Kinetics of Oxidation of L-Cysteine by trans- and cis-CoIII and FeIII Complexes based on α- and γ-Diimine Schiff Base Ligands

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Abstract. Kinetics of oxidation of L-cysteine by CoIII and FeIII complexes based on α- and γ-diimine Schiff base ligands were studied in aqueous solution. Pairs of trans and cis isomers of the metal complexes were used in the studies. Kinetic measurements were performed at 25 °C and constant pH and ionic strength under pseudo-first order condition, in which the concentration of cysteine was around two orders of magnitude greater than that of the metal complex. The observed rate constant was obtained by following the change in absorbance of the reaction mixture with time at a predetermined wavelength. The overall rate constant and order of the reaction with respect to cysteine and metal complex were determined. For both metal ions studied, the oxidation rate constant for the trans isomer was higher than that for the cis isomer. This was attributed to the contribution of the steric factor and the trans effect. The effects of substituents and the nature of the metal ion on the reaction rate are discussed.

Introduction

Kinetic studies of structural isomers of transition metal complexes provide important information on the influence of the arrangement (cis/trans) on their reactivity. Kinetic studies of the reduction of isomers by various reducing agents provide much of the experimental knowledge used to develop coordination theory. Two types of structural isomers are common among transition metal complexes: tetra- and hexacoordinate. In the tetracoordinate compounds, trans and cis isomers exist mainly in square-planar arrangement. However, the octahedral hexacoordinate compounds have several possible structural isomers. If some ligands are bidentate, the number of possible isomers is limited, which facilitates identification of the metal complex. In the present work, octahedral transition metal complexes of the type [M(L–L)2Cl2]Cl (where L–L is a bidentate ligand) were selected for kinetic studies.

Several research groups studied the effect of structural isomerism on the reactivity of transition metal complexes. Using optical rotatory dispersion, IR, and NMR spectroscopy, de Vekki et al. [1] studied the reaction of the optically active structural isomers of platinum(II) complex (–){Pt(Me-p-TolISO)-(Py)Cl2}, (TolISO = tolylsulfoxide), with several nucleophilic reagents (Py, Ph3PS, Ph3P, Ph3As, and Me2SO). Farrell et al. [2] reported a study on the activity of platinum complexes as anti-tumor agents. For dinuclear platinum cis-and trans- [{PtCl(NH3)2}2–μ–(NH2(CH2)3NH2)](NO3)2 (n = 4, 6), they found that the initial binding and reaction rates of the cis isomer were slower than those of the trans isomer. Toma et al. [3] reviewed the kinetics and mechanisms involved in linkage isomerization reactions. The biodegradation kinetics of structural isomers of naphthenic acid in water was studied by Peru et al. [4]. Rates of biodegradation of cis and trans isomers of 4-methylyclohexenylacetic acids, 4-methylyclohexanycarboxylic acids, and 3-methylyclohexenylcarboxylic acids by heterotrophic bacteria were compared.

Oxidation of amino acids by transition metal complexes were studied using different methods that include [5]: stopped-flow UV/Vis spectroscopy, chemical analysis of products, and the use of radioactive and stable isotope tracers. Several research groups reported studies on the oxidation of amino acids by transition metal complexes [6–17]. Olabe et al. [6] studied the reaction kinetics of ruthenium nitrosyl complexes with cysteine by UV/Vis spectroscopy using stopped-flow techniques. Vani et al. [7] reported on the kinetics and mechanism of the oxidation of l-methionine by 1,10-phenanthroline iron(III) complex in perchloric acid. The reactivity of iron(V) and iron(VI) complexes with several amino acids using stopped-flow techniques and pulse radiolysis were studied by Sharma and Bielski [8]. Laloo and Mahanti [9] investigated the kinetics of oxidation of lysine, arginine, and histidine by alkali hexacyanoferrate(III) in the temperature range 318–338 K. Anaerobic oxidation of cysteine to cystine by iron(III) complexes in acidic solution using stopped-flow techniques was reported by Jameson et al. [10, 11]. Mehrotra et al. [12] studied the oxidation of amino acids to aldehydes by alkali hexacyanoferrate(III) in the presence of OsVIII as a catalyst.

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