Europium(III) Catalysis for Reduction of Thionine Dye by Selenous Acid in Aqueous Sulfuric Acid Solutions: A Kinetic and Mechanistic Approach

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ABSTRACT: The catalytic effect of europium(III) on the reduction of thionine dye (Th) by selenous acid has been studied by spectrophotometry in aqueous sulfuric acid solutions at a constant ionic strength of 3.0 mol dm^{-3} and at different temperatures (283–313 K). A first-order dependence with respect to both [Th] and [Eu^{III}] was obtained, whereas the orders with respect to [Se^{IV}] and [H$^+$] were less than unity. Variation of ionic strength and dielectric constant of the reaction media did not affect the reaction rates. Probable mechanistic schemes for thionine reductions in both the absence and presence of europium(III) catalyst were proposed. The rate laws associated with the reaction mechanisms were derived, and the reaction constants were calculated. The activation parameters of the rate constants of the slow steps of both uncatalyzed and catalyzed reactions along with thermodynamic quantities of the equilibrium constants are computed and discussed. © 2016 Wiley Periodicals, Inc. Int J Chem Kinet 48: 531–543, 2016

INTRODUCTION

Thionine dye (Th) or thionine monochloride (ThCl), also known as Lauth's violet, has two hydrophilic amino groups symmetrically distributed on each side

with a planer aromatic structure (Scheme 1). It is considered as a strong staining metachromatic dye [1,2] that is widely used for biological staining. It was observed that Th gave color variation but not reliable differentiation among the substances. It is much used in tissue sections to distinguish empirically between mucin or mucoid (staining violet) and nuclei (blue). It can also be used in place of Schiff reagent in

quantitative Feulgen staining of DNA. Furthermore, Th is used to mediate electron transfer in microbial fuel cells [3]. When both the amino groups are dimethylated, the product tetramethyl thionine is known as methylene blue. The one-electron reduction of Th was investigated in the past using flash photolysis and radiolysis techniques [4]. The dye molecule accepts an electron from the reductant and converted into a semi- or leucoform of the dye. Also, the kinetics of the catalyzed oxidative mineralization of the Th dye with H_2O_2 has been studied [5]. A reaction mechanism was proposed with the formation of free radicals as reactive intermediates.

Selenium that is regarded as a metalloid is a relatively noble element. Selenium is an essential trace element in the human body. The nutrient is an important part of antioxidant enzymes, which protect cells against the effects of free radicals produced through oxygen metabolism. Selenium exhibits variable oxidation states, namely $+VI$, $+IV$, and $-II$, in the environment. The redox chemistry of this polyvalent element determines its solubility, bioavailability, and also its toxicity. Thus, understanding of the properties of the various oxidation states and transformations among them is of importance. One of the important compounds of selenium(IV) is SeO_2, an acidic oxide which dissolves in water to form selenous acid ($H_2Se^{IV}O_3$). Selenous acid is an important reagent in organic synthesis. It is a well-known and widely used oxidant in organic synthesis ($E_{H_2SeO_3} = 0.74$ V), but it has received much attention as a mild reducing agent ($E_{H_2SeO_4} = 1.15$ V) [6]. However, the kinetics of oxidation of selenium(IV) was studied in acid solutions by different oxidants such as neptunium(VII) [6], hydrogen peroxide [7], peroxydisulfate catalyzed by silver(I) [8], permanganate [9,10], cobalt(III) [11], cerium(IV) catalyzed by ruthenium(III) [12], and in alkaline medium by ferricyanide ion catalyzed by osmium(VIII) [13].

Europium, a lanthanide element, is the most reactive rare earth element. It dissolves readily in dilute sulfuric acid to form pale pink solutions of the hydrated Eu^{III}, which exists as a nonahydrate, $[Eu(H_2O)_9]^{3+}$ [14]. Lanthanide ions and their complexes were found to catalyze certain reactions [15,16]. Studies in homogeneously metal ion catalyzed oxidation of organic compounds in aqueous solutions are regarded as an important field of chemistry. Transition metal ions are shown to catalyze some oxidation–reduction reactions, because they have multiple oxidation states [17]. Catalysis by metal ions depends on the nature of the substrates, oxidant, and experimental conditions, and it is suggested [18,19] to proceed by one of several paths, such as formation of complexes with the reactants, oxidation of substrate itself, or formation of free radicals.

Owing to the significance of thionine dye and the dearth of literature on the reduction of this compound, I have carried out a detailed study on the kinetics and mechanism of reduction of thionine by selenous acid in sulfuric acid medium in the absence and presence of europium(III) catalyst. The present study aims to understand the redox chemistry of Th in a strong acid medium, to establish the optimum conditions affecting reduction of Th by selenous acid, to understand the active species of the oxidant, reductant, and catalyst in such a medium, to examine the catalytic activity of the catalyst and finally to elucidate probable reduction reaction mechanisms.

EXPERIMENTAL

Materials and Methods

Materials: The chemicals employed in the present investigation were of reagent grade, and doubly distilled water was used throughout the work. The thionine dye used in this study was obtained from Sigma Chemicals (Louis, USA) and was used as received. A solution of selenous acid was prepared by dissolving selenium dioxide sample (E. Merck, Germany) in doubly distilled water and was standardized by titration with permanganate [10]. Sulfuric acid, sodium sulfate, and acetic acid (BDH) were used to vary the acidity, ionic strength, and dielectric constant of the reaction media, respectively. Europium(III) solution was prepared by dissolving a known weight of $EuCl_3 \cdot 6H_2O$ (S.D. fine chem) in diluted HCl. Solutions of other reagent were prepared by dissolving the requisite amounts of the samples in doubly distilled water.

Kinetic Measurements: The reactants were formulated such that the reactions were of pseudo–first-order kinetics where the selenous acid was added in a large excess relative to Th. The progress of the uncatalyzed and Eu^{III}-catalyzed reactions was followed by tracing the decay in absorbance of Th at $\lambda_{max} = 605$ nm, maximum absorption wavelength belonging to Th [20], whereas the other reactants did not absorb significantly at this wavelength. The absorbance measurements were carried out using a Shimadzu UV–VIS-NIR-3600 double-beam spectrophotometer. Some kinetic runs were carried out after bubbling purified nitrogen and compared with those taken under air. The results were the same suggesting that the dissolved oxygen did not have any effect on the oxidation rate.

