Original Research Article

Kinetic Approach to the Reduction of Ethylenediaminetetraacetatoferrate(III) Complex by Iodide Ion in Aqueous Acidic Medium

ABSTRACT

The kinetic approach to the reduction of ethylenediaminetetraacetatoferrate(III) complex (hereafter $[Fe(III)EDTA]^-$) by iodide ion has been studied spectrophotometrically in an aqueous acidic medium. The study was carried out under pseudo-first order conditions of an excess of iodide ion concentration at 28 ± 1°C, I = 0.43 mol dm^{-3} (KNO_3) and $[H^+]$ = 5.0 × 10^{-2} mol dm^{-3}. The $[Fe(III)EDTA]^-$ complex was reduced according to the reaction;

$$2[Fe(III)EDTA]^- + 2I^- \rightarrow 2[Fe(II)EDTA]^{2-} + I_2$$

The rate law is $-d[Fe(III)EDTA^-]/dt = k[I^-][Fe(III)EDTA^-]$. The rate of the reaction is first order in oxidant and reductant concentrations. On the basis of catalysis by added anion, Michaelis-Menten plots and the absence of intermediates, the outer-sphere electron transfer mechanism is proposed for the reaction.

Keywords

Kinetics, Mechanism, Iodide, Reduction, Ethylenediaminetetraacetatoferrate(III) Complex

1. Introduction

The determination of the most common iodine-containing molecules and ions found in environmental waters such as iodine (I_2), iodide (I^-) and iodate (IO_3^-) is critical in fields such as biological and environmental sciences [1]. The iodide salts being mild reducing agents are easily oxidized and some enzymes readily convert it into electrophilic iodinating agents as required for biosynthesis of iodide-containing natural products. The iodide is functional as antioxidant reducing specie that can destroy reactive oxygen species such as hydrogen peroxide [2]. The usefulness of this iodide ion in electron transfer reactions is a key in gaining knowledge about its mechanistic pathways. The kinetics of oxidation of iodide ion with other species revealed the liberation of iodine gas [3,4,5]. The aminocarboxylatoferrate(III) complex has been reduced by a few number of substrates [6,7,8].

In this paper, we report the kinetics and mechanistic pathway of reduction of $[Fe(III)EDTA]^-$ by iodide ion in aqueous nitric acid medium.

2. Experimental

The $[Fe(III)EDTA]^-$ complex was prepared according to the method of Xiao-juan [6] and was characterized spectrophotometrically. The UV/Visible spectrum of $[Fe(III)EDTA]^-$ was scanned between ranges of 300 – 800 nm and gave λ_{max} of 308 and 470 nm.

Standard solution of nitric acid (Sigma-Aldrich) was prepared by diluting concentrated acid (70 %, specific gravity 1.413) using distilled water. KNO_3 (BDH) was used to maintain ionic strength. The complex stock solution had a concentration of about 0.05 mol dm^{-3}. A stock solution of calcium nitrate was prepared by weighing known amount and dissolving in known volume of distilled water.

2.1 Stoichiometric studies

The stoichiometry was determined by spectrophotometric titration using the mole ratio approach [9] under the reaction condition $[Fe(III)EDTA^-] = 4.0 \times 10^{-3}$ mol dm^{-3}, I = 0.1 mol dm^{-3}, $[H^+] = 5.0 \times 10^{-2}$ mol dm^{-3}, $[I^-] = (0.56 – 1.04) \times 10^{-2}$ mol dm^{-3}.

2.2 Kinetic measurements

The kinetic measurements were carried out at the wavelength of 470 nm by monitoring the decrease in absorbance of the reaction mixture as the reaction progressed. The reaction was carried out under Pseudo-first order conditions with the concentration of iodide ion 10-fold in excess over $[Fe(III)EDTA^-]$. Ionic strength of the reaction mixture was kept constant at 0.43 mole dm^{-3} (KNO_3) and $[H^+]$ at 5.0×10^{-2} mol dm^{-3}. A plot of $(A_t - A_\infty)$ versus time were linear for over 80 % extent of reaction. Pseudo-first order rate constants, k_1 were determined as the slopes of the above plots as given by the equation:

$$\log(A_t - A_\infty) = \frac{kt}{2.303} + \log(A_t - A_\infty) \qquad (1)$$

The second order rate constants, k_2 were obtained as the ratios of k_1 to $[I^-]$.

