

Interaction of Hemin and Hydrogen Peroxide: Effect of Media

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Maximum of catalytic activity of hemin (complex of iron(III) with protoporphyrin IX, FePP) in hydrogen peroxide decomposition is shown to correspond to an associated form (evidently, dimer) of FePP. Influence of NaHCO₃, Na₂HPO₄, cetyltrimethylammonium bromide and poly-N-vinylpyrrolidone on kinetics of hydrogen peroxide decomposition catalyzed by FePP and destruction of FePP was studied.

Keywords: Hemin, oxidative destruction, aggregation, hydrogen peroxide decomposition.

Introduction

Hemin (Fe^{III} complex of protoporphyrin IX, FePP) catalyses the decomposition of hydrogen peroxide. This process underlies the mechanism of action of oxidoreductases.^[1] Complex FePP isolated from apoenzyme is unstable in H₂O₂ systems. It is known that isolating of FePP from protein macromolecule results in decrease of the rate of H₂O₂ catalytic decomposition considerably.^[2] Both catalytic decomposition of H₂O₂ and oxidative destruction of FePP proceed simultaneously. Rate of these processes depends on aggregation state of FePP in solutions and changes in the presence of different compounds. At present the catalytic activity of FePP in H₂O₂ decomposition is well investigated.^[2,3] However insufficient attention are given to problem of stability of FePP in studied reaction systems containing H₂O₂.

In this work an influence of NaHCO₃, Na₂HPO₄, cetyltrimethylammonium bromide (CTAB) and poly-N-vinylpyrrolidone (PVP) on interaction FePP and H₂O₂ in 0.1 N NaOH was studied. Salts NaHCO₃ and Na₂HPO₄ are components of different buffer solutions and important constituent part of biological liquids. Micellar systems of CTAB and composition based on PVP are widely applied in pharmacology and biophysical modeling, for instance as solubilization agents. The question about association of FePP in these systems is of the particular interest.

Experimental

Hydrogen peroxide without stabilizers, chlorinated FePP, Na₂HPO₄, NaHCO₃, NaOH, CTAB («Reakhim», Russia) and PVP with average molecular weight 10000 g/mol («Sigma», USA) were used in experiment. Salts, CTAB or PVP were added to 50 ml of solution FePP of known concentration in 0.1 N NaOH. Then H₂O₂ was added to concentration 0.08 M at stirring. Concentration of H₂O₂ was determined by chemical titration using potassium permanganate. Concentration of FePP in solutions was calculated on value of their optical density in Soret band measured on spectrophotometer Beckman DU-8B using quartz cells (1 cm).

Results and Discussion

The rate of H₂O₂ decomposition catalyzed by FePP was determined from initial part of kinetic curves. Dependence of the rate of H₂O₂ decomposition (w) on FePP concentration is characterized by maximum corresponding $4.5 \cdot 10^{-4}$ M FePP (Figure 1). It was interesting to study an aggregation state of FePP in dependence on its concentration. The graph of change of optical density of FePP solutions in 0.1 N NaOH depending on FePP is represented in Figure 2. The straight line showing the Bouguer law on Figure 2 (value of molar extinction of FePP is 90000 l/mol·cm^[4]) coincides with the straight line constructed by least-squares method through points in the range of concentration $(0.3 - 1.5) \cdot 10^{-5}$ M. At the concentration of FePP $\geq 2 \cdot 10^{-5}$ mol/l a deviation from Bouguer law is observed (Figure 2). This feature testifies to process of FePP association, first of all FePP dimer formation.^[5]

As it was reported earlier,^[6,7] Fe^{III} porphyrins interact with H₂O₂ forming a particle of ferryl type. In this case its formula is PPFe^{IV}=O. This particle is highly reactive. First

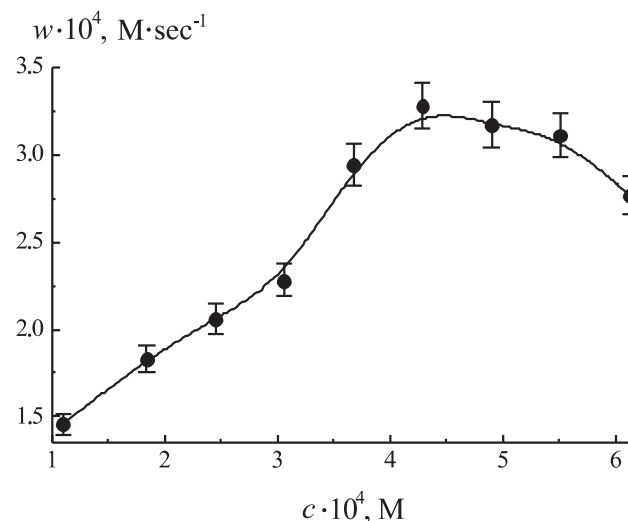


Figure 1. Dependence of rate of H₂O₂ decomposition on FePP concentration.

