Chemistry

STUDY OF THE INFLUENCE OF SOME ADDITIVES ON THE RATE OF HYDROGEN PEROXIDE DECOMPOSITION IN ALKALINE MEDIUM: I. INFLUENCE OF UNSATURATED CYANOLACTON AND DIMETHYL SULFOXIDE

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The influence of 2-cyano-3,4,4-trimethyl-2-butene-4-olyd (unsaturated cyanolacton, UCL) and DMSO on the rate of the reaction $H_2O_2 + HOO^-$ at room temperature was studied using gasometric method. Taking into consideration the solubility of H_2O_2 in water and solubility of UCL in oil, the UCL influence is studied in: a) water–EtOH solution; b) in water emulsions stabilized by either anionic (sodium dodecylsulfate, DDS) or cationic (dodecyltrimethylammonium chloride, DTAC) emulsifier. It is assumed that very polar groups, which are in UCL and DMSO molecules, favor the non-radical mechanism of the reaction.

Keywords: anionic emulsifier, cationic emulsifier, non-radical mechanism of the reaction.

Introduction. In our earlier publications [1, 2] was pointed out the importance of control of radical reactions making use compounds, which either have natural origin, for example vitamins, or are harmless for human life, as 2-cyano-3,4,4--trimethyl-2-butene-4-olyd (unsaturated cyanolacton, UCL) and DMSO. It was shown that the mentioned compounds really suppress radical-chain reactions. In this case a new question arises: is it possible that the mentioned compounds influence non-radical reactions, too? To answer this question, the influence of these compounds on the rate (W) of the $H_2O_2 + HOO^-$ (hereafter (∗)) reaction is studied.

The mechanism of the reaction (∗) in detail is studied in [3] using gasometric method. It is established: (i) W has maximum value at $[H_2O_2]_0:[NaOH]_0 = 2 : 1$ or $[HOOH]_0 = [HOO^-]_0$; (ii) the rate law is $W = k[HOOH]_0[HOO^-]_0$; (iii) studying the influence of EtOH, TEMPO and acryl amide it is established that the reaction occurs parallel by two mechanisms: non-radical and radical-chain.

The over-all reaction is:

$$2H_2O_2 \xrightarrow{\;HO^-\;} 2H_2O + O_2. \tag{1}$$
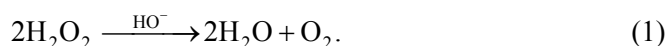
It is shown that $\dfrac{W_{nonrad.}}{W_{rad.ch.}} \cong 5$ [4, 5].

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The use of H_2O_2 (HP) as investigation test is well explained. On the one hand, the mechanism of its decomposition in alkaline medium is clear, on the other hand, HP has many applications in human life. It plays a very important role in the formation of natural waters quality [6]. The concentration of HP in natural waters is equal to $10^{-6} M$ approximately [7, 8]. When its concentration in human organism increases the antioxidant defense, in which vitamins are playing an important role, especially C vitamin, is organized [9]. In little quantities HP is useful. HP has large application in the economy [10]. It is used in waste waters cleaning [11, 12]. In combination with Me(n), especially with Fe(II) (Fenton reagent), HP is a good initiator for radical reactions, e.g. to initiate radical polymerization at low temperatures [13]. It is used in peracids [14, 15], epoxides [16, 17] synthesizing also.

Experimental Part. Kinetics of reaction (∗) was studied by gasometric method. The volume of O_2, evolved during the reaction (1) at the moment, was determined by the method described in [5]. Marked "for medical use" HP was used, which concentration was determined by permanganatometric method. The purity of sodium dodecylsulfate (DDC) and dodecyltrimethylammonium chloride (DTAC) emulsifiers (ES) was more than 99%, also 2,2′,6,6′-tetramethylpiperidine-1-oxyl (TEMPO, "Sigma Aldrich") was used.

Influence of UCL on the Rate of the Reaction (∗).

The Reactions are Carried out in Water–Ethanol Mixture. All experiments are carried out at $[H_2O_2]=[HOO^-]=0.5 M$ and $T=303 K$. The obtained kinetic data are presented on Fig. 1.

Fig. 1. Kinetic curves of the reaction (∗) at
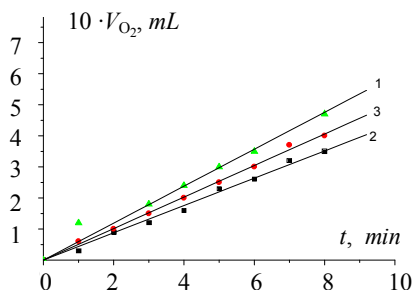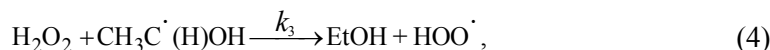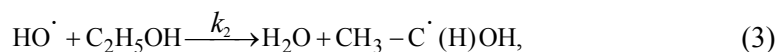
1. $[EtOH]_0=[UCL]_0=0$;
2. $[EtOH]_0=0.25 M$, $[UCL]_0=0$;
3. $[EtOH]_0=0.25 M$, $[UCL]_0=1.0·10^{-2} M$.

