

Summary of PhD Thesis

The oxidation of tris(phenanthroline)iron(II) and bis(terpyridine)iron(II) complexes and the corresponding ligands by peroxomonosulfate ion: kinetics and mechanism

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I. Introduction and objectives

The kinetics and mechanisms of the redox reactions of various inorganic species have extensively been studied in the Environmental Redox Mechanisms Research Group at the Department of Inorganic and Analytical Chemistry Chemistry of the University of Debrecen over the last two decades. Exploring the redox features of sulfur-containing species has been one of the main objectives of these studies. Within the frame of this research program, the oxidation reactions of peroxomonosulfate ion with various substrates have been studied: metal ions (Fe^{2+} , Ce^{3+} , VO^{2+}), halides or pseudohalides (Cl^- , Br^- , I^- , SCN^-), simple biomolecules (tryptophan and its derivatives, dopamine and its derivatives), drugs (isoniazid, ethambutol, pyrazinamide) and molecules relevant in environmental chemistry (chlorophenols, trichloroethylene) have been oxidized.

Peroxomonosulfate (HSO_5^-) is commercially available in the form of a triple salt, named Oxone ($2 \text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$). Apart from its wide industrial and consumer applications (such as decolorizing agent in denture cleansers, microetchant in electronics, shock-oxidizer for swimming pools, repulping agent in papermaking or oxidizer in wool treatment), the use of peroxomonosulfate ion is very common in organic reactions. It was shown to be a convenient and efficient oxidant for a great variety of synthetic purposes. The main reasons behind its popularity are favorable features such as stability, simple handling, nontoxic nature, good solubility in water, versatility of the reagent and low costs.

Detailed stoichiometric and kinetic studies on the redox reactions of this powerful nonchlorine oxidizing agent and elucidation of the often complex mechanisms of these reactions may contribute to the wider industrial application of peroxomonosulfate ion and help to gain a better understanding of advanced oxidation processes.

During the oxidation of aqueous $\text{Fe}(\text{II})$, unexpectedly complex kinetic phenomena were found partly due to the noncomplementary and inner-sphere features of the redox process. In order to get more insight into the intimate nature of such reactions, it seemed reasonable to study further iron(II) complexes that are more difficult to oxidize and whose oxidation is expected to proceed via outer-sphere electron transfer. Keeping this in mind, the aim of this work is the kinetic and mechanistic study of the oxidation of coordinatively saturated iron complexes and the corresponding N-heteroaromatic ligands (1,10-phenanthroline and 2,2':6',2''-terpyridine, Figure 1) by peroxomonosulfate ion. The investigation of the oxidation

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of the ligands was motivated by the preliminary experiments, in which it was found that the ligands are oxidized by peroxomonosulfate ion during the course of the reactions of the complexes.

Complexes containing iron and N-heteroaromatic ligands are of huge importance in analytical, coordination chemistry, as well as in biochemistry. They are often used for modeling the interactions between substrates and iron-containing metalloproteins. These complexes are good candidates as functional models of both heme enzymes, such as cytochrome c oxidase, and nonheme iron enzymes i.e. intradiol-cleaving catechol dioxygenase.

The study of the oxidation of the ligands can also be the subject of wide interest because N-heteroaromatic substrates readily form N-oxides with peroxo derivatives (hydrogen peroxide, peracetic acid, meta-chloroperoxybenzoic acid, peroxomonosulfate ion etc.). N-Oxides of heterocycles have received much attention due to their applicability as important intermediates in organic syntheses, as protecting groups, ligands in metal complexes, energetic materials, and biologically relevant molecules.

II. Instrumentation and computation

The primary source of kinetic information was **UV-Vis spectrophotometry**. The spectra and kinetic curves were recorded on *Perkin Elmer Lambda 25*, *Shimadzu UV 1800* scanning, and *HP-8543* diode-array spectrophotometers. Fast kinetic experiments were carried out in an *Applied Photophysics SX 18-MV* stopped-flow instrument. The constant temperature was maintained by the use of different thermostats with the various instruments. All measurements were performed at 25.0 ± 0.1 °C except for the temperature dependence studies. Standard 1.000 cm or 0.500 cm quartz cuvettes were used.

