

Kinetic Investigation of Hydroxide Ion Attack at High Spin Fe(II) Bromosalicylidine Chelates with Amino Acids in Binary Aqueous Solvents: Initial and Transition State Analysis¹

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Abstract—We have investigated the kinetics of hydroxide ion attack at iron(II) chelates with 5-bromosalicylidene derivatives of amino acids (alanine, phenylalanine, aspartic acid, histidine, and arginine) in binary aqueous mixed solvents at 298 K. The observed reactivity trends are discussed in connection with the complexes hydrophobicity/hydrophilicity, transfer chemical potentials of hydroxide ion and the complex, and the solvent effects.

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In bioinorganic chemistry, iron(II) complexes with the Schiff's bases serve as useful structural and electronic models of functional sites of heme-containing enzymes. Furthermore, such complexes may be used in asymmetric oxidation of organic substrates, since their structure and catalytic activity are similar to these of iron porphyrins [1]. The complexes of amino acids Schiff's bases act as perfect chelating agents [2, 3] and are highly biologically active [4, 5] and cytotoxic [6]. Additionally, they are regarded as new type of promising antibacterial and anticancer reagents [7].

The solvent effects on reactivity of transition metal complexes have been of interest recently. Most of reactions of inorganic complexes proceed differently in micellar and microemulsion systems as compared with homogeneous solutions. The appropriate use of microemulsions allows for kinetic studies of reactions involving water-insoluble or hydrophobic substrates like the above-described complexes of the amino acids Schiff's bases [8, 9]. The transfer chemical potentials of the inorganic complexes have been investigated in binary aqueous solvents with relation to the reactivity towards substitution and redox processes [10]. A new approach have been corroborated to understand the solvent effects on reactivity, involving analysis of the interaction of the solvent with the initial and the

transition reactant states [11]. The solvent effects on the rate constant and activation parameter are generally complex; however, their analysis in terms of the contributions from the initial and transition states can fully explain the trends [8, 9, 12]. Simultaneously, the solvation effects can be probed via changes of the activation volume as function of the solvent properties [13]. The two mentioned approaches are complementary: the analysis of the initial and transition states provides information on solvation changes in the case of reaction involving heterogeneous reactant transfer, whereas the activation volume analysis reflects solvation changes in the case of homogeneous processes [14]. Specifically, thermodynamic solubility data gives information on the initial state interphase transfer, and solvent effects on the transition state can be derived from the observed rate constants [13]. In this contribution, we applied the described approaches to investigate the solvent effects in the case of base hydrolysis of a series of hydrophobic high-spin iron(II) chelates with the amino acid Schiff's bases.

EXPERIMENTAL

The solid complexes of Fe(II) with the Schiff's base of amino acids were prepared by mixing aqueous solutions of the respective amino acids (L-alanine, L-phenylalanine, L-aspartic acid, L-histidine, or L-arginine) with equimolar amount of 5-bromosalicylic aldehyde in the hot solution in ethanol. The resulting

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