The influence of $[H^+]$ on the rate of the reaction was investigated using nitric acid in the range 6.0×10^{-2} mol dm^{-3} $\leq [H^+] \leq 1.0 \times 10^{-1}$ mol dm^{-3}, while the $[Fe(III)EDTA^-]$ and $[I^-]$ were kept constant. The reaction was carried out at 28 ± 1°C and I = 0.43 mol dm^{-3} (KNO_3).

The effect of ionic strength on the rate of the reaction was investigated in the range I = 0.05 – 0.07 mol dm^{-3} KNO_3, while the concentration of other reagents was kept constant. The effect of added oxalate ions on the rate of the reaction was investigated for Ca^{2+} = (5.0 – 6.4) x 10^{-3} mol dm^{-3} while the concentrations of all other reactants were kept constant.

2.3 Product analysis

The UV/Visible spectrum of the reaction product was scanned between wavelength ranges of 400 - 600 nm gave a λ_{max} of 520 nm, which is characteristic of the Fe(II) product [10,11], and the appearance of a brown solution which turns to soil precipitate on addition of potassium permanganate reveals the presence of Fe(II) product [12].

3. Results and discussion

The spetrophotometric titrations showed oxidant - reductant ratio of 1:1 represented by the stoichiometric equation;

$$2[Fe(III)EDTA]^- + 2I^- \rightarrow 2[Fe(II)EDTA]^{2-} + I_2 \quad (2)$$

Stoichiometry 1:1 obtained in this reaction has been documented with reaction involving iodide ions [3,4,5].

The pseudo-first order plot is linear for greater than 80 % extent of reaction. This implies that the order of the reaction is one with respect to $[Fe(III)EDTA]^-$ concentration (Figure 1). The rate of the reaction increases with increase in $[I^-]$ with a slope of 0.920, suggesting that the reaction is first-order in $[I^-]$ as shown in Table 1. A similar first order dependence of rate of reaction was observed for iodide ion [3,4,5] and for $[Fe(III)EDTA]^-$ [13,14,15,16,17].

The rate law for the reaction is given as equation (3)

$$-\frac{[Fe(III)EDTA^-]}{dt} = k[I^-][Fe(III)EDTA^-] \quad (3)$$

Within the range 6.0 x 10^{-2} mol dm^{-3} $\leq [H^+] \leq$ 1.0 x 10^{-1} mol dm^{-3} and constant ionic strength 0.43 mole dm^{-3} KNO_3. The rate of the reaction decreases with increase in $[H^+]$ (Table 1). The plot of k_2 versus $[H^+]^{-1}$ was linear with an intercept and the acid dependence of this nature indicates that there are two pathways for the electron transfer: one being independent of hydrogen ion concentration and the other has inverse dependence on the hydrogen ion concentration. The two rate-controlling paths are preceded by rapid deprotonation equilibrium, and both protonated and deprotonated forms are reactive [18].