The reaction between selenous acid and Th in sulfuric acid solution was found to proceed with a measurable rate in the absence of Eu^{III} catalyst, and the catalyzed reaction is thought to occur in a parallel
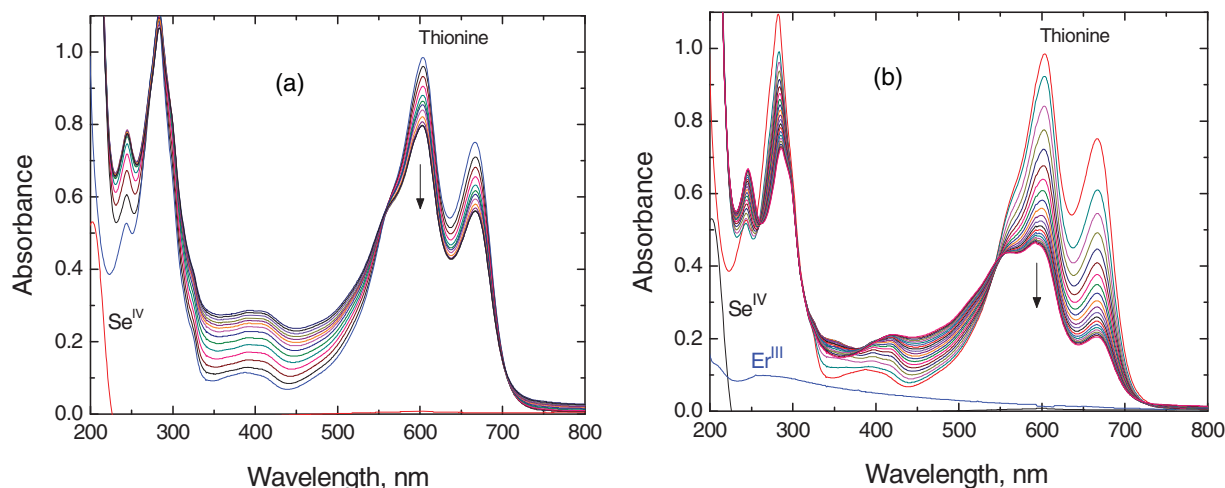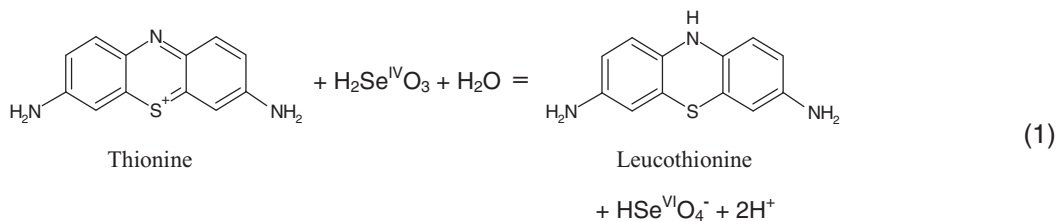
Figure 1 Time-resolved spectra for (a) uncatalyzed and (b) europium(III)-catalyzed reduction of thionine by selenous acid in sulfuric acid solutions. [Th] = 2.0×10^{-4}, [Se^{IV}] = 2.0×10^{-3}, [H$^+$] = 2.0 and $I = 3.0$ mol dm^{-3} at 20°C. [Eu^{III}] = 5.0×10^{-5}. Scan time interval = 2 min.

path, with contributions from both uncatalyzed and catalyzed reactions. Thus, the total rate constant (k_T) is equal to the sum of the rate constants of the uncatalyzed (k_U) and catalyzed (k_C) reactions, so $k_C = k_T - k_U$. First-order plots of ln(absorbance) versus time of both uncatalyzed and Eu^{III}-catalyzed reactions were found to be linear for more than about 80% of the reactions completion, and the observed first-order rate constants were calculated as the gradients of such plots. Average values of at least two independent runs of the rate constants were taken for the analysis. The runs were reproducible to within ±4%. The orders of the reactions with respect to the reactants were evaluated from the slopes of log k_U and log k_C versus log(concentration) plots by varying the concentrations of the substrate, acid, and catalyst in turn, while keeping other conditions constant.

RESULTS

Time-Resolved Spectra

The spectral scans through the reduction of Th by selenous acid in sulfuric acid solutions in the absence and presence of europium(III) catalyst are shown in Figs. 1a

and 1b, respectively. In both cases, the scanned spectra indicate gradual disappearance of Th at its absorption maximum with time as a result of its reduction to leucothionine. It is shown that the decay of Th during the catalyzed reaction is significantly faster than that of uncatalyzed one. Furthermore, a careful examination of the spectral scans of the catalyzed reaction confirms the presence of two isosbestic points located at 543 and 259 nm.

Stoichiometry

At fixed acidity, ionic strength, and temperature, the stoichiometry of both uncatalyzed and catalyzed reactions, determined spectrophotometrically, was found to be 1:1, as shown in the following equation:

$$\text{Thionine} + H_2Se^{IV}O_3 + H_2O = \text{Leucothionine} + HSe^{VI}O_4^- + 2H^+ \quad (1)$$

The products were identified by spectral data and elemental analysis as described elsewhere [5,21]. A similar oxidation product of Th with different experimental conditions was reported earlier [5].

Effect of [Th] on the Reduction Rates

The oxidant, thionine, was varied in both uncatalyzed and catalyzed reactions in the range of 5.0×10^{-5} to

Table I Effects of Variation of [Th], [Se^{IV}], [H$^+$], and [Eu^{III}] on the Observed First-Order Rate Constant Values in the Uncatalyzed and Europium(III)-Catalyzed Reduction of Thionine by Selenous Acid in Sulfuric Acid Solutions. I = 3.0 mol dm^{-3} at 20°C

10^4 [Th] (mol dm^{-3})	10^3 [Se^{IV}] (mol dm^{-3})	[H$^+$] (mol dm^{-3})	10^5 [Eu^{III}] (mol dm^{-3})	$10^5\, k_T$ (s^{-1})	$10^5\, k_U$ (s^{-1})	$10^5\, k_C$ (s^{-1})
0.5	2.0	2.0	5.0	98.3	21.5	76.8
1.0	2.0	2.0	5.0	100.1	23.2	76.9
1.5	2.0	2.0	5.0	100.9	21.2	79.7
2.0	2.0	2.0	5.0	100.3	22.1	78.2
2.5	2.0	2.0	5.0	100.3	22.3	78.0
3.0	2.0	2.0	5.0	102.1	23.0	79.1
3.5	2.0	2.0	5.0	100.8	21.6	79.2
2.0	**0.5**	2.0	5.0	33.4	8.2	25.2
2.0	**1.0**	2.0	5.0	55.7	12.8	42.9
2.0	**1.5**	2.0	5.0	79.2	17.2	62.0
2.0	**2.0**	2.0	5.0	100.3	22.1	78.2
2.0	**2.5**	2.0	5.0	117.4	25.6	91.8
2.0	**3.0**	2.0	5.0	142.6	30.4	112.2
2.0	**3.5**	2.0	5.0	161.8	35.1	126.7
2.0	2.0	**0.5**	5.0	35.0	6.8	28.2
2.0	2.0	**1.0**	5.0	55.7	11.9	43.8
2.0	2.0	**1.5**	5.0	81.3	17.2	64.1
2.0	2.0	**2.0**	5.0	100.4	22.2	78.2
2.0	2.0	**2.4**	5.0	121.4	26.1	95.3
2.0	2.0	**2.7**	5.0	135.0	29.9	105.1
2.0	2.0	**3.0**	5.0	147.9	33.6	114.3
2.0	2.0	2.0	**3.0**	67.3	22.1	45.2
2.0	2.0	2.0	**5.0**	100.3	22.1	78.2
2.0	2.0	2.0	**7.0**	131.9	22.1	109.8
2.0	2.0	2.0	**9.0**	160.4	22.1	138.3
2.0	2.0	2.0	**12.0**	204	22.1	181.9
2.0	2.0	2.0	**16.0**	260.2	22.1	238.1
2.0	2.0	2.0	**20.0**	313.1	22.1	291.0

Experimental error ±4%.

3.5×10^{-4} mol dm^{-3} at fixed concentrations of se^{IV}, Eu^{III}, and Na$_2$SO$_4$, pH, and temperature. Straight lines for ln(absorbance) versus time plots were obtained for about 80% of the reactions completion. Furthermore, the increase in the initial oxidant concentration did not change significantly the reduction rates of Se^{IV} as shown in Table I. These results indicate that the order of reactions with respect to the oxidant is unity.