Electrospray ionization (ESI) and occasionally **collision induced dissociation (CID)** mass spectrometric analysis was carried out by a *Bruker MicrOTOF-Q* instrument in the positive ion mode to identify the oxidation products of the ligands and complexes.

The oxidation products of phenanthroline were confirmed by **$^1\text{H-NMR}$ spectroscopic** measurements run on a *Bruker 360 MHz* spectrometer. The NMR spectra were referenced on the residual signal of the solvent (D_2O).

The **pH metric and iodometric measurements** were performed using a *Metrohm 785 DMP Titrino* automatic titrator equipped with 6.0262.100 and 6.0451.100 combination electrodes, respectively. The HSO_5^- -content of Oxone was standardized by iodometric titration, while the purity of the ligands was tested by pH metric titration. To determine the molar absorptivities and the pKs of the ligands, a **combined pH potentiometric and spectrophotometric** method was used, whereby the UV-Vis spectra of phen, phenO and HSO_5^- were recorded as a function of measured pH. In all cases the pH readings were converted to hydrogen ion concentration as described by Irving et al.

The primary data were evaluated by *Microsoft Excel*, *Micromath Scientist 2.01*, *Matlab 4.2c.1* and *ZiTa 4.01* softwares. To analyze the kinetic data in complex systems, we utilized the initial rate method using *Microsoft Excel*. Non-linear least squares fittings of the titration curves and the kinetic traces at a given wavelength were performed by the software *Micromath Scientist*. The linear algebraic decomposition of the spectral changes was carried out by the software *Matlab*. In certain cases, multiple kinetic curves recorded under different initial reactant conditions were simultaneously evaluated with the program package *ZiTa*.

III. Studied ligands and complexes

The structural formulae of the two studied N-heteroaromatic ligands are given in Figure 1: 1,10-phenanthroline ($\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$, POCH, Polskie Odczynniki Chemiczne) and 2,2':6',2''-terpyridine ($\text{C}_{15}\text{H}_{11}\text{N}_3$, Aldrich). The ligands were of analytical reagent grade, purchased from commercial sources and used as received without further purification.

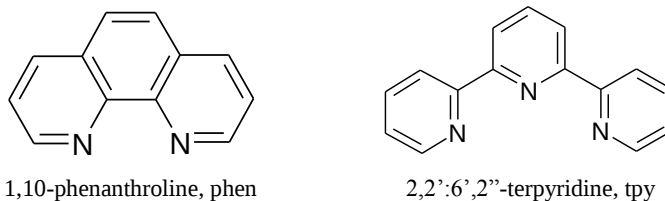


Figure 1. Structural formulae of the studied ligands

The iron(II) complexes were prepared by directly reacting iron(II) sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Reanal) and the corresponding ligand at controlled acidity by using small ligand excess. The solid complexes were precipitated with a large excess of perchlorate ion from the concentrated solution. The product was soluble enough in pure water to prepare samples with the concentration required in the kinetic study. The stock solutions of the iron(II) complexes were stable for months.

The iron(II) complexes are easily prepared by mixing iron(II) and the ligand at a suitable pH. The iron(III) complexes, however, can only be synthesized by oxidizing the corresponding iron(II) complex. The oxidants used for this purpose were solid lead(IV) oxide and Ce(IV).

The oxidation by Ce(IV) provides a rapid and quantitative conversion of the iron(II) complex. However, from preparative point of view this is not the most advantageous way to produce the iron(III) complexes because the excess of oxidant and the by-product of the oxidation, Ce(III), may be a source of unwanted problems. The use of lead(IV) oxide, on the other hand, has distinct advantages: the oxidant is solid, and the oxidation byproduct lead(II) sulfate is also insoluble in the sulfuric acid medium used for the reaction. Therefore, a reasonably pure solution of $\text{Fe}(\text{phen})_3^{3+}$ can be obtained in this way, but the stock solution should be freshly prepared every time.