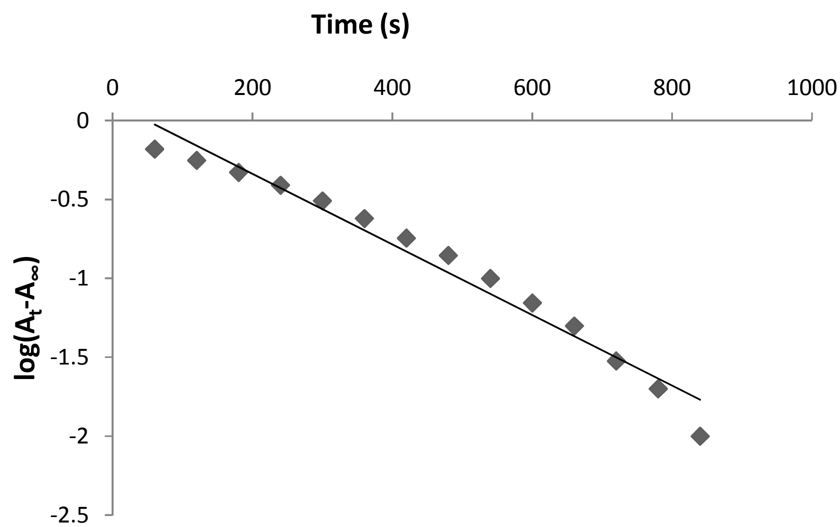

Figure 1: Typical Pseudo-first Order Plot for the Reaction of $[Fe(III)EDTA]^-$ and I^- at $[Fe(III)EDTA^-] = 4.0 \times 10^{-3}$ mol dm^{-3}, $[I^-] = 9.0 \times 10^{-2}$ mol dm^{-3}, I = 0.43 mol dm^{-3} (KNO_3), $[H^+] = 5.0 \times 10^{-2}$ mol dm^{-3}, T = 28 ± 1°C, and λ_{max} = 470 nm.

Table 1: Pseudo-first Order and Second Order Rate Constants for the Reaction of $[Fe(III)EDTA]^-$ and I^- at $[Fe(III)EDTA^-] = 4.0 \times 10^{-3}$ mol dm^{-3}, I = 0.43 mol dm^{-3} (KNO_3), $[H^+] = 5.0 \times 10^{-2}$ mol dm^{-3}, T = 28 ± 1°C and λ_{max} = 470 nm.

$10^2[I^-]$, mol dm^{-3}	$10^1[H^+]$	I, mol dm^{-3}	10^3k_1, s^{-1}	10^2k_2, dm^3 mol^{-1} s^{-1}
2.0	0.5	0.43	1.04	5.18
3.0	0.5	0.43	1.54	5.14
4.0	0.5	0.43	2.33	5.81
5.0	0.5	0.43	2.93	5.84
6.0	0.5	0.43	2.97	4.95
7.0	0.5	0.43	3.39	4.84
8.0	0.5	0.43	3.75	4.69
9.0	0.5	0.43	4.31	4.79
9.0	0.6	0.43	2.88	3.19
9.0	0.7	0.43	2.72	3.02
9.0	0.8	0.43	2.56	2.84
9.0	0.9	0.43	2.33	2.58
9.0	1.0	0.43	2.17	2.41
9.0	0.5	0.50	4.56	5.07
9.0	0.5	0.54	4.89	5.43

9.0	0.5	0.58	5.26	5.84
9.0	0.5	0.62	5.37	5.97
9.0	0.5	0.66	5.90	6.56
9.0	0.5	0.70	6.21	6.90