Effect of [Se^{IV}] on the Reduction Rates

The observed rate constants (k_U and k_C) were measured at different initial concentrations of Se^{IV} while other variables were kept constant. It was found that increasing [Se^{IV}] increased the rates (Table I). Plots of the observed rate constants versus [Se^{IV}] were linear with positive intercepts (figure not shown). This confirms the fractional first-order dependences with respect to Se^{IV} for both the uncatalyzed and catalyzed reactions.

Effect of [H$^+$] on the Reduction Rates

To explore the effect of hydrogen ion concentration on the rates of the reactions, kinetic runs were carried out by varying the hydrogen ion concentration in the range of 0.5–3.0 mol dm^{-3} at constant [Th], [Se^{IV}], [Eu^{III}] (for the catalyzed reaction), ionic strength, and temperature. It was observed that the increase in [H$^+$] increased the reduction rates (Table I). Plots of k_U and k_C versus [H$^+$] were linear with positive intercepts as shown in Fig. 2 confirming fractional first-order dependences with respect to [H$^+$].

Effect of [Eu^{III}] on the Reduction Rate

The europium(III) catalyst concentration was varied from 3.0×10^{-5} to 20.0×10^{-5} mol dm^{-3} while maintaining other variables constant. The reaction rate
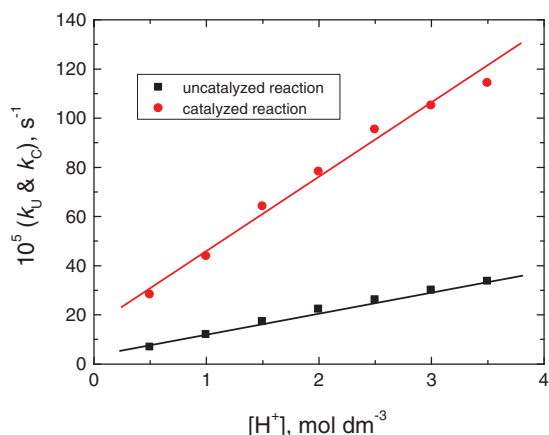
Figure 2 Plots of k_U and k_C versus [H$^+$] in the uncatalyzed and europium(III)-catalyzed reduction of thionine by selenous acid in sulfuric acid solutions. [Th] = 2.0×10^{-4}, [Se^{IV}] = 2.0×10^{-3}, and $I = 3.0$ mol dm^{-3} at 20°C. [Eu^{III}] = 5.0×10^{-5} mol dm^{-3}.
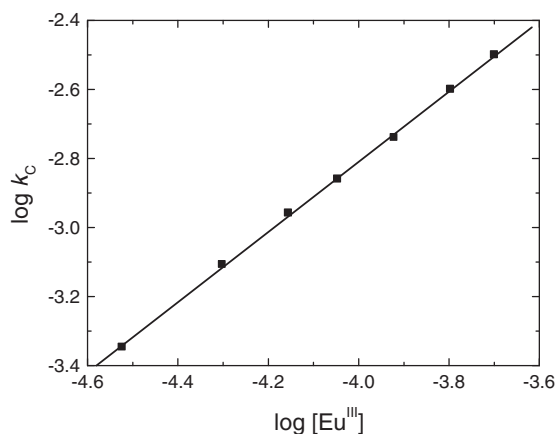

Figure 3 Plot of log k_C versus log [Eu^{III}] in the europium(III)-catalyzed reduction of thionine by selenous acid in sulfuric acid solution. [Th] = 2.0×10^{-4}, [Se^{IV}] = 2.0×10^{-3}, [H$^+$] = 2.0, and $I = 3.0$ mol dm^{-3} at 20°C.

was found to increase with increasing [Eu^{III}] (Table I). The order with respect to [Eu^{III}] was found to be unity as the slope of log k_C versus log [Eu^{III}] plot (Fig. 3).

Effect of Ionic Strength and Dielectric Constant

The effect of the ionic strength on both uncatalyzed and catalyzed reactions was studied by varying the concentration of Na$_2$SO$_4$ at constant other variables. The rates of the reactions were found to unaffected significantly with increasing the ionic strength of the reaction media.

The dielectric constant of the medium was varied by addition of acetic acid to the reaction media in the range of 0–40% (v/v). There was no effect of dielectric constant on the reactions as the k_U and k_C values remain unaffected.

Effect of Temperature

The rates of the uncatalyzed and europium(III)-catalyzed reactions were measured at four different temperatures in the range of 283–313 K under varying selenium(IV) reductant and acid concentrations. Both rates increased with increasing temperature. In both cases, the activation parameters of the rate constants of the slow steps (k_1 and k_2) along with thermodynamic parameters of the equilibrium constants involved in the reaction mechanisms were evaluated and are listed in Tables III, IV, VI and VII.
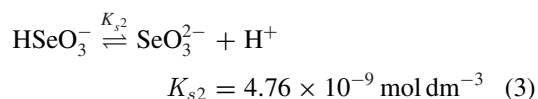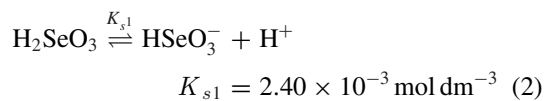
Polymerization Test

The intervention of free radical that may be generated from Th was examined by a polymerization test. In this test, acrylonitrile was used as a free radical scavenger and tested in the reaction mixtures as follows: A known quantity of acrylonitrile monomer was mixed with the reaction mixtures and kept for about 6 h in an inert atmosphere, with the results of formation of white precipitates of polymers in the whole reaction mixtures, indicating the presence of free radicals during the oxidation reactions. The experiments of either Th or Se^{IV} with acrylonitrile alone did not induce polymerization under similar condition as those induced with reaction mixtures. These results indicate that the reactions were proceeded through free radical paths.

DISCUSSION

Zhao et al. [22] reported that thionine dye in acid media is usually present in the form of purple monochloride (singly protonated Th, ThHCl$^+$, or ThH^{2+}). Throughout reduction of Th, the singly protonated species ThH$^+$ takes up an electron from the reductant leading to a semithionine radical ThH$^+$ (half reduced state). The latter gives up an electron to convert into leucothionine ThH (Scheme 1). The semithionine free radical, which is yellow in color, is most stable in concentrated sulfuric acid (5.0–12.5 mol dm^{-3}).

Selenium(IV) in the form of selenium dioxide in aqueous solutions [23] exists in selenous acid (H$_2$Se^{IV}O$_3$). The stepwise dissociation constants of the

acid are shown in the following equilibria:

$$H_2SeO_3 \overset{K_{s1}}{\rightleftharpoons} HSeO_3^- + H^+$$

$$K_{s1} = 2.40 \times 10^{-3} \, \text{mol dm}^{-3} \quad (2)$$

$$HSeO_3^- \overset{K_{s2}}{\rightleftharpoons} SeO_3^{2-} + H^+$$

$$K_{s2} = 4.76 \times 10^{-9} \, \text{mol dm}^{-3} \quad (3)$$

The values of the dissociation constants indicate that first deprotonation occurs, to a significant extent, in aqueous acid solutions, but because of its very low value the second deprotonation does not occur under the acid condition of the present study. Therefore, in acid medium [11] selenium dioxide exists as selenous acid which will be in equilibrium with the $HSeO_3^-$ species. Furthermore, the observed catalysis by H^+ indicates that selenous acid is the predominant reac-

tive species. Also, selenium(IV) is known to dimerize [24] in its concentrated solutions, but in the concentration range employed in the present investigation the monomer is the predominant species. In view of these reports, Se^{IV} may be present in the form of H_2SeO_3.