Our synthetic efforts showed that two aspects, not usually emphasized in the relevant literature, are crucial in the process. First of all, the synthesis reaction

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needs to be carefully timed. The optimal reaction time depends on the initial concentration of the iron(II) complex, the amount of PbO_2 , acidity, overall reactor volume and stirring speed. Even a relatively small deviation from the optimal reaction time could result in significant difference in the iron(III) complex concentration and seriously decrease the reproducibility of later kinetic experiments. The need for careful reaction timing is most probably due to the proton-assisted dissociations of the complexes which result in uncoordinated iron that cannot return into the complex form. Thus, the yield of the iron(III) complex decreases. In light of the aforementioned reasons, optimizing the conditions of the oxidation by lead(IV) oxide is of crucial importance.

The other important factor is the method of filtration. Contact with filter paper must be entirely avoided, glass filters should be used only. This second criterion is quite understandable as the iron(III) complexes are strong oxidants and filter paper is an oxidizable material.

IV. New scientific results

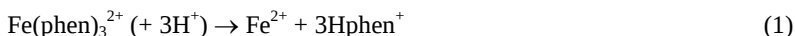
IV.1. Reaction between HSO_5^- and $\text{Fe}(\text{phen})_3^{2+}$

A model was proposed to interpret experimental observations in the redox reaction of HSO_5^- with $\text{Fe}(\text{phen})_3^{2+}$ based on detailed studies. The formation of an intermediate, a 1:1 adduct between peroxomonosulfate ion and tris-(1,10-phenanthroline)iron(II) complex was detected.

IV.1.1. The formation and decomposition of the adduct

The reaction features complex kinetic behavior. The initial rate method was used to study the early phase of the reaction. The rate showed saturation with respect to the concentration of the oxidant. Our findings can be interpreted with the following mechanism:

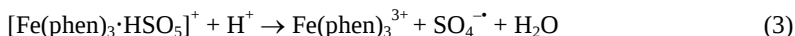
- acid catalyzed dissociation of $\text{Fe}(\text{phen})_3^{2+}$ (1);
- the ion pair formation between the reactants that is considered a fast pre-equilibrium (2);
- the dissociation of the adduct into the corresponding Fe(III) complex and sulfate ion radical ($\text{SO}_4^{\cdot-}$) (3);
- fast oxidation of another Fe(II) complex by the $\text{SO}_4^{\cdot-}$ (4).



$$v = k_1[\text{Fe}(\text{phen})_3^{2+}]$$



$$K = \frac{[\text{Fe}(\text{phen})_3 \cdot \text{HSO}_5^+]}{[\text{Fe}(\text{phen})_3^{2+}][\text{HSO}_5^-]}$$



$$v = k_3[\text{Fe}(\text{phen})_3 \cdot \text{HSO}_5^+]$$



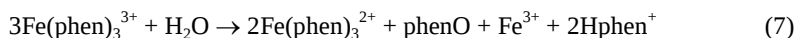
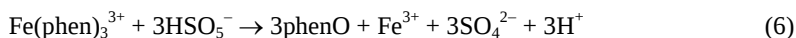
$$v = \text{fast}$$

The formation of an adduct between HSO_5^- and the coordinatively saturated $\text{Fe}(\text{phen})_3^{2+}$ might seem quite puzzling. However, there are two independent experimental findings that support this proposal: the rate equation found perfectly fits the experimental data and the peaks corresponding to the adduct were identified in the ESI-MS spectra.

IV.1.2. Interpretation of the unusual kinetic phenomena in the later stages of the reaction

Under proper initial conditions, the absorbance change of the reaction features two extrema. However, the linear algebraic decomposition of the spectral series detected during the reaction showed that the temporary increase in the absorbance is due to the re-formation of the initial complex and not the production of a new absorbing species. This finding is quite surprising in view of the fact that the oxidizing agent was used in large excess. A further interesting feature of the system is that the oxidation product of the ligand was detected in the reaction mixture with several methods (UV-Vis, ESI-MS, ^1H -NMR) and identified as 1,10-phenanthroline-mono-N-oxide (phenO). The N-oxide was proved to have a significant inhibiting effect on the oxidation reaction of the complex and plays an important role in the unusual kinetic behavior. We interpreted the observations by the following general model which can qualitatively describe the experimental data:

- oxidation of the $\text{Fe}(\text{II})$ complex to the corresponding $\text{Fe}(\text{III})$ complex by HSO_5^- (5) (see: initial stage of the reaction),
- formation of the oxidized ligand and $\text{Fe}(\text{III})$ from $\text{Fe}(\text{phen})_3^{3+}$, probably via the proton-induced dissociation of the complex, then the oxidation of the free ligand (6),
- formal disproportionation reaction of the $\text{Fe}(\text{III})$ complex, which is (auto)catalyzed by phenO and results in the formation of the initial $\text{Fe}(\text{II})$ complex and the oxidized ligand (7).



