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THE INFLUENCE OF THE REACTION MEDIUM ON THE CLEAVAGE OF HYDROGEN PEROXIDE CATALYZED WITH COBALT IONS

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Received: January 10, 2008

Abstract. Using the method of inhibitors the peculiarities of H₂O₂ cleavage catalyzed by cobalt (II)acetylacetonate in different hydrophilic solvents was studied. As was established, physical-chemical properties of the reaction medium can significantly affect the rate of peroxide decomposition and catalyst oxidation.

Key words: catalytic cleavage, hydrogen peroxide, cobalt (II) ions, solvents, inhibitor.

1. Introduction

A solvent can affect the kinetics of the homogeneous oxidation processes by influencing their elementary steps [1, 2]. As a rule, the range of these changes does not exceed one order of magnitude (usually 200-300 %). In spite of relatively low sensitivity of such processes towards the nature of a solvent, accelerating the velocity of certain elemental steps can notably influence the target products yield. An initiation stage is one of the elementary stages which are most sensitive to the reaction medium. Thus studying the role of this stage in the general mechanism of oxidation is of great importance.

Commonly, decomposition of peroxide-like compounds is responsible for the initiation. Due to the generally accepted opinions the decomposition of peroxides occurs along the two parallel routes – heterolytic (non-radical) and induced (radical) [3]. The role of the solvent in this type of reactions is conditioned by its solvating properties [4], which particularly affect the heterolytic decomposition. At the same time the induced moiety is mainly dependent on the solvent's self-association value (density of cohesion energy) [5]. The increase of the last member accelerates the rate supposedly by enforcing the "cage" effect in the "solvent-solvent" and "solvent-peroxide" system [6]. The last effect causes decreasing of the reaction barrier and increases the rate of the induced moiety of the cleavage [7].

This work continues the study of the peculiarities of the peroxides catalytic cleavage in organic solvents that has been started in [8]. The selection of H₂O₂ as an object of investigation is due to its unique qualities (ecological safety, technological versatility and economical attractiveness), that allow applying it as a relevant oxidant for numerous organic substrates oxifunctionalization. The kinetics results have been obtained by using the method of inhibitors as one of the most proven, informative and accepted tools for radical reactions studying.

2. Experimental

The kinetics of H₂O₂ consumption has been studied at 308 K in a thermostatted 25 ml glass cell. The reaction mixture (total volume 20 ml) was stirred with a Teflon covered magnetic stirring bar. In the beginning (prior to adding H₂O₂) nitrogen was being bubbled through the reaction mixture for 5–10 min. Following that a determinate volume of peroxide was injected into the deaerated mixture by a syringe and this moment was taken as the start of the reaction. The content of H₂O₂ in the reaction medium during the experiment was being monitored by the titration of the probes withdrawn from the reaction mixture with defined intervals. 0.01N water solution of Na₂S₂O₃ was used as a titrant. The probe (1 ml) withdrawn with a pipette was poured into 250 ml conical flask that initially contained 2 ml of H₂SO₄ (4N aq solution) and 2 ml of KI (saturated aq solution) in 100 ml of distilled water. The resulted brown mixture was being preserved in a dark place for 30 min and then titrated with sodium tiosulphate under vigorous stirring till light-yellow color was obtained. Following that 2-3 drops of 10 % aq solution of starch was added and the flask content was titrated colorless. Before each experiment the "blank" titration (without a probe) was conducted in order to abate the influence of dissolved oxygen on the results of the analysis. Usually, the error of

measurement caused by the presence of dissolved O_2 was <1 % from the total (including H_2O_2) consumption of titrating agent.

In order to avoid probable exceeding consumption of hydrogen peroxide in the reaction with the solvents capable of oxidizing in the experimental conditions (morpholine) "blank" titrations (in the absence of Co^{2+}) of H_2O_2 solution in such solvents have been carried out. The obtained results were taken into account for calculation of the rate of hydrogen peroxide decomposition catalyzed by cobalt ions.