On the other hand, oxidation of Se^{IV} to Se^{VI} takes place according to the following equation [25]:

$$H_2SeO_3 + H_2O = HSeO_4^- + 3H^+ + 2e \quad (4)$$

Kinetics and mechanistic patterns of the oxidation of selenium(IV) [26,27] by one-electron oxidants such as neptunium(VII) and cerium(IV) proceeds, in general, through two successive one-electron steps, whereas oxidation by two-electron oxidants such as chloramine-T, N-chlorosuccinimide, and N-bromosuccinimide takes place in a simultaneous two-electron step. Oxidation
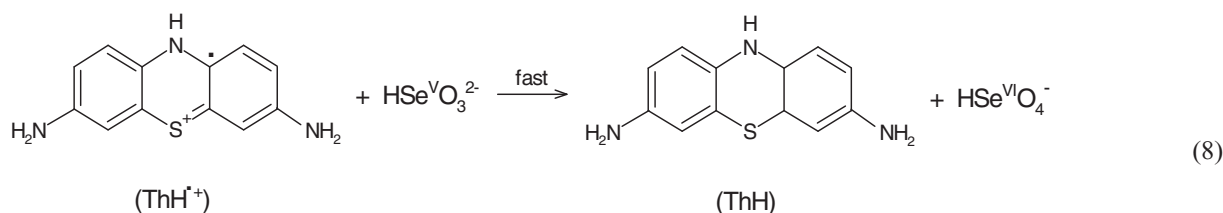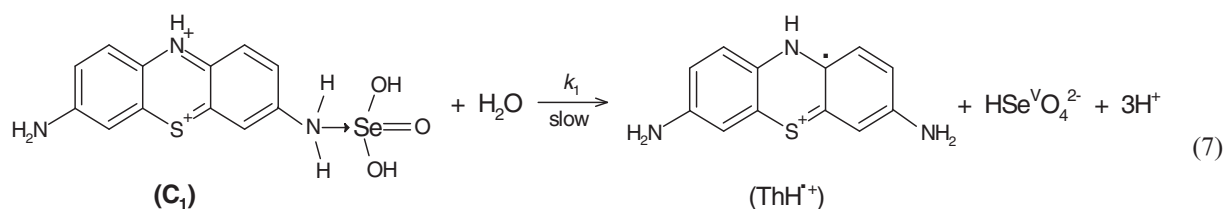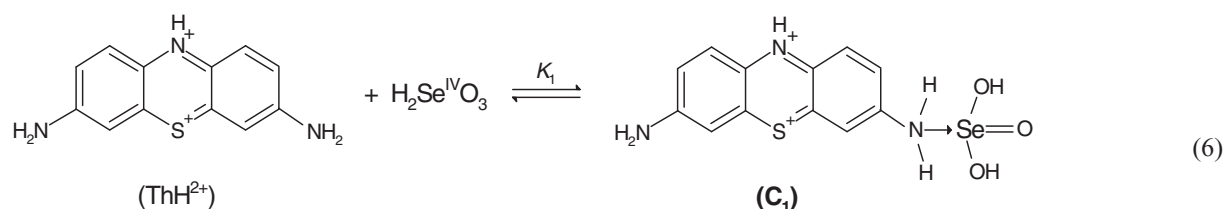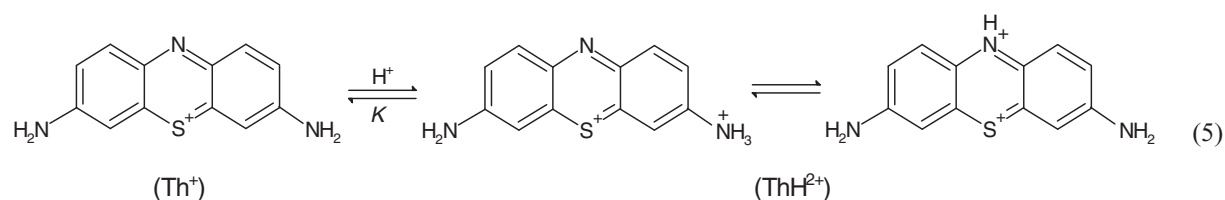
Scheme 1   Mechanism of the uncatalyzed reduction of thionine by selenous acid in sulfuric acid solution.

by oxygenated two-electron oxidants, such as hydrogen peroxide and periodate, seems to involve an oxygen atom transfer from the oxidant to selenium(IV) substrate. Oxidation of selenium(IV) by multielectron oxidant, permanganate, takes place in acid, neutral, and alkaline media. The rate-determining step involves a one-electron change in all three media, but the stoichiometry is different, being 5:2 in acid, 3:2 in neutral, and 1:2 in alkaline medium. Unstable Se^V intermediate species in the form of $HSe^VO_4^{2-}$ has been reported [13] to generate throughout Os^{VIII}-catalyzed oxidation of Se^{IV} by alkaline ferricyanide, which is then attacked by Os^{VIII} catalyst to give the oxidized product $HSe^{VI}O_4^-$. The reduced form of osmium rapidly reacts with another molecule of ferricyanide to regenerate Os^{VIII}.

Mechanism of the Uncatalyzed Reduction Reaction

Thionine reduction by selenium(IV) was found to occur in a slow rate in the absence of Eu^{III} catalyst in sulfuric acid solution. The stoichiometry of the reaction was 1:1. The reaction exhibited first-order dependence on [Th] and less than unit order each with respect to both $[Se^{IV}]$ and $[H^+]$. The acceleration of the reaction rate by hydrogen ion can be interpreted by either direct involvement of H^+ in any one of the steps of the mechanism or due to the existence of prior protonation equilibria. Thus, thionine is suggested [22] to protonate by the acid in a preequilibrium step to form a more reactive species of the oxidant (ThH^{2+}). Furthermore, the rate of reaction is not significantly affected by variation of ionic strength or solvent polarity of the medium. According to the principle of salt effect [28], there must be a neutral molecule in the rate-determining (slow) step, which confirms selenous acid (H_2SeO_3) as the kinetically active species of Se^{IV} in the present study.

On the other hand, the less than unit order in $[Se^{IV}]$ may be an indication of complex formation between the protonated species of Th and Se^{IV} before the slow step. The formation of a complex was kinetically proved by the nonzero intercept of the plot $1/k_U$ versus $1/[Se^{IV}]$ (Fig. 4) [29]. The formed complex was slowly decomposed in the rate-determining step to give the initial oxidation products as the oxidant radical (ThH^+) and unstable $HSe^VO_4^{2-}$. The oxidant radical reacts again with $HSe^VO_4^{2-}$ in a subsequent fast step to yield the final products as leucothionine (ThH) and Se^{VI} (Scheme 1). Such a mechanism accords with the principle of noncomplementary oxidations occurring in a sequence of one-electron steps in which the reaction between the substrate and oxidant would afford a radical intermediate as was obtained experimentally. Mechanistic Scheme 1 presents such equations.