IV.2. Reactions of the $\text{Fe}(\text{phen})_3^{3+}$ complex

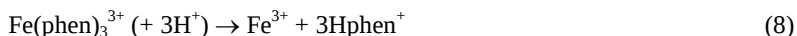
1,10-Phenanthroline-mono-N-oxide (phenO) and $\text{Fe}(\text{phen})_3^{2+}$ were shown to be a product of the decomposition of $\text{Fe}(\text{phen})_3^{3+}$ and phenO had an autocatalytic effect on the reaction producing it.

The critical evaluation of the spectral changes revealed that only a small fraction of $\text{Fe}(\text{phen})_3^{3+}$ produces $\text{Fe}(\text{phen})_3^{2+}$, and most iron(III) complex dissociates by the proton assisted route (8) without redox decomposition. We envisage the redox decomposition in two steps. The first is the actual disproportionation of the

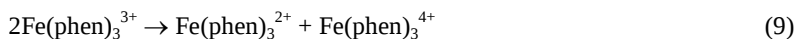
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metal center into iron(II) and iron(IV) complexes (9). The rate of this reaction was studied carefully and it was shown that phenO has an accelerating effect. Experimental support for the involvement of a Fe(phen)_3^{4+} species was provided by ESI-MS. The occurrence of this species was postulated earlier in order to interpret kinetic observations, but without any experimental evidence.

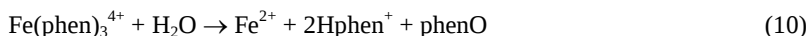
The second, subsequent rapid reaction produces phenO, free metal, and protonated ligand from the iron(IV) complex and water (10). Fe(phen)_3^{3+} can, as well, oxidize Fe(II) in a fast reaction (11):



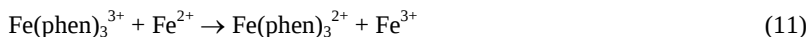
$$v = k_8[\text{Fe(phen)}_3^{3+}]$$



$$v = k_9[\text{Fe(phen)}_3^{3+}][\text{phenO}]$$



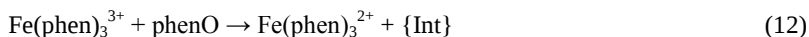
$$v = \text{fast}$$



$$v = k_{11}[\text{Fe(phen)}_3^{3+}][\text{Fe}^{2+}] = \text{fast}$$

Processes 9-11 play an important role in the unusual kinetic phenomena observed during the oxidation of the iron(II) complex and the net stoichiometry of these reactions is shown in equation 7. The role of these steps in the overall mechanism is important when a significant amount of Fe(III) is still present in the form of the phenanthroline complex and a considerable amount of phenO is already produced in order to exert its autocatalytic effect.

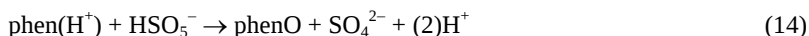
The catalytic role of phenO may be explained by assuming that it can be oxidized to a radical by Fe(phen)_3^{3+} (12), which can in turn oxidize another Fe(phen)_3^{3+} to Fe(phen)_3^{4+} completing a catalytic cycle for the N-oxide (13).



IV.3. Reaction between HSO_5^- and phenanthroline

The reaction between 1,10-phenanthroline and peroxomonosulfate ion follows a net second-order kinetics and the primary oxidation product is the mono-N-oxide derivative of the substrate (phenO). The temperature dependence study of the rate of the reaction revealed that the oxidation is more likely to proceed via oxygen atom transfer.

The photometric determination of the stoichiometry of the reaction between phen and HSO_5^- in both acidic and neutral media showed a 1:1 ratio consistent with equation 14. The identification of the product was made by $^1\text{H-NMR}$, ESI-MS and UV-Vis measurements.



