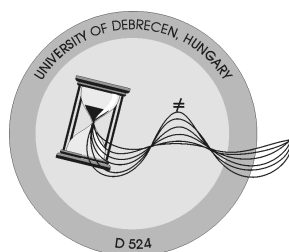


REACTIONS OF THE IRON(III) HYDROXO DIMER WITH INORGANIC LIGANDS

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1. Introduction and research objectives

Iron is the most abundant transition element in the solar system and on the earth. In the oxidative atmosphere of our planet it mostly occurs in the oxidation state of +3. The metal has been known to humankind since ancient times and has had an immense impact on history and culture. Iron is classified as essential in biological systems, where it is often found in oxo- or hydroxo-bridged di- or oligonuclear structures. Numerous enzymes with dinuclear iron(III) centers are known and their structural motifs can be used to design protein-free dinuclear iron(III) catalysts.

Iron(III) gives rise to polynuclear species in aqueous solution over a characteristic pH range. Mononuclear hydrolytic species are important in the kinetics and mechanism of substitution and redox reactions. It seems to be reasonable that polynuclear hydrolytic complexes may also have similar roles.

The major goal of this thesis was to characterize the kinetics and equilibrium of direct ligand substitution reactions of the aqueous iron(III) hydroxo dimer, $\text{Fe}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_8^{4+}$, with simple inorganic ligands and draw structural and mechanistic conclusions from the results. A further objective was to explore the possible role of $\text{Fe}_2(\text{OH})_2^{4+}$ in redox reactions between iron(III) and inorganic species with special emphasis on the iron(III)–sulfur(IV) system because of its outstanding environmental significance. Because of the complexity of the studied reactions, the traditional kinetic evaluation method based on pseudo first-order curves could only be employed in a few cases, and the rate constants in other systems were calculated by fitting the experimental kinetic traces directly to the simultaneous differential equations defined by the kinetic model.

2. Results

2.1. It was established that only the species $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{OH})(\text{H}_2\text{O})_5^{2+}$, and $\text{Fe}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_8^{4+}$ are present at considerable concentration levels in aqueous iron(III) solutions in the reproducibly accessible pH and concentration range. The relevant equilibrium constants were determined.

2.2. A novel, extended mechanism was proposed to interpret the kinetics of the hydrolytic reactions of iron(III). This work proved that a third pathway should be taken into account in addition to the two pathways proposed in an earlier study. The new mechanism interprets the experimental data satisfactorily in the entire accessible pH-range.

2.3. A simple test method was developed in order to determine whether $\text{Fe}_2(\text{OH})_2^{4+}$ reacts directly with a particular ligand or not. The mono- and dinuclear iron(III) hydroxo complexes in aqueous solutions of iron(III) ion cannot be separated, and it is often unclear which form reacts in the process monitored in a particular system. The test method solves this problem based on a comparison of initial rates of absorbance change measured in two complementary kinetic experiments. Some 30 inorganic ligands were tested, and only hypophosphite, phosphite, phosphate, arsenite, arsenate, dithionite, sulfite, sulfate, selenite and periodate ions were found to react directly with $\text{Fe}_2(\text{OH})_2^{4+}$.

2.4. Direct reactions between $\text{Fe}_2(\text{OH})_2^{4+}$ and the ligand were detected to produce transient dinuclear complexes with the compositions $\text{Fe}_2(\text{OH})(\text{H}_2\text{PO}_2)(\text{H}_2\text{O})_8^{4+}$, $\text{Fe}_2(\text{OH})(\text{HPO}_3)(\text{H}_2\text{O})_8^{3+}$, $\text{Fe}_2(\text{OH})(\text{SO}_3)(\text{H}_2\text{O})_8^{3+}$, and $\text{Fe}_2(\text{OH})(\text{SeO}_3)(\text{H}_2\text{O})_8^{3+}$ in the initial phase of the reactions between iron(III) ion and hypophosphite, phosphite, sulfite, and selenite ions at high iron(III) concentrations (> 1 mM). The rate law and the rate constants were determined in each system.