According to the suggested mechanism, the relationship between the rate constant and the reductant, oxidant, and hydrogen ion concentrations can be expressed by the following rate law (see the Appendix A),

$$\text{Rate} = \frac{k_1 K K_1 [Se^{IV}][Th^+][H^+]}{1 + K[H^+] + K K_1 [Se^{IV}][H^+]} \quad (9)$$

This equation is consistent with all the observed orders with respect to different species.

Under the pseudo–first-order condition,

$$\text{Rate} = \frac{-d[Th^+]}{dt} = k_U [Th^+] \quad (10)$$

Comparing Eqs. (9) and (10),

$$k_U = \frac{k_1 K K_1 [Se^{IV}][H^+]}{1 + K[H^+] + K K_1 [Se^{IV}][H^+]} \quad (11)$$

Equation (11) can be verified by rearranging it to Eqs. (12) and (13),

$$\frac{1}{k_U} = \left(\frac{1}{k_1 K K_1 [H^+]} + \frac{1}{k_1 K_1} \right) \frac{1}{[Se^{IV}]} + \frac{1}{k_1} \quad (12)$$

$$\frac{1}{k_U} = \left(\frac{1}{k_1 K K_1 [Se^{IV}]} \right) \frac{1}{[H^+]} + \frac{1}{k_1 K_1 [Se^{IV}]} + \frac{1}{k_1} \quad (13)$$

Thus, plots of $1/k_U$ versus $1/[Se^{IV}]$ at constant $[H^+]$, and $1/k_U$ versus $1/[H^+]$ at constant $[Se^{IV}]$ should be linear with positive intercepts and were found to be so, Figs. 4 and 5, respectively. The values of the rate constant of the slow step k_1 at different temperatures, obtained as the intercepts reciprocal of $1/k_U$ versus $1/[Se^{IV}]$ plots, are listed in Table II. The activation parameters of k_1 were calculated from Arrhenius and Eyring plots and are listed in Table III. Similarly, on the basis of Eq. (13), plots of $1/k_U$ versus $1/[H^+]$ yielded straight lines with slopes and intercepts equal to $1/k_1 K K_1 [Se^{IV}]$ and $1/k_1 K_1 [Se^{IV}] + 1/k_1$, respectively. Now, using the slopes and intercepts of such plots, the values of the equilibrium constants associated with the mechanistic Scheme 2 (K and K_1) at different temperatures came and are listed in Table II. The van't Hoff plots were made for variation of K and K_1 with temperature. The values of enthalpy, entropy, and free
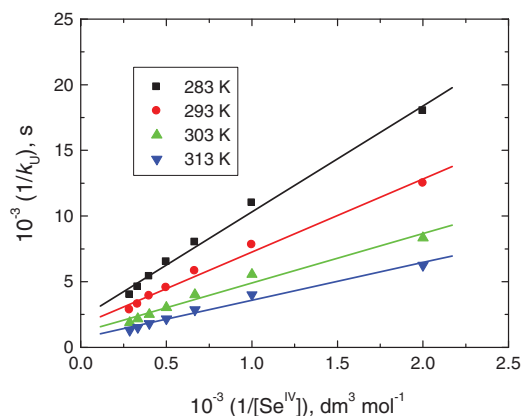
Figure 4 Plots of $1/k_U$ versus $1/[Se^{IV}]$ for the uncatalyzed reduction of thionine by selenous acid in sulfuric acid solution at different temperatures. $[Th] = 2.0 \times 10^{-4}$, $[H^+] = 2.0$ and $I = 3.0$ mol dm^{-3}.
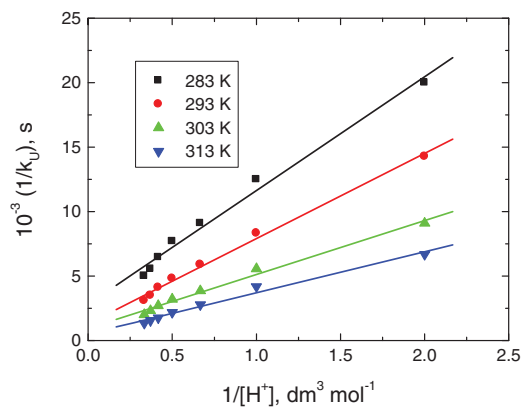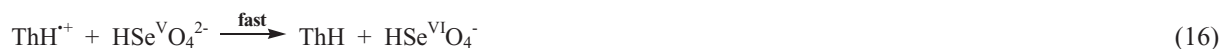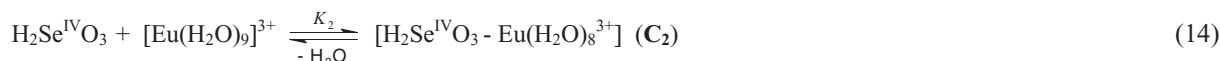

Figure 5 Plots of $1/k_U$ versus $1/[H^+]$ for the uncatalyzed reduction of thionine by selenous acid in sulfuric acid solutions at different temperatures. $[Th] = 2.0 \times 10^{-4}$, $[Se^{IV}] = 2.0 \times 10^{-3}$, and $I = 3.0$ mol dm^{-3}.

Table II Values of the Rate Constant of the Slow Step (k_1) and the Equilibrium Constants (K and K_1) in the Uncatalyzed Reduction of Thionine by Selenous Acid in Sulfuric Acid Solution at Different Temperatures. $[Th] = 2.0 \times 10^{-4}$, $[Se^{IV}] = 2.0 \times 10^{-3}$, $[H^+] = 2.0$, and I = 3.0 mol dm^{-3}

Constant	Temperature (K)			
	283	293	303	313
$10^4 k_1$ (s^{-1})	4.66	6.64	11.12	20.81
$10^3 K$ (dm^3 mol^{-1})	17.6	22.21	31.02	42.10
$10^{-3} K_1$ (dm^3 mol^{-1})	6.95	5.04	3.02	1.97

Experimental error = ±4%.

a decrease in the randomness during the oxidation process due to formation of compacted intermediate complex, and the one-electron transfer mechanism of inner-sphere nature was suggested to be the probable mechanism [30]. On the other hand, the positive values of both enthalpy of activation ($\Delta H^{\neq}$) and free energy of activation ($\Delta G^{\neq}$) indicated that the complex formation was endothermic and nonspontaneous, respectively.

Mechanism of Europium(III)-Catalyzed Reduction Reaction

It is reported [14] that in sulfuric acid solutions, Eu^{III} exists as a nonahydrate cation, $[Eu(H_2O)_9]^{3+}$. In the present study, the reaction between Th and Se^{IV} in sulfuric acid solution in the presence of small amounts of europium(III) catalyst is similar to the uncatalyzed reaction with respect to stoichiometry, reaction orders, ionic strength, and solvent polarity. In addition, the reaction was first order with respect to europium(III) catalyst. The mechanism is therefore likely to be similar, except for the participation of the catalyst. Thus, Eu^{III} species, $[Eu(H_2O)_9]^{3+}$, was suggested to react with Se^{IV} prior to the slow step to yield a complex (C$_2$), which was proved kinetically by a nonzero intercept of $[Eu^{II}]/k_C$ versus $1/[Se^{IV}]$ plots (Fig. 6). Then,

energy of the reaction were calculated and are listed in Table IV.

