha \ll 1$ the reaction occurs by nonradical-chain mechanism (Bray–Gorin mechanism) [8].

$$H_2O_2 + Fe^{2+} \rightarrow H_2O + \underset{\text{ferryl cation}}{FeO^{2+}} \Rightarrow FeO^{2+} + H_2O_2 \rightarrow Fe^{2+} + H_2O + O_2 . \tag{3}$$
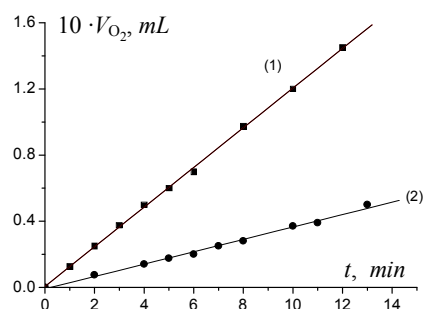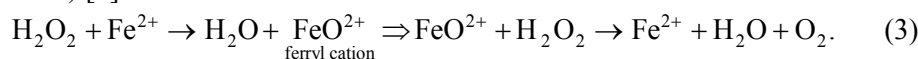
Fig. 1. The kinetic data at: pH 3.5; $[H_2O_2] = 7 \cdot 10^{-2}$ *M*; $[Fe(II)]_0 = 5 \cdot 10^{-2}$ *M* and *T*=298.15 *K*. $[FA]_0$=0 (1); $2.28 \cdot 10^{-3}$ *M* (2).

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

FA influence is studied in the following conditions: pH 3.5; $[H_2O_2]=7 \cdot 10^{-2} M$; $[Fe(II)]_0 = 5 \cdot 10^{-4} M$ 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 $2 \leq pH \leq 4$ [10]. The obtained kinetic data are presented in Fig. 1. It follows that FA decreases $H_2O_2+HOO^-$ 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 $[H_2O_2]_0=[HOO^-]_0=0.5$ *M*. $[TA]_0$ is changed in the range 0–$2.5 \cdot 10^{-4}$ *M*. The obtained kinetic data are presented in Fig. 2.

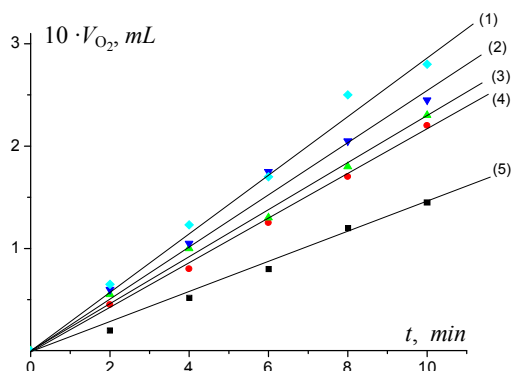Fig. 2. [TA] influence on kinetics of $H_2O_2+HOO^-$ reaction, *T*=303.15 *K*. $[TA]_0$=0 (1); $0.25 \cdot 10^{-4}$ (2); $0.75 \cdot 10^{-4}$ (3); $1.25 \cdot 10^{-4}$ (4); $2.50 \cdot 10^{-4}$ (*M*) (5).

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.
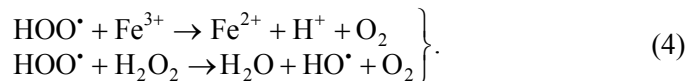
b) *In Acidic Medium.* In this case the reaction's conditions are: $[H_2O_2]=7 \cdot 10^{-2}$ *M*; $[Fe(II)]_0=5 \cdot 10^{-3}$ *M*, pH 3.5, *T*=303.15 *K*. In acidic medium TA is present as hydrochloric salt (TA·HCl).

It is established that at $[TA·HCl]_0 \geq 1 \cdot 10^{-4}$ *M* there is not O_2 evolvement. Therefore, TA·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: $[H_2O_2]=7 \cdot 10^{-2}$ *M*; $[Fe(II)]_0=5 \cdot 10^{-3}$ *M*, pH 3.5, *T*=298.15 *K*.

