



Novel mechanistic aspects on the reaction between low spin Fe(II) Schiff base amino acid complexes and hydrogen peroxide—Spectrophotometric tracer of intraperoxo intermediate catalyzed reaction

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Abstract

The kinetics and mechanism of the reaction of hydrogen peroxide with some Fe(II) Schiff base complexes were investigated spectrophotometrically in aqueous solution at pH 8 and 35 °C under pseudo-first-order conditions. The used ligands were derived from salicylaldehyde or *o*-hydroxynaphthaldehyde and some amino acids (L-leucine, L-iso-leucine, L-serine, L-methionine and DL-tryptophan). It was found that the formation of the purple intraperoxo complex appears only above pH 7.5. The reaction consists of two steps. The first step involves reversible formation of the intraperoxo intermediate which renders irreversible at pH 8. The second step consists of inner-sphere electron transfer. The suggested scheme illustrated first-order kinetics at low [H₂O₂] and zero-order at high [H₂O₂]. Moreover, the activation parameters of the reaction were evaluated. © 2008 Elsevier B.V. All rights reserved.

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1. Introduction

Schiff base complexes have extensive importance as radio-tracers [1], biologically active reagents [2–5], catalysts for oxidation [6,7], epoxidation [8], polymerization [9] and decomposition reactions [10,11]. On the other hand the decomposition of H₂O₂ has recently been extensively used in fundamentally clean processes and in end-of-pipe treatment of effluent of chemical industries [12,13]. It was found that, many complexes of transition metals are more effective catalysts than their aqua metal ions in catalyzing the decomposition of H₂O₂ in both homogenous [14] and heterogeneous [15] media. There are two general types of mechanisms have been postulated for the decomposition of H₂O₂ in the presence of metal complexes, the radical mechanism [16] and the peroxide complex mechanism [17]. Moreover, the redox chemistry of iron plays an important role in the oxygen activation and transfer reactions mediated by heme and non-heme iron proteins [18]. Crystallographic and

spectroscopic data of non-heme iron sites support both penta- and hexa-coordination with nitrogen, oxygen and sulfur donors derived from amino acid residues and exogenous ligands [19].

The different pathways concerning the decomposition of H₂O₂ catalyzed by Fe(II) and Fe(III) ions and their complexes stimulated our interest in the actual mechanism of hydrogen peroxide activation by Fe(II) Schiff base amino acid complexes. Our previous data [20] on the base hydrolysis of our recent complexes and their observed stability in pH range (4–10) encouraged us to continue our investigation with the effects of H₂O₂ on these complexes in the stability pH range. Therefore, in the present contribution, a detailed kinetic investigation of the reaction between Fe(II) Schiff base amino acid complexes and H₂O₂ in the aqueous solution at pH 8 was performed.

2. Experimental

The complexes were prepared as reported elsewhere [21] from iron(II) ammonium sulphate, 2-hydroxy-1-naphthaldehyde or salicylaldehyde and some amino acids, viz. L-leucine, L-iso-leucine, L-serine, L-methionine and DL-tryptophan. An aqueous solution of the α -amino acid was mixed

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