Activation parameters listed in Table III may be discussed as follows: The obtained large negative value of the entropy of activation ($\Delta S^{\neq}$) showed

$$H_2Se^{IV}O_3 + [Eu(H_2O)_9]^{3+} \underset{-H_2O}{\overset{K_2}{\rightleftharpoons}} [H_2Se^{IV}O_3 - Eu(H_2O)_8{}^{3+}] \ (C_2) \tag{14}$$

$$[H_2Se^{IV}O_3 - Eu(H_2O)_8{}^{3+}] + ThH^{2+} + 2H_2O \xrightarrow[\text{slow}]{k_2} ThH^{\bullet+} + HSe^VO_4{}^{2-} + 3H^+ + [Eu(H_2O)_9]^{3+} \tag{15}$$

$$ThH^{\bullet+} + HSe^VO_4{}^{2-} \xrightarrow{\text{fast}} ThH + HSe^{VI}O_4{}^- \tag{16}$$

Scheme 2 Mechanism of the europium(III)-catalyzed reduction of thionine by selenous acid in sulfuric acid solution.

Table III Activation Parameters Associated with k_1 in the Uncatalyzed Reduction of Thionine by Selenous Acid in Sulfuric Acid Solution

$\Delta S^{\neq}$ (J mol^{-1}K^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta G^{\neq}_{293}$ (kJ mol^{-1})	$E_a^{\neq}$ (kJ mol^{-1})	A (mol^{-1} s^{-1})
-188.72	33.84	89.14	26.07	20.08

Experimental error $= \pm 4\%$.

Table IV Thermodynamic Parameters Associated with K and K_1 in the Uncatalyzed Reduction of Thionine by Selenous Acid in Sulfuric Acid Solution

Equilibrium Constant	ΔH^o (kJ mol^{-1})	ΔG^o_{293} (kJ mol^{-1})	ΔS^o (J mol^{-1}K^{-1})
K	21.37	9.28	41.25
K_1	-31.22	-20.75	-35.72

Experimental error $= \pm 5\%$.

the protonated form of Th oxidant ThH^{2+} attacks the formed intermediate in the rate-determining step leading to a free radical derived from Th and Se^V with regeneration of the catalyst Eu^{III}. The radical intermediate reacts again with Se^V in a subsequent fast step forming the final oxidation products. The results are presented in Scheme 2.

The suggested mechanism leads to the following rate laws expression (see the Appendix B),

$$\text{Rate} = \frac{k_2 K K_2 [\text{Se}^{IV}][\text{Th}^+][\text{Eu}^{III}][\text{H}^+]}{1 + K[\text{H}^+] + K_2[\text{Se}^{IV}] + K K_2[\text{Se}^{IV}][\text{H}^+]} \tag{17}$$

Equation (17) is also consistent with all the observed orders with respect to different species.

Under the pseudo–first-order condition,

$$\text{Rate} = \frac{-d[\text{Th}^+]}{dt} = k_C [\text{Th}^+] \tag{18}$$

comparing Eqs. (17) and (18), the following relationship is obtained:

$$k_C = \frac{k_2 K K_2 [\text{Se}^{IV}][\text{Eu}^{III}][\text{H}^+]}{1 + K[\text{H}^+] + K_2[\text{Se}^{IV}] + K K_2[\text{Se}^{IV}][\text{H}^+]} \tag{19}$$

Equation (19) can be rearranged into the following equations:

$$\frac{[\text{Eu}^{III}]}{k_C} = \left(\frac{1}{k_2 K K_2[\text{H}^+]} + \frac{1}{k_2 K_2} \right) \frac{1}{[\text{Se}^{IV}]}$$

$$+ \frac{1}{k_2 K[\text{H}^+]} + \frac{1}{k_2} \tag{20}$$

$$\frac{[\text{Eu}^{III}]}{k_C} = \left(\frac{1}{k_2 K K_2[\text{Se}^{IV}]} + \frac{1}{k_2 K} \right) \frac{1}{[\text{H}^+]}$$

$$+ \frac{1}{k_2 K_2[\text{Se}^{IV}]} + \frac{1}{k_2} \tag{21}$$

According to Eqs. (20) and (21), plots of $[\text{Eu}^{III}]/k_C$ versus $1/[\text{Se}^{IV}]$ at constant $[\text{H}^+]$ and $[\text{Eu}^{III}]/k_C$ versus $1/[\text{H}^+]$ at constant $[\text{Se}^{IV}]$ to be linear with positive intercepts as were obtained experimentally as illustrated in Figs. 6 and 7, respectively. The values of the rate constant of the slow step (k_2) and the equilibrium constants (K and K_2) at different temperatures were calculated (Table V). The activation parameters of k_2 and thermodynamic parameters of K and K_2 were evaluated (Tables V–VII).

An alternative mechanism for the europium(III)-catalyzed reduction reaction based on the formation of the ternary complex (C$_3$) between reductant,
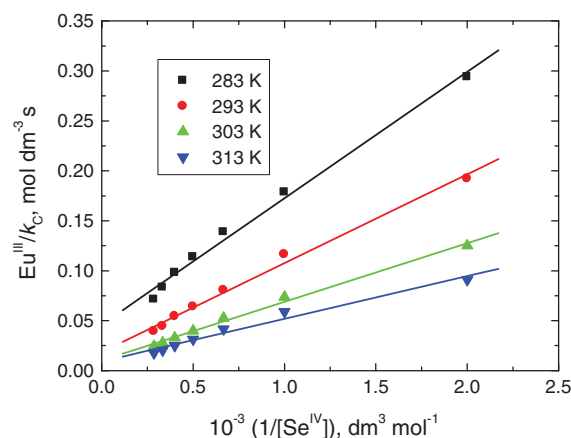

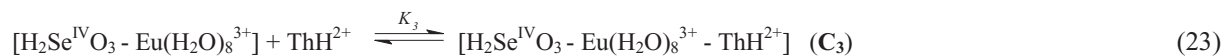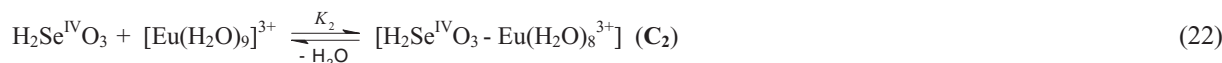**Figure 6** Plots of $[\text{Eu}^{III}]/k_C$ versus $1/[\text{Se}^{IV}]$ for the europium(III)-catalyzed reduction of thionine by selenous acid in sulfuric acid solution at different temperatures. [Th] $= 2.0 \times 10^{-5}$, $[\text{H}^+] = 2.0$, $[\text{Eu}^{III}] = 5.0 \times 10^{-5}$, and $I = 3.0$ mol dm^{-3}.

$$H_2Se^{IV}O_3 + [Eu(H_2O)_9]^{3+} \underset{-H_2O}{\overset{K_2}{\rightleftharpoons}} [H_2Se^{IV}O_3 - Eu(H_2O)_8^{3+}] \ (\mathbf{C_2}) \tag{22}$$

$$[H_2Se^{IV}O_3 - Eu(H_2O)_8^{3+}] + ThH^{2+} \overset{K_3}{\rightleftharpoons} [H_2Se^{IV}O_3 - Eu(H_2O)_8^{3+} - ThH^{2+}] \ (\mathbf{C_3}) \tag{23}$$

$$[H_2Se^{IV}O_3 - Eu(H_2O)_8^{3+} - ThH^{2+}] + 2H_2O \underset{slow}{\overset{k_3}{\longrightarrow}} ThH^{\bullet+} + HSe^{V}O_4^{2-} + 3H^+ + [Eu(H_2O)_9]^{3+} \tag{24}$$

$$ThH^{\bullet+} + HSe^{V}O_4^{2-} \overset{fast}{\longrightarrow} ThH + HSe^{VI}O_4^- \tag{25}$$