From Fig. 1 it follows:

(i) in the presence of EtOH the reaction rate decreases, O_2 evolution is continued. The increase of $[EtOH]_0$ up to 0.75 M does not act on the reaction rate. Therefore, EtOH inhibits only the radical-chain run of the reaction. O_2 evolution is continued as a result of the non-radical run. The following kinetic data confirm this conclusion:

$$HO^· + H_2O_2 \xrightarrow{k_1} H_2O + HOO^·, \tag{2}$$

$$HO^· + C_2H_5OH \xrightarrow{k_2} H_2O + CH_3 - C^·(H)OH, \tag{3}$$

$$H_2O_2 + CH_3C^·(H)OH \xrightarrow{k_3} EtOH + HOO^·, \tag{4}$$

where $k_1 = 7.0·10^7$ [18], $k_2 = 1.0·10^9$ [19], $k_3 = 1.8·10^3 (M·s)^{-1}$ [20].

(ii) In the presence of UCL $W_{\substack{UCL=0 \\ EtOH=0}} > W_{EtOH+UCL} > W_{\substack{UCL=0 \\ EtOH}}$.

(iii) In [1] it is established that UCL inhibits radical-chain reactions. Therefore, UCL cannot increase the reaction rate favouring the radical-chain run. It is assumed that both reagents H_2O_2 and HOO^- may be activated on a very polar $-C\equiv N$ group, which is in the UCL molecules:

$$— C \overset{\delta+}{=\!\!=} C — C \cdots ^-OOH$$
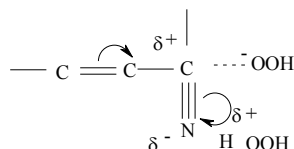
This interaction can favour the non-radical path of the reaction. The reaction is carried out in emulsion. The obtained kinetic data are presented in Fig. 2.
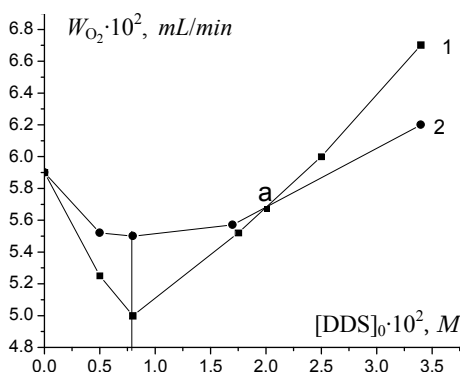
Fig. 2. The reaction rate dependence on $[DDS]_0$:

$[H_2O_2]_0=[HOO^-]_0=0.5\ M$,
1. $[UCL]_0=0$;
2. $[UCL]_0=1.0\cdot10^{-2}\ M$.

Identical curves are obtained when ES DTAC is used. In this case also the reaction has minimum value at $[DTAC]_0=CCM$.

From Fig. 2 it follows:

(i) in the presence of $[ES]_0<CCM$ W decreases, but remains greater than $W_{UCL}=0$. It is assumed that ES reacts with free radicals $HO^\cdot$ and $HOO^\cdot$ as a usual organic compound thus breaking the radical-chain run. As it is mentioned above $W_{UCL}>W_{[UCL]=0}$, because the polar $-C\equiv N$ group in UCL molecule favours the activation of H_2O_2 and HOO^-.

But in general with $[ES]_0$ increase its negative action increases.

(ii) At $[ES]_0 > CCM$ micelles are being formed in the reaction medium. The reaction begins to occur in Stern's layer of micelles, which is being considered as favourable reaction loci.

In this case also, with the increase of $[ES]_0$ after $[ES]_0=a$ (in the case of DTAC $a \approx 3.0\cdot10^{-2}\ M$) the micelles positive action begins to decrease. It is assumed that with $[ES]_0$ increase, increases the competition between ES ions and reagent particles (H_2O_2 and HOO^-) to interact with UCL polar group:

$$— C =\!\!=\!\!= C — C \overset{\delta+}{\equiv\!\!\equiv} N \cdots N(CH_3)_3C_{12}H_{25} .$$
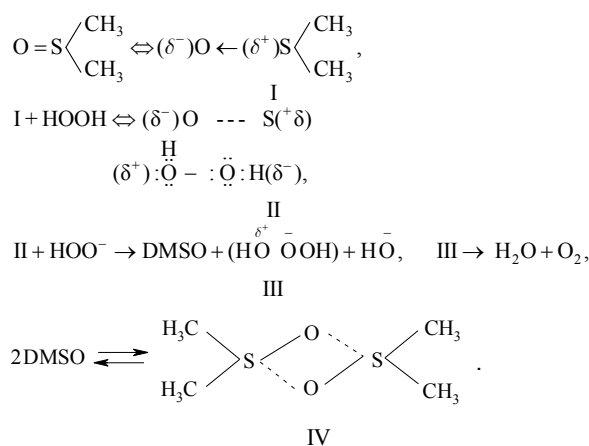$$^-OSO_3C_{12}H_{25}$$
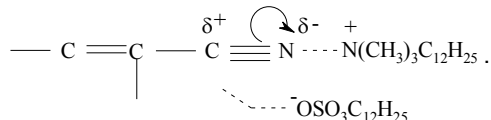
These interactions prevent the simultaneous activation of both reagents on the same polar group. It is very probable that UCL interaction with charged micelles heads more than with ES ions.

Influence of DMSO on the Rate of Reaction (∗). The conditions are: $[H_2O_2]_0=[HOO^-]_0=0.25\ M,\ T=298\ K.$ $[DMSO]_0$ is changed in the range 0–0.1 M [20, 21].

The rate dependence on $[DMSO]_0$ is presented in the Table.

$[DMSO]_0 \cdot 10^3$, M	0	0.5	2.5	5.0	20.0	25.0	40.0	100.0
$W \cdot 10^2$, mL/min	4.8	5.0	5.4	5.4	5.6	5.6	5.2	5.2

From these data it follows, that $W=f([DMSO]_0)$ may be presented by bell shape curve. The optimum range of the $[DMSO]_0$ is $(5.0–25.0)\cdot10^{-3}$ M. The activation energies (E_a) in DMSO absence is equal to 60.6 and is equal to 55.6 *KJ/mol* in its presence. This shows that DMSO decreases the reaction E_a. It is assumed that the polar $O=S<$ group in DMSO molecule favours the activation of HP molecule:

$$O=S\begin{array}{c}CH_3\\CH_3\end{array} \Leftrightarrow (\delta^-)O \leftarrow (\delta^+)S\begin{array}{c}CH_3\\CH_3\end{array},$$
$$I$$
$$I+HOOH \Leftrightarrow (\delta^-)O \ --- \ S(^+\delta)$$
$$H$$
$$(\delta^+):\ddot{O} - \ :\ddot{O}:H(\delta^-),$$
$$II$$
$$II+HOO^- \rightarrow DMSO+(HO \ \overset{\delta^+}{O}\overset{-}{OH})+H\overset{-}{O}, \quad III \rightarrow H_2O+O_2,$$
$$III$$

$$2\,DMSO \rightleftharpoons \begin{array}{c}H_3C\\H_3C\end{array}>S\overset{O}{\underset{O}{<}}S<\begin{array}{c}CH_3\\CH_3\end{array}.$$
$$IV$$

In this case DMSO favours the non-radical run of the reaction. It must be noted that in all cases the antioxidant activity of DMSO remains which results in decrease of over all rate of the reaction decreasing the radical-chain run rate. The W decrease at $[DMSO]_0 \geq 1.0\cdot10^{-2}$ M may be explained assuming that it favours the dimerisation of DMSO. HP molecule cannot interact with IV.

So, on one side DMSO acts as antioxidant and decreases the over-all rate of the reaction decreasing the rate of the radical-chain run, on the other side increases the over-all rate of the non-radical run. It is due to the activation of HP molecule on the polar $O=S<$ group, which is in DMSO molecule.

Conclusion.

1. The influence of unsaturated cyanolacton and DMSO is discussed considering the fact that the reaction (∗) occurs simultaneously by two mechanisms: non-radical (~84%) and radical-chain (~16%).

2. In absence of UCL ethanol decreases the over-all rate of the reaction, decreasing the rate of the radical-chain run.

3. In the presence of UCL+EtOH mixture the over-all rate of reaction in some extent increases, but remains lower when UCL and EtOH are absent. It is explained assuming that the polar $-C=C-C\equiv N$ group in UCL molecule favours the reaction non-radical run activating both reagents H_2O_2 and HOO^-.

4. In the presence of micelle-forming ionic ES (sodium dodecylsulfate and dodecyltrimethylammonium chloride) the over-all rate decreases. The rate has minimum value at $[ES]_0 = CCM$.

5. At $[ES]_0 > CCM$ the reaction rate increases, because the reaction loci is being changed. In this case the reaction mainly occurs in micelles.

6. Even in the presence of ES UCL polar group continues to favour the reaction increasing the non-radical run rate of the reaction.

7. DMSO exhibits its autoxidant behaviour, which results in rate decrease. At the same time DMSO favours non-radical run of the reaction. It is due to the activation of HP interaction with the polar O=S< group. The increase of $[DMSO]_0$ results in the increase of DMSO dimerisation possibility. The dimer is not able to activate HP molecule.

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