It is established that in AA absence, $W=0.10$ $M^{-1}min^{-1}$. In its presence ($[AA]_0=1.25 \cdot 10^{-3}$ *M*) $W=0.033$ $M^{-1}min^{-1}$. *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:

$$\left. \begin{array}{l} HOO^{\bullet} + Fe^{3+} \rightarrow Fe^{2+} + H^+ + O_2 \\ HOO^{\bullet} + H_2O_2 \rightarrow H_2O + HO^{\bullet} + O_2 \end{array} \right\} . \qquad (4)$$

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

$$\left. \begin{array}{l} H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^- + HO^{\bullet} \\ HO^{\bullet} + H_2O_2 \rightarrow H_2O + HOO^{\bullet} \end{array} \right\} . \qquad (5)$$
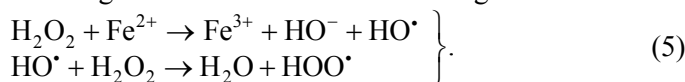
It is evident that AA reacting with $HO^{\bullet}$ will suppress the O_2 formation.

The product of AA oxidation is DHAA:

$$\text{I} \xrightarrow[-H_2O]{HO^\bullet} O=C-\underset{OH}{\underset{|}{C}}\overset{\overset{O}{\frown}}{=}\underset{O^\bullet}{\underset{|}{C}}-\underset{H}{\underset{|}{C}}-\underset{OH}{\underset{|}{\overset{\overset{H}{|}}{C}}}-CH_2OH \xrightarrow{\underset{-H_2O}{HO^\bullet}} O=C-C\overset{\overset{O}{\frown}}{=}C-\underset{O^\bullet}{\underset{|}{C}}-\underset{OH}{\underset{|}{\overset{\overset{H}{|}}{C}}}-CH_2OH. \quad (7)$$

(III) → (II)

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

$$HO^\bullet + \text{I} \xrightarrow[-H_2O]{} O=C-\underset{OH}{\underset{|}{C}}\overset{\overset{O}{\frown}}{=}\underset{OH}{\underset{|}{C}}-\underset{^\bullet OH}{\overset{\overset{H}{|}}{C}}-CH_2OH \xrightarrow{O_2} O=C-\underset{HO}{\underset{|}{C}}\overset{\overset{O}{\frown}}{=}\underset{OH}{\underset{|}{C}}-\underset{OO^\bullet}{\underset{|}{C}}-\underset{OH}{\overset{\overset{H}{|}}{C}}-CH_2OH. \quad (8)$$

(IV) → (III)   (V) → (II)

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 $H_2O_2+Fe^{2+}$ 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 $-\overset{|}{\underset{|}{C}}^\bullet$ [15] as it is in IV.

In following initial conditions: $[H_2O_2]=7\cdot10^{-2}$ M; $[Fe(II)]_0=5\cdot10^{-4}$ M, pH 3.5, $[AA]_0=1.25\cdot10^{-3}$ M, $T=298.15$ K and $[TEMPO]_0=1\cdot10^{-4}$ M, $W= 0.040$ $M^{-1}min^{-1}$, which is less than W at $[AA]_0=0$ and $[TEMPO]_0=0$, but more than

In TEMPO presence: $\longrightarrow$

IV+ TEMPO(RNO)$^\bullet$

$$O=C-\underset{HO}{\underset{|}{C}}\overset{\overset{O}{\frown}}{=}\underset{OH}{\underset{|}{C}}-\underset{ONR}{\underset{|}{C}}-\underset{OH}{\overset{\overset{H}{|}}{C}}-CH_2OH. \quad (9)$$

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: $RNO^\bullet + {^\bullet}\overset{|}{\underset{|}{C}}-$ $(10^9\,M^{-1}s^{-1})$; $O_2 + {^\bullet}\overset{|}{\underset{|}{C}}-$ $(10^8–10^9\,M^{-1}s^{-1})$ [16].

It must be considered that $[RNO^\bullet]_0/[O_2]_{solub} \gg 1$ (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 $H_2O_2+HOO^-$ 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.

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