The first step of the reaction follows second-order kinetics and the order with respect to both reactants is unity. According to the pH dependence of the rate (Figure 2) two oxidation pathways can be distinguished:

$$v = k_{15}[\text{Hphen}^+][\text{HSO}_5^-] \quad (15)$$

$$v = k_{16}[\text{phen}][\text{HSO}_5^-] \quad (16)$$

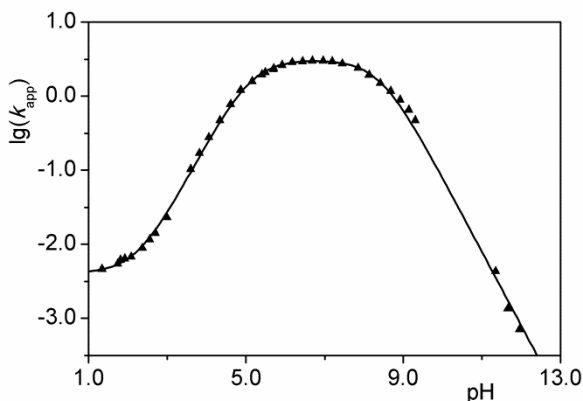


Figure 2. The pH dependence of the apparent rate constant (k_{app} , $\text{M}^{-1} \text{s}^{-1}$) of the reaction of phen with HSO_5^- . $[\text{HSO}_5^-]_0 = 5.0 \text{ mM}$, $[\text{phen}]_0 = 0.250 \text{ mM}$, $[\text{buffer}]_{\text{tot}} = 50.0 \text{ mM}$, $I = 1.00 \text{ M}$, $T = 25.0 \text{ }^\circ\text{C}$, $\lambda = 375 \text{ nm}$.

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The effect of pH on the rate was studied by the initial rate method. For the evaluation of the results we determined the molar absorptivities and the pKs of phen and phenO by a combined pH potentiometric and spectrophotometric technique.

The oxidation of the deprotonated substrate occurs approximately 3 orders of magnitude faster than the one of the protonated form which is interpreted by the intermolecular hydrogen bond in Hphen^+ giving little opportunity for the oxidative attack on the nitrogen atom. Similarly, under basic conditions, the oxidation decelerates, which can be explained by the deprotonation of HSO_5^- resulting in the formation of SO_5^{2-} , which, apparently, cannot oxidize phen. According to the results, the faster reaction occurs between the deprotonated phenanthroline (phen) and the monoprotic form of Caro's acid (HSO_5^-). This finding is supported by the observation that the rate of the reaction at about pH 6.6 is practically independent of the ionic strength, since the charge product of the reactants in the dominant reaction path is zero.

The temperature dependencies of both oxidation pathways were studied. The results are listed in Table 1. The activation entropies are essentially identical large negative values which suggest that the oxidations are more likely to proceed via an initial $2e^-$ oxidation, involving concerted heterolytic O–O bond cleavage and N–O bond formation.

Table 1. Activation parameters of the two pathways of the $\text{phen(H}^+)$ and HSO_5^- reaction.

Reaction	$\Delta S^\ddagger$ ($\text{J mol}^{-1} \text{K}^{-1}$)	$\Delta H^\ddagger$ (kJ mol^{-1})
$\text{Hphen}^+ + \text{HSO}_5^-$ (R15)	-134 ± 1	45.7 ± 0.3
$\text{phen} + \text{HSO}_5^-$ (R16)	-134 ± 3	30.6 ± 0.9

IV.4. Formation of 1,10-phenantroline-di-N-oxide (phenO₂) in the HSO_5^- -phen reaction

We found that as the primary oxidation product (phenO) deprotonates ($\text{pK}_a = 7.30$) in the reaction of HSO_5^- with phen, further oxidation occurs resulting in the formation of phenO₂.

Up to now there is only one known method in the literature for the synthesis of phenO₂, which uses extreme conditions, and all the previous attempts using peroxo compounds were unsuccessful. In the only published method, the mixture of F_2 , H_2O and CH_3CN was used as the oxidizing agent (S. Rozen, S. Dayan. *Angew. Chem.*, 1999, 38, 3471). The behavior of phen in oxidation reactions was explained

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by its rigid structure and the limited space in the bay area of the molecule that cannot accommodate two oxygen atoms.