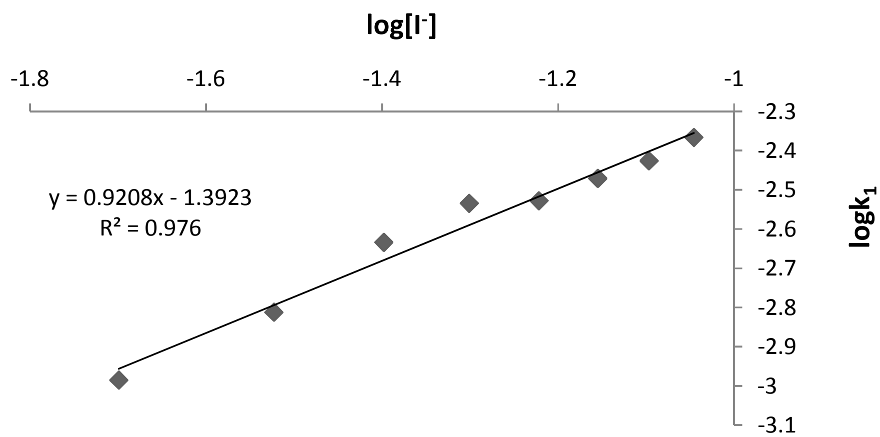

Figure 2: Plot of log k_1 versus log $[I^-]$ for the Reaction of $[Fe(III)EDTA]^-$ and I^- at $[Fe(III)EDTA^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, $[I^-] = (2.0 – 9.0) \times 10^{-2}$ mol dm^{-3}, I = 0.43 mol dm^{-3} (KNO_3), $[H^+] = 5.0 \times 10^{-2}$ mol dm^{-3} , T = 28 ± 1℃, and λ_{max} = 470 nm

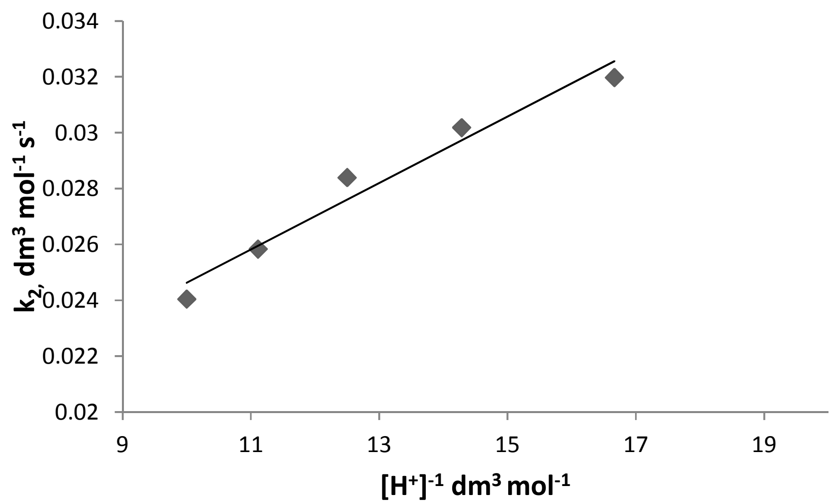

Figure 3: Plot of k_2 versus $[H^+]^{-1}$ for the Reaction of $[Fe(III)EDTA]^-$ and I^- at $[Fe(III)EDTA^-] = 5.0 \times 10^{-3}$ mol dm^{-3}, $[I^-] = 9.0 \times 10^{-2}$ mol dm^{-3}, I = 0.43 mol dm^{-3} (KNO_3), $[H^+] = (0.6 – 1.0) \times 10^{-1}$ mol dm^{-3} , T = 28 ± 1℃, and λ_{max} = 470 nm

The change in ionic strength from 0.5 to 0.7 mol dm^{-3} led to a progressive increase in the observed rate constant, k_1 (Table 1). Since the reductant and oxidant are anions, the observation is consistent with positive Bronsted–Debye salt effect, implying that the activated complex is composed of reactants of like charges [19].