The electronic absorption spectra of the investigated solutions were recorded using Hewlett Packard 8453 and SF-20 spectrophotometers (1 cm quartz cuvettes).

Quinone (InH) was synthesized from hydroquinone by the method described in [9] and purified by double recrystallization from ethanol.

The solvents (for the analysis) were purified by conventional methods [10] and distilled before each series of experiments.

Cobalt (II)acetylacetonate ($Co(acac)_2$) (99% grade, Aldrich) was used as purchased.

The contribution of the non-radical (heterolytic) moiety of the rate of hydrogen peroxide cleavage can be calculated using the following equation:

$$W = W_{ind} + W_{het}$$

where: W – total rate of H_2O_2 cleavage, $M \cdot s^{-1}$; W_{ind} – induced (radical) moiety of total rate of cleavage, $M \cdot s^{-1}$;

W_{het} – non-radical (heterolytic) component of total rate of H_2O_2 cleavage in the presence of free-radical inhibitor (quinone), $M \cdot s^{-1}$.

3. Results and Discussion

The experimental rates of pseudo-first order of H_2O_2 cleavage catalyzed with Co^{2+} indicate the significant influence of solvents on the process under consideration (Fig. 1, Table 1).

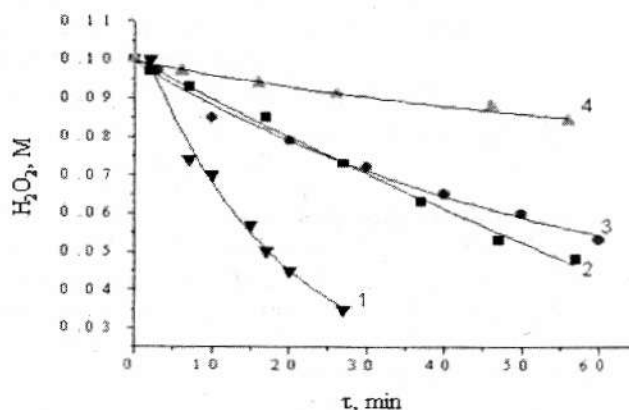


Fig. 1. Kinetics of Co^{2+} catalyzed cleavage of H_2O_2 in THF (1), MeCN (2), AcOH (3), and morpholine (4) at 308 K

Table 1

Total rate of hydrogen peroxide consumption (W) and it heterolytic (W_{het}) and induced (W_{ind}) moieties

Solvent	$W \cdot 10^5, M \cdot s^{-1}$	$W_{het} \cdot 10^5, M \cdot s^{-1}$	$W_{ind} \cdot 10^5, M \cdot s^{-1}$	$W_{ind}/W, \%$
<i>i</i> -PrOH	19.0	2.5	16.5	87
<i>t</i> -BuOH	18.0	2.1	15.9	88
HOAc	6.2	0.8	5.4	87
H_2O	1.4	0.4	1.0	71
Dioxane	1.2	0.7	0.5	42
Morpholine	1.4	0.6	0.8	57
MeCN	5.5	0.8	4.7	75
THF	18.0	3.5	14.5	81

Note: $[H_2O_2]_0 = 100 \text{ mM}$; $[Co^{2+}]_0 = 5 \text{ mM}$; $[Quinone]_0 = 10 \text{ mM}$; the temperature is 308 K

In the solvents containing hydroxyl groups – 2-propanol (*i*-PrOH) and 2-methyl-2-propanol (*t*-BuOH) the cleavage rate is so high ($W \approx 2 \cdot 10^{-3} M \cdot s^{-1}$) that after approximately 20 min from the insertion of peroxide into the reaction mixture the concentration of the last one verged towards zero. At the same time in water and acetic acid (AcOH) the cleavage of H_2O_2 is notably slower. The reaction under consideration runs even slower in electron-donating dioxane and particularly in morpholine. The discovered experimental fact correlates with the dependence of the rate of peroxide cleavage upon specific

(ability to form donor-acceptor complexes) and non-specific (electrostatic) solvation of H_2O_2 by the molecules of the solvent [11]. Hence the solvents with hydroxyl groups (alcohols) and, to a bit less degree acids and water facilitate the cleavage of peroxide. At the same time electron-donating solvents (morpholine and dioxane) stabilize it.