2.5. Direct reactions between $\text{Fe}_2(\text{OH})_2^{4+}$ and the ligand were detected to produce transient tetranuclear complexes with the compositions $\text{Fe}_4(\text{PO}_4)(\text{OH})_2(\text{H}_2\text{O})_{16}^{7+}$ and $\text{Fe}_4(\text{AsO}_4)(\text{OH})_2(\text{H}_2\text{O})_{16}^{7+}$ in the initial phase of the reactions between iron(III) ion and phosphate or arsenate ions at high iron(III) concentrations (> 1 mM). The rate law indicated that the

processes might proceed via the dinuclear intermediates $\text{Fe}_2(\text{OH})(\text{HPO}_4)(\text{H}_2\text{O})_8^{3+}$ and $\text{Fe}_2(\text{OH})(\text{HAsO}_4)(\text{H}_2\text{O})_8^{3+}$, which are always present at very low concentration levels.

2.6. Kinetic models were proposed to interpret the full course of reactions between iron(III) ion and hypophosphite, phosphite, phosphate, arsenate, and selenite ions. The relevant rate constants were determined. A common characteristic feature of these reactions is that the multinuclear intermediates are transformed into mononuclear complexes, the formations of which were also studied independently under conditions where the reactions of $\text{Fe}_2(\text{OH})_2^{4+}$ are negligible ($[\text{Fe(III)}] < 0.2 \text{ mM}$). The individual pathways for each reaction in the general model were identified based on pH-dependence.

2.7. The fast formation of the intermediate $\text{Fe}_2(\text{OH})(\text{SO}_4)(\text{H}_2\text{O})_8^{3+}$ was verified in the initial phase of the iron(III) ion – sulfate ion reaction. It was shown that the decomposition of this species should also be taken into account to interpret later processes during the reaction.

2.8. Arsenite ion was confirmed to catalyze the hydrolytic reactions of iron(III) ion, and this finding was interpreted assuming the formation and decomposition of the dinuclear complex $\text{Fe}_2(\text{OH})(\text{H}_2\text{AsO}_3)(\text{H}_2\text{O})_8^{4+}$, which is formed at very low concentration levels.

2.9. The direct substitution reactions of $\text{Fe}_2(\text{OH})_2^{4+}$ with inorganic ligands were proposed to proceed via a dissociative interchange (I_d) mechanism. The second-order rate constants for these reactions were primarily dependent on the charge of the ligand, and the neutral or uninegative protonated forms reacted with similar rate constants. The difference between the rate constants for uninegative and neutral ligand forms could be interpreted considering the stability of ion pairs formed between the reactants.

2.10. A kinetic model was proposed for the reaction between iron(III) ion and sulfite ion at large metal ion excess. The key rate step in the overall redox process was the decomposition of the complex $\text{Fe}(\text{SO}_3)(\text{H}_2\text{O})_5^+$ to give iron(II) and sulfite ion radical. The dinuclear complex $\text{Fe}_2(\text{OH})(\text{SO}_3)(\text{H}_2\text{O})_8^{3+}$ did not take part in redox reactions directly.

3. Potential uses of the results

The findings presented in this thesis may be important for future mechanistic research on iron(III) reactions. The test method developed for the identification of the reactions of the hydroxo dimer could be used with any (organic or inorganic) ligand. The information obtained on the general reactivity patterns of the dinuclear iron(III) center may be of significant interest for the ongoing research on the biological functions of iron(III), and may help reveal the mechanisms of reactions catalyzed by diiron(III) enzymes.

The results in the iron(III) – sulfur(IV) system might be significant in optimizing and developing new methods for the desulfurization of plume gases, and could also provide important information for atmospheric models to clarify the role of sulfur dioxide. The results also serve as examples illustrating that reliable evaluation of kinetic curves is possible using numerical integration of kinetic models and least-squares fitting in cases where the traditional approach based on finding pseudo first-order conditions fails or yields very imprecise estimates.

4. Final remark

The thesis was written in English. The full text, the English and the Hungarian abstracts of the thesis were published on the Internet. They can be downloaded from the personal homepage of the author (<http://www.klte.hu/~lente/index.html>). The site has recorded 6 full text downloads from outside institutions from September to November in 2001.