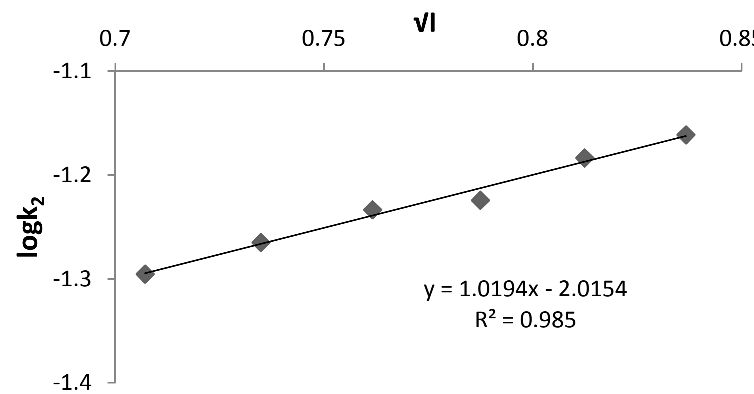

Figure 4: Plot log k_2 versus √I for the Reaction of $[Fe(III)EDTA]^-$ and I^- at $[Fe(III)EDTA^-]$ = 5.0×10^{-3} mol dm^{-3}, $[I^-] = 9.0 \times 10^{-2}$ mol dm^{-3}, I = (0.5 – 0.7) mol dm^{-3}, $[H^+] = 5.0 \times 10^{-2}$ mol dm^{-3}, T = 28 ± 1°C, and λ_{max} = 470 nm

The plot of k_1^{-1} versus $[I^-]^{-1}$ gave a negligible intercept, suggesting unstable binuclear intermediate formation. Also, the added Ca^{2+} ions had effect on the rate of reaction by initiating an increase in the reaction rate. Since the reactant species are negatively charged, Ca^{2+} ion is expected to accelerate the rate by acting as a bridge between the reactants through an outer-sphere complex formation [20].

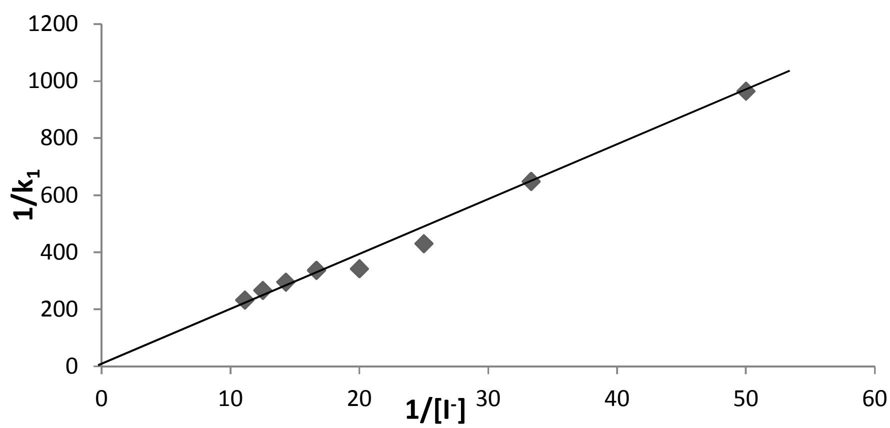

Figure 5: Michaelis-Menten Plot of $1/k_1$ versus $1/[I^-]$ for the Reduction of $[Fe(III)EDTA]^-$ by I^-

The outer-sphere mechanism is proposed for this reaction on ground that there was no detectable binuclear intermediate and the reaction is catalyzed by added ion.

$$I^- + H^+ \underset{}{\overset{K_{eq}}{\rightleftharpoons}} HI \tag{4}$$

$$[Fe(III)EDTA]^- + I^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(III)EDTA^-, I^-] \tag{5}$$

$$[Fe(III)EDTA^-, I^-] \xrightarrow[slow]{k_2} [Fe(II)EDTA]^{2-} + I^{\bullet} \tag{6}$$

$$[Fe(III)EDTA]^- + HI \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Fe(III)EDTA^-, HI] \tag{7}$$

$$[Fe(III)EDTA^-, HI] \xrightarrow[slow]{k_4} [Fe(II)EDTA]^{2-} + I^{\bullet} + H^+ \tag{8}$$

$$I^{\bullet} + I^{\bullet} \xrightarrow[fast]{k_5} I_2 \tag{9}$$

$$Rate = k_2[Fe(III)EDTA^-, I^-] + k_4[Fe(III)EDTA^-, HI] \tag{10}$$

From equation (6);

$$k_{-1}[Fe(III)EDTA^-, I^-] = k_1[Fe(III)EDTA^-][I^-] \tag{11}$$

$$[Fe(III)EDTA^-, I^-] = \frac{k_1}{k_{-1}}[Fe(III)EDTA^-][I^-] \tag{12}$$

From equation (9);