Under acidic conditions (1.00 M H_2SO_4), only a one-step oxidation occurs producing phenO even in the presence of large excess of the oxidant and at higher temperature (70 °C). However, when the pH is increased, HphenO^+ loses a proton giving rise to further oxidation, which clearly leads to the conclusion that the oxidation involves the liberated N atom. This assumption was confirmed by experimental data: 1,10-phenanthroline- $\text{N,N}'$ -dioxide was identified by $^1\text{H-NMR}$ and ESI-MS methods. At low pH, the intermolecular hydrogen bond in the HphenO^+ species shields the second N atom and protects it from N-oxidation.

Apparently, selecting appropriate (neutral) pH is the key to the synthesis. Bearing this in mind, we also tried to oxidize phen by O_3 , H_2O_2 , $\text{S}_2\text{O}_8^{2-}$ and MnO_4^- under neutral conditions, but these attempts were unsuccessful and no phenO_2 was produced.

Under nearly neutral conditions (pH = 6.7) and in the presence of excess HSO_5^- , four consecutive steps were resolved. In the early stage of the reaction, the stepwise oxidation results in the formation of phenO and phenO_2 . The model used for fitting the traces includes the second-order decomposition reaction of HSO_5^- , whose rate is largest at the pH identical to its pK_a (8.43).

IV.5. Reaction between HSO_5^- and Fe(tpy)_2^{2+}

A kinetic model was proposed to interpret the kinetic observations on the redox reaction between HSO_5^- and Fe(tpy)_2^{2+} , the autocatalytic behavior of the oxidation was proved and Fe(tpy)_2^{3+} was found to be the autocatalyst.

Similarly to the oxidation of the iron(II) phenanthroline complex, the reaction shows complex kinetic behavior. The dependence of the initial rate of the reaction on HSO_5^- revealed saturation tendency which was interpreted by ion pair formation. The proposed mechanism of this stage of the oxidation is analogous to the one shown by reactions 1-4.

We proved that the oxidation is autocatalyzed by Fe(tpy)_2^{3+} . The concentration loss of the initial complex becomes almost perfectly linear in the final stage of the oxidation (Figure 3) which implies that the order with respect to the Fe(II) complex is zero at this phase of the reaction.

The proton-assisted dissociation of Fe(tpy)_2^{3+} was studied in independent experiments because it is of huge importance to describe the oxidation reaction. It

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was found that in contrast to $\text{Fe}(\text{phen})_3^{3+}$, the loss of $\text{Fe}(\text{tpy})_2^{3+}$ occurs via only the acid-catalyzed pathway without participating in any redox reactions.

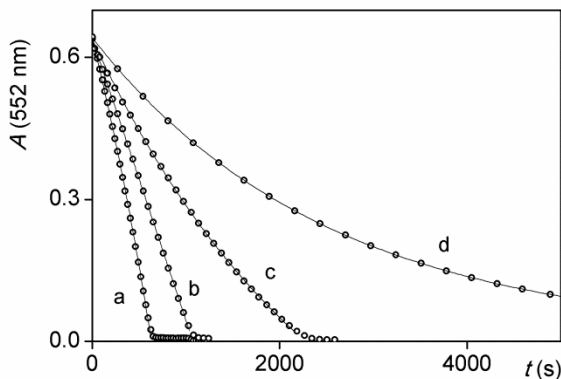


Figure 3. Measured and fitted kinetic traces in the reaction between $\text{Fe}(\text{tpy})_2^{2+}$ and HSO_5^- . $[\text{Fe}(\text{tpy})_2^{2+}]_0 = 52.3 \mu\text{M}$; $[\text{HSO}_5^-]_0 = 24.1 \text{ mM}$ (a); 9.39 mM (b); 2.68 mM (c); no HSO_5^- is added (d); $[\text{H}_2\text{SO}_4] = 0.323 \text{ M}$; $T = 25.0 \text{ }^\circ\text{C}$; $\lambda = 552 \text{ nm}$; $l = 1.000 \text{ cm}$.