The presence of the inhibitor (quinone) significantly changes the picture observed for the non-inhibiting process (Fig. 2, Table 1). It is known that in free-radical processes free-valent species are able to induce decomposition of the compounds with the weakened O–O bonds. The free-

radicals inhibitors slow this route [12] enabling the quantitative estimation of each route's input (heterolytic and induced) in the total rate of peroxide consumption.

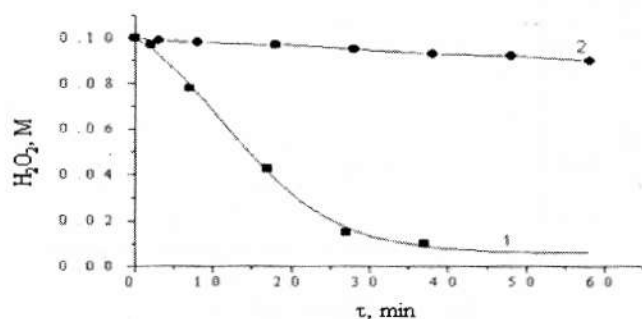


Fig. 2. Kinetics of catalyzed with Co^{2+} cleavage of H_2O_2 in *i*-PrOH without InH (1) and in the presence of 20 mM of quinone (2) at 308 K

As was determined experimentally (Fig. 3) exceeding quinone concentration over 10 mM has practically no influence on the rate of H_2O_2 cleavage any more. At the same time such content of InH in the reaction mixture (10–20 % from the initial concentration of H_2O_2) can not noticeably influence the titrating agent ($\text{Na}_2\text{S}_2\text{O}_3$) consumption and radical component of hydrogen peroxide decomposition rate. (Quinones, by analogy with alkylphenols [12] can be oxidized with free-radical products of H_2O_2 cleavage with the formation of their peroxide-like derivatives). Hence it can be assumed that at such concentration of InH cleavage of peroxide in the tested solvents occurs mainly along the non-radical route. This enables experimental determination of heterolytic moiety of H_2O_2 decomposition.

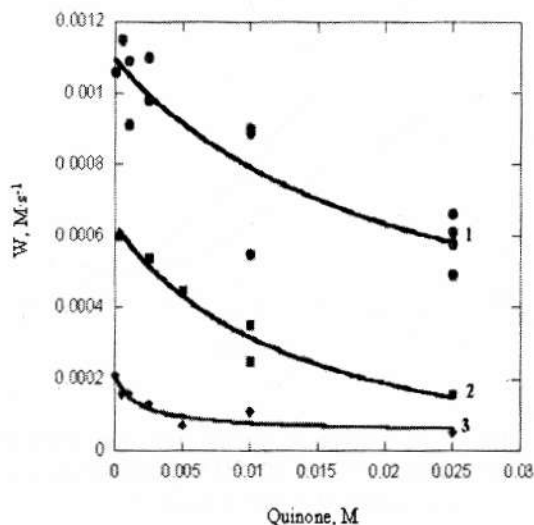


Fig. 3. Rates of H_2O_2 decomposition catalyzed by 10 mM (1), 5 mM (2) and 2.5 mM (3) Co^{2+} depending on quinone concentration. $[\text{H}_2\text{O}_2]_0 = 50\text{mM}$, $T = 308\text{ K}$, AcOH medium

H_2O_2 decomposition rate in the solvents which are prone to self-association is more sensitive to the presence of quinone as compared to those containing no hydroxyl groups (Table 1). For example in alcohols and acetic acid the induced moiety of decomposition is about 90 %, followed by acetonitrile (MeCN) and tetrahydrofuran (THF) (the reviewed value is equal $\approx 80\%$), and then water, morpholine and dioxane (40–70 %). The aloof position of water in this range apparently is explained by the concerted influence of several electrochemical properties characteristic of H_2O . Their combination can be responsible for different behavior of this solvent as compared to alcohols and acids.