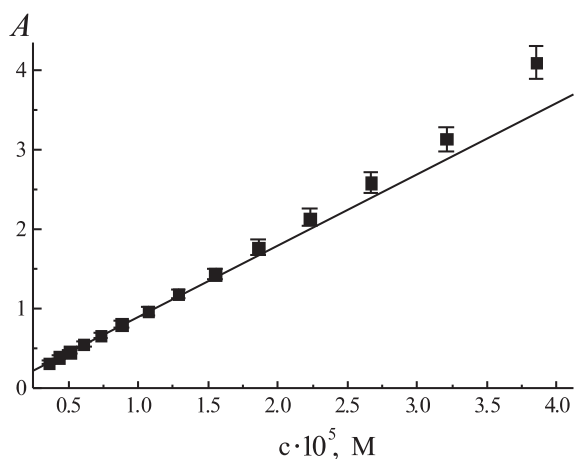


Figure 2. Dependence of optical density of FePP solutions on their concentration.

of all FePP complex is subjected to oxidative destruction by ferryl transients. Particles $\text{PPFe}^{\text{IV}}=\text{O}$ are easily formed, if complex FePP is in the monomer form. In dimer state generation of less active μ -oxodimers $(\text{PPFe}^{\text{III}})_2\text{O}$ competes to $\text{PPFe}^{\text{IV}}=\text{O}$ formation. Consequently FePP in dimer form oxidizes and is spent as the catalyst to a smaller extent.

The given feature of interaction FePP and H_2O_2 allows to explain the decrease of the rate of H_2O_2 decomposition catalyzed by FePP at addition of cationic surfactant CTAB (Figure 3).

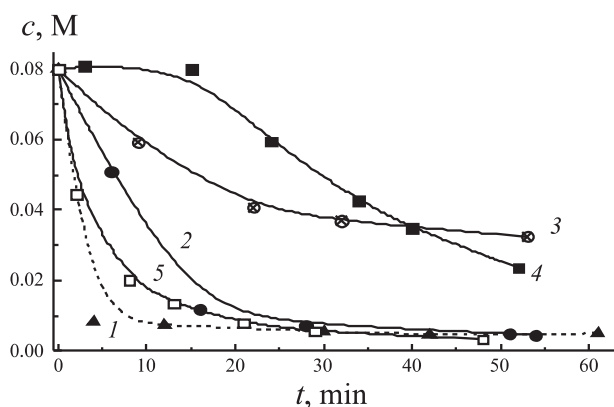


Figure 3. Kinetics of H_2O_2 decomposition catalyzed by FePP in 0.1 N NaOH without additives (1), in the presence of 0.1 M NaHCO_3 (2), 0.1 M Na_2HPO_4 (3), 3 mM CTAB (4) and 0.5 mM PVP (5).

Addition of CTAB (3 mM) lowers process of FePP dimer formation because FePP molecule contains negatively charged propionic acid residues in alkaline solutions. So FePP destruction accelerates in these systems (Figure 4).

Formation of $\text{PPFe}^{\text{IV}}=\text{O}$ is facilitated in the presence of acceptors of O^{2-} anions,^[6] as well as at decrease of pH. In the presence of the salts Na_2HPO_4 and NaHCO_3 (0.1 M) leading to the reduction of pH value FePP destruction increases (Figure 4). Hence the decrease of the rate of H_2O_2 decomposition is observed (Figure 3). However it is visible that FePP destruction does not allow to explain the decrease of the rate of H_2O_2 decomposition fully. For instance, the decrease of the rate of H_2O_2 decomposition in NaHCO_3 solution is not explained by lesser concentration of destructed FePP. We assume that

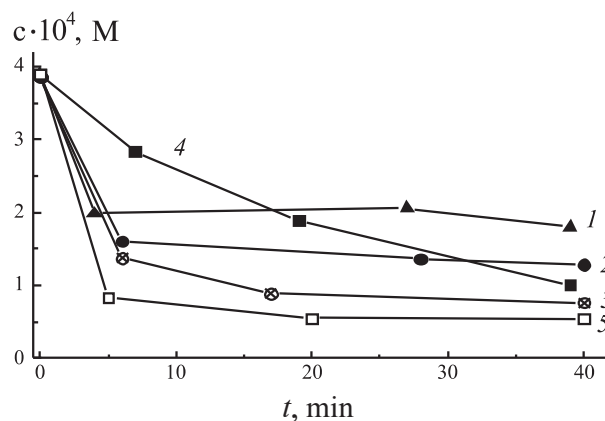


Figure 4. Decrease of FePP concentration during interaction with H_2O_2 in 0.1 N NaOH without additives (1), in the presence of 0.1 M NaHCO_3 (2), 0.1 M Na_2HPO_4 (3), 3 mM CTAB (4) and 0.5 mM PVP (5).

deceleration of H_2O_2 decomposition in bicarbonate solution is caused also by formation of peroxocarbonates,^[8] which are relatively stable concerning FePP catalysis.

Strengthening of FePP interaction with H_2O_2 occurs also at addition of water-soluble polymer PVP to solution (0.5 mM) (Figure 4). Binding of FePP complexes with PVP macromolecules obviously results in being of FePP mainly in a monomer state. Destruction of FePP increases in this case. At the same time it is known that PVP absorbs 50-60% H_2O_2 on weight.^[9,10] So combined coordination of H_2O_2 and FePP is possible. Therefore rate of decay H_2O_2 decomposition practically does not decrease.

Conclusions

Studied additives influence on aggregation states of hemin and decrease the rate of H_2O_2 decomposition catalyzed by hemin. However a strict correlation of this effect with FePP destruction is not observed because there are specific action of each systems, e.g. peroxocarbonates formation from HCO_3^- , significant binding of H_2O_2 by PVP macromolecules and others. Observable features of interaction FePP and H_2O_2 in the presence of various compounds are necessary to consider at discussion of H_2O_2 role in biological processes, and also by working out of the artificial systems modeling these processes.

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