Taking into consideration the proton-assisted dissociations of both tpy complexes and the noncatalyzed and catalyzed pathways of the oxidation, a differential rate equation system was derived which successfully describes the kinetic observations on the $\text{Fe}(\text{tpy})_2^{3+} - \text{HSO}_5^-$ reaction.

Although to our best knowledge, the oxidation of terpyridine by peroxomonosulfate ion is of little significance in the oxidation of the iron(II) complex, the process was investigated in independent experiments. Its minor role in the overall mechanism is most probably due to the fact that under the applied strongly acidic conditions, the oxidation proceeds at a very low rate. The oxidation products of the reaction were identified by ESI-MS method: apart from the mono-N-oxide, the di-N-oxide (tpyO_2) derivative of terpyridine was also detected in small amounts when slight excess of oxidant was used.

V. Possible applications of the results

In this work, we studied the reactions of peroxomonosulfate ion with N-heteroaromatic ligands (1,10-phenanthroline and 2,2':6',2''-terpyridine) and their iron complexes (Fe(phen)_3^{2+} and Fe(tpy)_2^{2+}) in detail. The investigations cover mainly basic research. In all studied systems, complex kinetic behavior was found including consecutive, parallel and reversible processes.

The mechanism of numerous inorganic reactions consists of concurrent and parallel elementary steps. To develop the understanding of such complex systems, thorough studies should be carried out from both kinetic and stoichiometric points of view. For a long time, our research group has been engaged in the exploration of the mechanisms of reactions relevant in oxidation and disinfection methods. Generally, these investigations involve the study of components present in communal and industrial wastewater with strong oxidizing agents frequently used in advanced oxidation processes (AOP) such as H_2O_2 , O_3 , OCl^- , ClO_2 or HSO_5^- .

The detailed study of the reactions of HSO_5^- may provide valuable information on reactive intermediates, confirm mechanistic considerations regarding the autoxidation of various substrates and explore important aspects of industrial applications.

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Ph.D. List of Publications

Candidate: Gábor Bellér

Neptun ID: O1K6MD

Doctoral School: Doctoral School of Chemistry

List of publications related to the dissertation

Foreign language scientific article(s) in international journal(s) (2)

1. **Bellér, G.**, Bátki, G., Lente, G., Fábrián, I.: Unexpected adduct formation in the reaction of peroxomonosulfate ion with the tris-(2,2'-bipyridine)iron(II) and tris-(1,10-phenanthroline)iron(II) complexes.
J. Coord. Chem. 63 (14/16), 2586-2597, 2010. ISSN: 0095-8972.
DOI: <http://dx.doi.org/10.1080/00958972.2010.493213>
IF: 1.932
2. **Bellér, G.**, Lente, G., Fábrián, I.: Central Role of Phenanthroline Mono-N-oxide in the Decomposition Reactions of Tris(1,10-phenanthroline)iron(II) and -iron(III) Complexes.
Inorg. Chem. 49 (9), 3968-3970, 2010. ISSN: 0020-1669.
DOI: <http://dx.doi.org/10.1021/IC902554b>
IF: 4.325

Total IF of journals (all publications): 6,257

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The Candidate's publication data submitted to the IDEa Tudóstér have been validated by DEENK on the basis of Web of Science, Scopus and Journal Citation Report (Impact Factor) databases.

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Publications

Papers related to the thesis

4. Gábor Bellér, Gábor Lente, István Fábán

Detailed kinetics and mechanism of the autocatalytic oxidation of bis(terpyridine)-iron(II) by peroxomonosulfate ion in acidic medium
(to be submitted)

3. Gábor Bellér, Gábor Lente, István Fábán

Unexpected formation of 1,10-phenanthroline-di-N-oxide under mild conditions: the kinetics and mechanism of the oxidation of 1,10-phenanthroline by peroxomonosulfate ion
(submitted)

2. Gábor Bellér, Gabriella Bátki, Gábor Lente, István Fábán

Unexpected adduct formation in the reaction of peroxomonosulfate ion with the tris-(2,2'-bipyridine)iron(II) and tris-(1,10-phenanthroline)iron(II) complexes
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