As follows from Table 1 the maximal ratio of brutto-rates of H_2O_2 decomposition in the selected solvents is about 16 ($W_{i\text{-PrOH}}/W_{\text{Dioxane}}$). For heterolytic decomposition this value is 9 ($W_{\text{THF}}/W_{\text{Water}}$) and in case of the induced one – 33 ($W_{i\text{-PrOH}}/W_{\text{Dioxane}}$). Thus in the testing conditions the reaction medium stronger affects the induced moiety of peroxide cleavage notably (≈ 4 times) than the non-radical one.

For additional clarification of the role of the solvent's nature in Co^{2+} ions transformation the electronic spectra of these ions in the selected solvents have been recorded before and after H_2O_2 treatment. The absorption maximums attributed to Co^{2+} and Co^{3+} (Table 2) as well as the velocity of these cations transformation after peroxide addition depended on physical-chemical properties of the solvent. According to the obtained data (Fig. 4, Table 2) in the solvents that are able to form strong intermolecular hydrogen bonds (alcohols) maximum absorption is observed at 490 and 605 nm. The rate of Co^{2+} to Co^{3+} transformation after H_2O_2 addition in such solvents as well as in MeCN is diffusion-controlled. Interestingly, in AcOH and water, which by analogy with alcohols, are capable of creating associates, [7, 13] the bathochromic shift of Co^{2+} ions absorption was observed (Table 2).

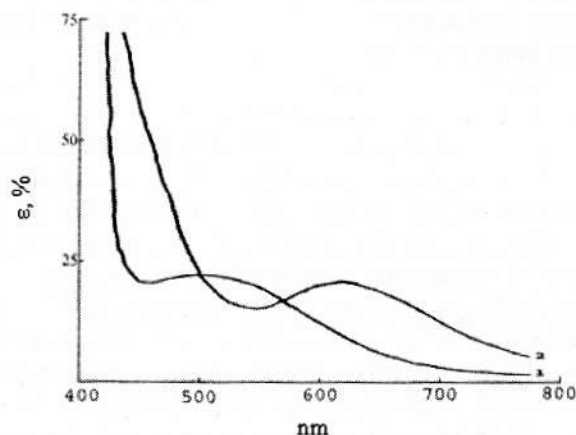


Fig. 4. Electronic absorption spectra of 1mM Co^{2+} in *i*-PrOH (1) and in the presence of 50 mM H_2O_2 (2) at 293 K

Table 2

Maximums of absorption (nm) of Co^{2+} and Co^{3+} ions in the tested solvents at 293 K

λ_{cation} , nm	<i>i</i> -PrOH	HOAc	H ₂ O	Dioxane	Morpholine	MeCN	THF
$\lambda_{\text{Co}^{2+}}$	490	545	530	520	550	510	525
$\lambda_{\text{Co}^{3+}}$	605	610	610	610	570	610	610

In electron-donating solvents – morpholine, dioxane, and acetonitrile (Fig. 5) changes in Co^{2+} absorption spectrum occurred almost instantly (in 10–20 s) after H_2O_2 addition. However there are some inconsistencies between the rates of Co^{3+} formation and peroxide decomposition, which are still hard to explicate.