$$k_{-3}[Fe(III)EDTA^-, HI] = k_3[Fe(III)EDTA^-][HI] \tag{13}$$

$$[Fe(III)EDTA^-, HI] = \frac{k_3}{k_{-3}}[Fe(III)EDTA^-][HI] \tag{14}$$

From equation (4);

$$[HI] = K_{eq}[H^+][I^-] \tag{15}$$

Substitute equation (15) into (14);

$$[Fe(III)EDTA^-, HI] = \frac{k_3 K_{eq}[H^+]}{k_{-3}}[Fe(III)EDTA^-][I^-] \tag{16}$$

Substitute equation (12) and (16) into (10);

$$\text{Rate} = \frac{k_2 k_1}{k_{-1}}[\text{Fe(III)EDTA}^-][\text{I}^-] + = \frac{k_4 k_{3K_{eq}[H^+]}}{k_{-3}}[\text{Fe(III)EDTA}^-][\text{I}^-] \quad (17)$$

$$\text{Rate} = \frac{k_2 k_1}{k_{-1}} + \frac{k_4 k_{3K_{eq}[H^+]}}{k_{-3}}\left([\text{Fe(III)EDTA}^-][\text{I}^-]\right) \quad (18)$$

$$\text{Rate} = \text{k}[\text{Fe(III)EDTA}^-][\text{I}^-] \quad (19)$$

$$\text{Where k} = \frac{k_2 k_1}{k_{-1}} + \frac{k_4 k_{3K_{eq}[H^+]}}{k_{-3}}$$

The equation (19) conforms to the experimental rate law at equation (3).

4. Conclusion

The kinetics of reduction of ethylenediaminetetraacetatoferrate(III) complex by iodide ion was studied in aqueous acidic medium. A mole ratio of 1:1 (Complex: Oxidant) was obtained. The analysis of other kinetic data obtained under the pseudo-first order condition gave an overall order of second order; first order with respect to the concentration of the oxidant and reductant. Rationalizing the pieces of evidence obtained in the study favors the outer-sphere mechanism and a plausible mechanistic pathway which explains the kinetic data obtained is proposed.

References

[1] S. Fierro, C. Comninellis, Y. Einaga, Simultaneous detection of iodine and iodide on boron doped diamond electrodes, *Talanta*, 103 (2012) 33 – 37. http://dx.doi.org/10.1016/j.talanta.2012.10.002.

[2] F.C. Küpper, L.J. Carpenter, G.B. McFiggans, Iodide accumulation provides kelp with an inorganic antioxidant impacting atmospheric chemistry, *Proceedings of the National Academy of Sciences of the United States of America*, 105 (2008) 6954–6958. http://dx.doi.org/10.1073/pnas.0709959105.

[3] G. Nord, B. Pedersen, O. Farver, Outer-sphere oxidation of iodide and thiocynate by tris(2,2'-bipyridyl)- and tris(1, 10-phenanthroline) osmium(III) in aqueous solutions, *Inorganic Chemistry*, 17 (1978) 2233 – 2238. http://dx.doi.org/10.1021/ic50186a043.

[4] I. Fabian, G. Gordon, The kinetics and mechanism of the chlorine dioxide – iodide ion reaction, *Inorganic Chemistry*, 36 (1997) 2494 – 2497. http://dx.doi.org/10.1021/ic961279g.

[5] C.D. Hubbard, A. Gerhard, E. Rudivan, Electrostriction and counter ion effects on an outer-sphere electron transfer reaction, kinetics of the reduction of hexachloroiridate(IV) by iodide ion, *Journal of Chemical Society, Dalton Transaction*, (2001) 1069 – 1075, http://dx.doi.org/10.1039/b009363g.

[6] Y. Xiao-juan, Y. Lin, D. Li, L. Xiang-Li, Y. Wei-Kang, Kinetics of the [Fe(III)EDTA]$^-$ reduction by sulfite under the catalysis of activated carbon, *Journal of American Chemical Society* 25 (2011) 4248 – 4255, https://doi.org/10.1021/ef2006063.