Scheme 3 An alternative mechanism of the europium(III)-catalyzed reduction of thionine by selenous acid in sulfuric acid solution.
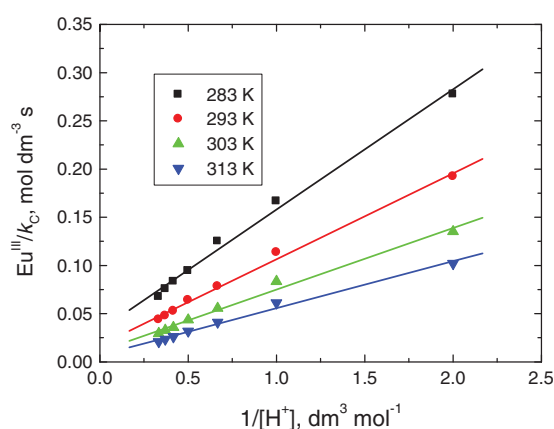

Figure 7 Plots of $[Eu^{III}]/k_C$ versus $1/[H^+]$ for the europium(III)-catalyzed reduction of thionine by selenous acid in sulfuric acid solutions at different temperatures. $[Th] = 2.0 \times 10^{-5}$, $[Se^{IV}] = 2.0 \times 10^{-3}$, $[Eu^{III}] = 5.0 \times 10^{-5}$, and $I = 3.0$ mol dm^{-3}.

Table V Values of the Rate Constant of the Slow Step (k_2) and the Equilibrium Constants (K and K_2) in the Europium(III)-Catalyzed Reduction of Thionine by Selenous Acid in Sulfuric Acid Solution at Different Temperatures. $[Th] = 2.0 \times 10^{-5}$, $[Se^{IV}] = 2.0 \times 10^{-3}$, $[H^+] = 2.0$, $[Eu^{III}] = 5.0 \times 10^{-5}$, and $I = 3.0$ mol dm^{-3}

	Temperature (K)			
Constant	288	293	298	303
k_2 (s^{-1})	31.25	45.45	83.31	150.81
$10^3\, K$ (dm^3 mol^{-1})	39.01	44.93	51.98	61.78
$10^{-3}\, K_2$ (dm^3 mol^{-1})	3.61	2.75	2.01	1.31

Experimental error = ±4%.

catalyst, and oxidant prior to the rate-determining step could be suggested. Spectroscopic evidence for such complex formation was obtained from UV–Vis spectra (appearance of two isosbestic points) shown in

Fig. 1b. The suggested mechanism is illustrated in Scheme 3.

The rate-law expression associated with the mechanistic Scheme 3 may be deduced to give the following equations:

$$Rate = \frac{k_2 K K_2 K_3 [Se^{IV}][Th^+][Eu^{III}][H^+]}{1 + K[H^+] + K_2[Se^{IV}] + K K_2[Se^{IV}][H^+]} \tag{26}$$

$$k_C = \frac{k_2 K K_2 K_3 [Se^{IV}][Eu^{III}][H^+]}{1 + K[H^+] + K_2[Se^{IV}] + K K_2[Se^{IV}][H^+]} \tag{27}$$

and with rearrangement, the following two equations are obtained:

$$\frac{[Eu^{III}]}{k_C} = \left(\frac{1}{k_2 K K_2 K_3 [H^+]} + \frac{1}{k_2 K_2 K_3} \right) \frac{1}{[Se^{IV}]} + \frac{1}{k_2 K K_3 [H^+]} + \frac{1}{k_2 K_3} \tag{28}$$

$$\frac{[Eu^{III}]}{k_C} = \left(\frac{1}{k_2 K K_2 K_3 [Se^{IV}]} + \frac{1}{k_2 K K_3} \right) \frac{1}{[H^+]} + \frac{1}{k_2 K_2 K_3 [Se^{IV}]} + \frac{1}{k_2 K_3} \tag{29}$$

The relationships (28) and (29) are quite similar to Eqs. (20) and (21), which requires that plotting $[Eu^{III}]/k_C$ versus $1/[Se^{IV}]$ at constant $[H^+]$ and $[Eu^{III}]/k_C$ versus $1/[H^+]$ at constant $[Se^{IV}]$ to be linear with positive intercepts on $[Eu^{III}]/k_C$ axes as shown also in Figs. 6 and 7, respectively. These results may be considered as a good support for the validity of the proposed mechanism.

Table VI Activation Parameters Associated with k_2 in the Europium(III)-Catalyzed Reduction of Thionine by Selenous Acid in Sulfuric Acid Solution

$\Delta S^{\neq}$ (J mol^{-1}K^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta G^{\neq}{}_{293}$ (kJ mol^{-1})	$E_a{}^{\neq}$ (kJ mol^{-1})	A (mol^{-1} s^{-1})
−87.29	36.33	61.91	38.79	2.41×10^8

Experimental error $= \pm 4\%$.

Table VII Thermodynamic Parameters Associated with K and K_2 in the Europium(III)-Catalyzed Reduction of Thionine by Selenous Acid in Sulfuric Acid Solution

Equilibrium Constant	ΔH^o (kJ mol^{-1})	$\Delta G^o{}_{298}$ (kJ mol^{-1})	ΔS^o (J mol^{-1}K^{-1})
K	11.14	7.55	12.24
K_2	−24.53	−19.29	−17.87

Experimental error $= \pm 5\%$.

APPENDIX A: DERIVATION OF THE RATE-LAW EXPRESSION FOR THE UNCATALYZED OXIDATION REACTION

According to the suggested mechanism and regarding to reaction (7),

$$\text{Rate} = \frac{-d[\text{C}_1]}{dt} = k_1 [\text{C}_1] \tag{A1}$$

Regarding to reactions (5) and (6),

$$K = \frac{[\text{ThH}^{2+}]}{[\text{Th}^+][\text{H}^+]}, \quad [\text{ThH}^{2+}] = K [\text{Th}^+][\text{H}^+] \tag{A2}$$

$$K_1 = \frac{[\text{C}_1]}{[\text{ThH}^{2+}][\text{Se}^{\text{IV}}]}, \quad [\text{C}_1] = K_1 [\text{ThH}^{2+}][\text{Se}^{\text{IV}}] \tag{A3}$$

Substituting Eq. (A2) into Eq. (A3) and rearrangement leads to

$$[\text{C}_1] = K K_1 [\text{Se}^{\text{IV}}][\text{Th}^+][\text{H}^+] \tag{A4}$$

Substituting Eq. (A4) into Eq. (A1) gives

$$\text{Rate} = k_1 K K_1 [\text{Se}^{\text{IV}}][\text{Th}^+][\text{H}^+] \tag{A5}$$

The total concentration of Se$^{\text{IV}}$ is given by

$$[\text{Se}^{\text{IV}}]_{\text{T}} = [\text{Se}^{\text{IV}}]_{\text{F}} + [\text{C}_1] \tag{A6}$$

where T and F stand for total and free concentrations, respectively.