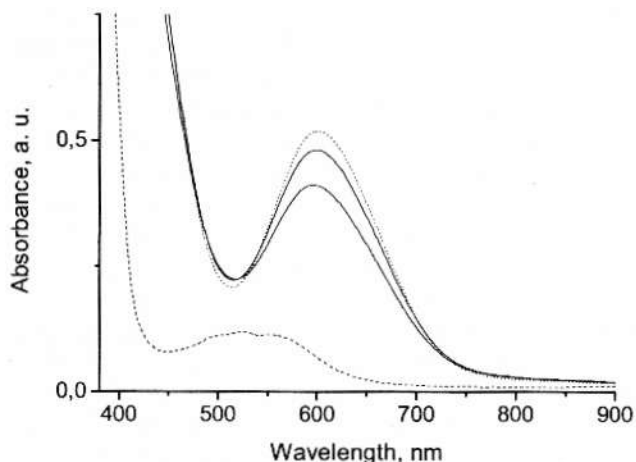


Fig. 5. Time-depending changes of UV-vis spectra of 5mM solution $\text{Co}(\text{acac})_3$ in 2 ml MeCN in the presence of H_2O_2 at 293 K. The dash lines depict the initial spectrum of $\text{Co}(\text{acac})_3$, the dot line – the last spectrum taken after 2 μl H_2O_2 injection

Eventually it is explained by the fact that Co^{2+} oxidation in such solvents is mainly by $\cdot\text{OH}$ -radicals. Unlike in the mentioned solvents the electronic spectrum of Co^{2+} in acetic acid solution remained unchanged for at least several hours after H_2O_2 addition (Fig. 6).

Absorption maximum of Co^{2+} in morpholine (550 nm), tetrahydrofuran (525 nm), dioxane (520 nm), and acetonitrile (510 nm) are shifted to bathochromic (as compared to alcohols) region (Table 2). The wavelengths at which the absorption maximum is observed for Co^{3+} in THF, dioxane, and MeCN (610 nm) also coincide with the ones in the solvents capable of forming the hydrogen bonds (Table 2). The absorption maximum of Co^{3+} in morpholine (570 nm) is situated close to the characteristic peak of Co^{2+} in this solvent. Such a noticeable hypsochromic shift (which has been observed for more polar Co^{3+} ions) is explained by stronger electron-donating properties of morpholine and its lower polarity as compared to MeCN [14].

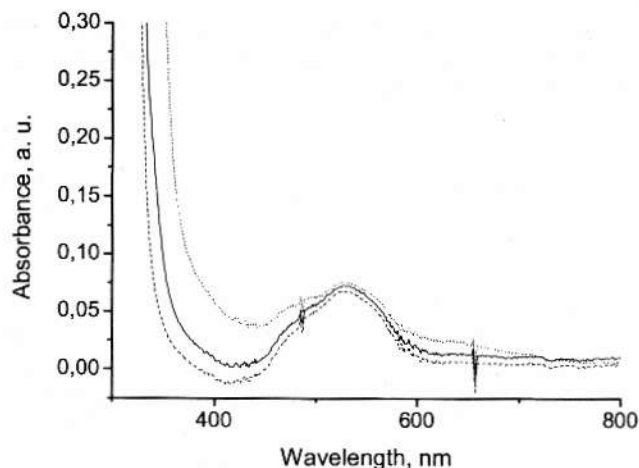


Fig. 6. Time-depending changes of UV-vis spectra of 5mM solution $\text{Co}(\text{acac})_3$ in 2 ml AcOH in the presence of H_2O_2 at 293 K. The dash lines depict the initial spectrum of $\text{Co}(\text{acac})_3$, the dot line – the last spectrum taken after 2 μl H_2O_2 injection. Inset – time-traces of spectra taken at 530 nm

The addition of hydrogen peroxide to the solution of Co^{2+} ions in 2-propanol that initially contains 10 mM of quinone does not lead to the formation of oxidized form of these ions – the Co^{3+} absorption peak is absent (Fig. 7). The spectrum has remained unchanged during more than 1 h after mixing the solution with H_2O_2 which indicates the noticeable free radicals ($\cdot\text{OH}$) contribution to Co^{2+} cations oxidation.