[7] T.T. Suchecki, B. Mathews, H. Kumazawa, Kinetic study of ambient-temperature reduction of Fe(III)-edta by $Na_2S_2O_4$, *Industrial & Engineering Chemistry Research,* 44 (2005) 4249. https://doi.org/10.1021/ie0493006.

[8] M.H. Mendelsohn, J.B.L. Harkness, Enhanced flue-gas denitrification using ferrous-EDTA and a polyphenolic compound in an aqueous scrubber system, *Energy Fuel*, 5 (1991) 244.10. https://doi.org/1021/ef00026a003.

[9] A.D. Onu, J.F. Iyun, S.O. Idris, Oxidation of ethylenediaminetetraactatocobaltate(II) complex by hydrogen peroxide in aqueous acidic medium: A kinetic study, *Journal of Nigerian Chemical Society*, 41 (2016) 81 – 86.

[10] J.F. Iyun, The oxidation of some tris-(diimine)iron(II) and tris-(substituted diimine)iron(II) complexes by aqueous acidic bromine solution. An assessment of the marcus model for non - complimentary reactions, *ChemClass Journal,* (2004) 59 - 63.

[11] S.O. Idris, J.F. Iyun, E.B. Agbaji, Kinetics and mechanism of oxidation of thiosulfate ion by tetrakis(2,2-bipyridine)-μ-oxodiiron(III) ion in aqueous acidic medium, *ChemClass Journal*, (2008) 103 – 108.

[12] Stephen, M. (1997). *Identification of Iron(II) and (III) Cations by Precipitation Reactions*. Retrieved from http://www.marz-kreations.com/Chemistry/Cation-ID/162k-Iron.html.

[13] T.S. Tomasz, M. Barbara, K. Hidehiro, Kinetic study of ambient-temperature reduction of Fe^{111}edta by $Na_2S_2O_4$*, Industrial & Engineering Chemistry Research,* 44 (2005) 4249 – 4253. https://doi.org/10.1021/ie0493006.

[14] M.M. Taqui Khan, A.E. Martell, The kinetics of the reaction of iron(III) chelate of aminopolycarboxylic acid with ascorbic acid, *Journal of the American Chemical Society*, 90 (1968) 3386 – 3389. https://doi.org/10.1021/ja01015a016.

[15] H.J. Wubs, A.A.C.M. Beenackers, Kinetics of H_2S absorption into aqueous ferric solutions of EDTA and HEDTA, *AlChE Journal*, 40 (1994) 433 – 444. https://doi.org/10.1002/aic.690400307.

[16] W. Cheves, E.P. Richard, W. Tomas, Kinetics of the decomposition of hydrogen peroxide catalyzed by ferric ethylenediaminetetraacetate complex, *Proceedings of the National Academy of Sciences of the USA*, 72 (1974) 140 – 142.

[17] C. Bull, G.J. McClune, J.A. Fee, (1983). The mechanism of Fe-EDTA catalyzed superoxide dismutation*, Journal of American Chemical Society*, 105 (1983) 5290 – 5300. https://doi.org/10.1021/ja00354a019.

[18] A.D. Onu, J.F. Iyun, S.O. Idris, The kinetics of the reduction of tetraoxoiodate(VII) by *n*-(2-hydroxylethyl)ethylenediaminetriacetatocobaltate(II) ion in aqueous perchloric acid. *Transition Metal Chemistry*, 34 (2009) 849 – 853, https://doi.org/10.1007/s11243-009-9273-1.

[19] J.M. Brønsted, Activities of ions in solution, *Journal of Physical Chemistry*, (1922) 102: 106.

[20] T.J. Pryztas, N. Sutin, (1973). Kinetics studies of anion – assisted outer-sphere electron transfer reactions. *Journal of American Chemical Society*, 95 (1973) 5545.