Substituting Eq. (A4) into Eq. (A6) and rearrangement gives

$$[\text{Se}^{\text{IV}}]_{\text{T}} = [\text{Se}^{\text{IV}}]_{\text{F}} \left(1 + K K_1 [\text{Th}^+][\text{H}^+]\right) \tag{A7}$$

Therefore,

$$[\text{Se}^{\text{VI}}]_{\text{F}} = \frac{[\text{Se}^{\text{IV}}]_{\text{T}}}{1 + K K_1 [\text{Th}^+][\text{H}^+]} \tag{A8}$$

In view of low [Th$^+$], the term $K K_1[\text{Th}^+][\text{H}^+]$ in the above equation can be neglected. Thus,

$$[\text{Se}^{\text{IV}}]_{\text{F}} = [\text{Se}^{\text{IV}}]_{\text{T}} \tag{A9}$$

Similarly, total [Th$^+$] can be calculated as,

$$[\text{Th}^+]_{\text{T}} = [\text{Th}^+]_{\text{F}} + [\text{ThH}^{2+}] + [\text{C}_1] \tag{A10}$$

Therefore,

$$[\text{Th}^+]_{\text{F}} = \frac{[\text{Th}^+]_{\text{T}}}{1 + K[\text{H}^+] + K K_1[\text{Se}^{\text{IV}}][\text{H}^+]} \tag{A11}$$

In view of high [H$^+$],

$$[\text{H}^+]_{\text{F}} = [\text{H}^+]_{\text{T}} \tag{A12}$$

Substituting Eqs. (A8), (A11), and (A12) into Eq. (A5) (and omitting T and F as subscripts) leads to

$$\text{Rate} = \frac{k_1 K K_1[\text{Se}^{\text{IV}}][\text{Th}^+][\text{H}^+]}{1 + K[\text{H}^+] + K K_1[\text{Se}^{\text{IV}}][\text{H}^+]} \tag{A13}$$

Under pseudo–first-order conditions, the rate law can be expressed by Eq. (A14),

$$\text{Rate} = \frac{-d[\text{Th}^+]}{dt} = k_{\text{U}} [\text{Th}^+] \tag{A14}$$

Comparing Eqs. (A13) and (A14) gives the following relationship:

$$k_{\text{U}} = \frac{k_1 K K_1[\text{Se}^{\text{IV}}][\text{H}^+]}{1 + K[\text{H}^+] + K K_1[\text{Se}^{\text{IV}}][\text{H}^+]} \tag{A15}$$

and with rearrangement, the following two equations are obtained:

$$\frac{1}{k_U} = \left(\frac{1}{k_1 K K_1 [H^+]} + \frac{1}{k_1 K_1} \right) \frac{1}{[Se^{IV}]} + \frac{1}{k_1} \quad (A16)$$

$$\frac{1}{k_U} = \left(\frac{1}{k_1 K K_1 [Se^{IV}]} \right) \frac{1}{[H^+]} + \frac{1}{k_1 K_1 [Se^{IV}]} + \frac{1}{k_1} \quad (A17)$$

APPENDIX B: DERIVATION OF RATE-LAW EXPRESSION FOR EUROPIUM(III)-CATALYZED REDUCTION REACTION

According to the suggested mechanism and on the light of reaction (15),

$$\text{Rate} = \frac{-d[C_2]}{dt} = k_2 [C_2] [ThH^{2+}] \quad (B1)$$

Regarding to reactions (5) and (14),

$$K = \frac{[ThH^{2+}]}{[Th^+][H^+]}, \quad [ThH^{2+}] = K [Th^+] [H^+] \quad (B2)$$

$$K_2 = \frac{[C_2]}{[Se^{IV}][Eu^{III}]}, \quad [C_2] = K_2 [Se^{IV}] [Eu^{III}] \quad (B3)$$

Substituting Eqs. (B2) and (B3) into Eq. (B1) gives

$$\text{Rate} = k_2 K K_2 [Se^{IV}] [Th^+] [Eu^{III}] [H^+] \quad (B4)$$

The total concentration of Se^{IV} is given by

$$[Se^{IV}]_T = [Se^{IV}]_F + [C_2] \quad (B5)$$

Substituting Eq. (B3) into Eq. (B5) and rearrangement gives

$$[Se^{IV}]_T = [Se^{IV}]_F (1 + K_2 [Eu^{III}]) \quad (B6)$$

Therefore,

$$[Se^{IV}]_F = \frac{[Se^{IV}]_T}{1 + K_2 [Eu^{III}]} \quad (B7)$$

In view of low $[Eu^{III}]$, the term $K_2[Eu^{III}]$ in the above equation can be neglected. Thus,

$$[Se^{IV}]_F = [Se^{IV}]_T \quad (B8)$$

Similarly, total $[Th^+]$ can be calculated as,

$$[Th^+]_T = [Th^+]_F + [ThH^{2+}] \quad (B9)$$

Therefore,

$$[Th^+]_F = \frac{[Th^+]_T}{1 + K[H^+]} \quad (B10)$$

Also, total $[Eu^{III}]$ is given by

$$[Eu^{III}]_T = [Eu^{III}]_F + [C_2] \quad (B11)$$

Therefore,

$$[Eu^{III}]_F = \frac{[Eu^{III}]_T}{1 + K_2[Se^{IV}]} \quad (B12)$$

In view of high $[H^+]$,

$$[H^+]_F = [H^+]_T \quad (B13)$$

Substituting Eqs. (B8) and (B10), (B12) and (B13) into Eq. (B4) (and omitting T and F subscripts) leads to

$$\text{Rate} = \frac{k_2 K K_2 [Se^{IV}][Th^+][Eu^{III}][H^+]}{(1 + K[H^+])(1 + K_2[Se^{IV}])} \quad (B14)$$

$$\text{Rate} = \frac{k_2 K K_2 [Se^{IV}][Th^+][Eu^{III}][H^+]}{1 + K[H^+] + K_2[Se^{IV}] + K K_2[Se^{IV}][H^+]} \quad (B15)$$

Under the pseudo–first-order condition, the rate law can be expressed by Eq. (B16),

$$\text{Rate} = \frac{-d[Th^+]}{dt} = k_C [Th^+] \quad (B16)$$

Comparing Eqs. (B15) and (B16) gives the following relationship:

$$k_C = \frac{k_2 K K_2 [Se^{IV}][Eu^{III}][H^+]}{1 + K[H^+] + K_2[Se^{IV}] + K K_2[Se^{IV}][H^+]} \quad (B17)$$

and with rearrangement, the following two equations are obtained:

$$\frac{[Eu^{III}]}{k_C} = \left(\frac{1}{k_2 K K_2 [H^+]} + \frac{1}{k_2 K_2} \right) \frac{1}{[Se^{IV}]}$$
$$+ \frac{1}{k_2 K [H^+]} + \frac{1}{k_2} \quad (B18)$$

$$\frac{[\text{Eu}^{\text{III}}]}{k_{\text{C}}} = \left(\frac{1}{k_2 K K_2 [\text{Se}^{\text{IV}}]} + \frac{1}{k_2 K} \right) \frac{1}{[\text{H}^+]}$$
$$+ \frac{1}{k_2 K_2 [\text{Se}^{\text{IV}}]} + \frac{1}{k_2} \qquad \text{(B19)}$$

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