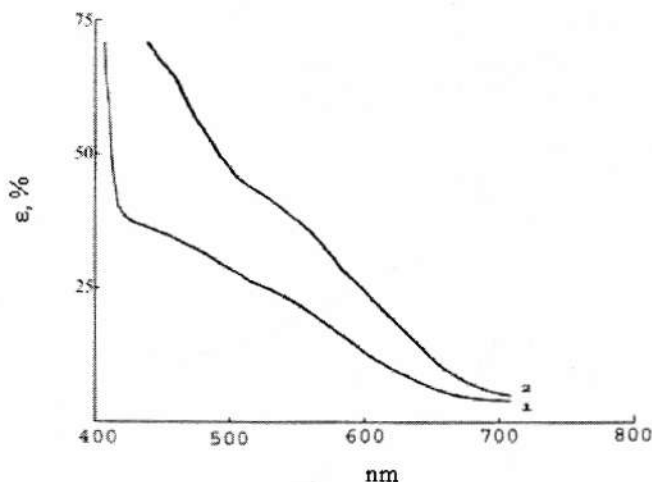


Fig. 7. Electronic absorption spectra of mixture 1mM Co^{2+} and 20 mM quinone in 2 ml *i*-PrOH before (1) and after (2) of 2 μl H_2O_2 injection at 293 K

It is necessary to note that according to the classic researches [15] the Co^{2+} with H_2O_2 reaction rate constant is by more than two orders of magnitude higher as compared to Co^{3+} . This is explained by the low reduction ability of hydrogen peroxide. In addition to this HOO^\cdot radical concentration which are also generated during H_2O_2 decomposition is so slight that the contribution of the reverse reaction of Haber-Weiss cycle (Co^{3+} reduction) can be neglected.

All of the mentioned features of hydrogen peroxide catalytic decomposition in different solvents imply that there is a combinatorial effect of several physical-chemical factors that characterize the reaction medium similarly as it is observed during the peracids decomposition [16]. To pursue the study of the established dependencies in more detail further thorough researches are planned.

3. Conclusions

The obtained experimental data prove the critical influence of the reaction medium on the routes of H_2O_2 cleavage. The hydroxyl radicals induced route makes significant contribution into the general process of hydrogen peroxide decomposition. On the other hand the same route has a determining influence on the valent transformations of d -elements in the medium characterized by high specific solvation. It is necessary to note that the influence of the physical-chemical properties of the solvents on the total rate of H_2O_2 catalytic decomposition has an ambiguous and complicated character.

Acknowledgements

A part of the presented work has been done under the financial support of NATO grant CLG No. 982510. The authors (particularly O. Pokutsa) express their thanks to Prof. H.-U. Siehl (University of Ulm) for the opportunity to present the preliminary results of the research on 7th European Symposium on Organic Reactivity (1999, Ulm, Germany).

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ВПЛИВ РЕАКЦІЙНОГО СЕРЕДОВИЩА НА РОЗКЛАД ПЕРОКСИДУ ВОДНЮ, КАТАЛІЗОВАНИЙ ІОНАМИ КОБАЛЬТУ

Анотація. Розклад H_2O_2 каталізованого кобальт (II) ацетилацетонатом, в ряді гідрофільних розчинників було вивчено методом інгібіторів. Встановлено, що фізико-хімічні властивості реакційного середовища можуть помітно впливати на швидкість розпаду пероксиду та окислення катіону металу. Ефект середовища є пропорційним його полярності та електрофільності. Наведені особливості каталітичного розкладу пероксиду водню в розчинниках вказують на присутність комбінаторного ефекту від впливу різноманітних фізико-хімічних факторів, що характеризують реакційне середовище.

Ключові слова: каталітичний розклад, пероксид водню, кобальт (II) йони, розчинники, інгібітор.