

Selective oxidation of thiourea with H₂O₂ catalyzed by [Ru^{III}(edta)(H₂O)]⁻: kinetic and mechanistic studies†Cite this: *Dalton Trans.*, 2013, **42**, 4725Debabrata Chatterjee,^{*a,b} Sabine Rothbart^b and Rudi van Eldik^{*b}

Reported here is the first example of a ruthenium complex, [Ru^{III}(edta)(H₂O)]⁻ (edta⁴⁻ = ethylenediaminetetraacetate), that catalyzes the oxidation of thiourea (TU) in the presence of H₂O₂. The kinetics and mechanism of this reaction were investigated in detail by using rapid-scan spectrophotometry as a function of both the hydrogen peroxide and thiourea concentrations at pH 4.9 and 25 °C. Spectral analyses and kinetic data clearly support a catalytic process in which hydrogen peroxide reacts directly with thiourea coordinated to the Ru^{III}(edta) complex. HPLC product analyses revealed the formation of formamidine disulfide (TU₂) as a major product at the end of the catalytic process, however, formation of other products like thiourea dioxide (TUO₂), thiourea trioxide (TUO₃) and sulfate was also observed after longer reaction times. Catalytic intermediates such as [Ru^{III}(edta)(OOH)]²⁻ and [Ru^V(edta)(O)]⁻ were evidently found to be non-reactive in catalyzing the oxidation of thiourea by H₂O₂ under the specified conditions.

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Introduction

Thiourea (NH₂CSNH₂, TU), a sulfur-containing compound, is extensively used in chemistry and biochemistry.^{1,2} In the recent past, efficacy of thiourea and 1,3-dimethyl-2-thiourea (DMTU) in scavenging reactive oxygen intermediates (ROIs),³ and preventing ROI-induced lung injury has been reported.⁴ In addition, it has immense industrial potential. Reactions of thiourea with hydrogen peroxide under certain conditions produce a powerful reductive bleaching agent, which is routinely used in the textile industry.⁵⁻⁷ Apart from the mechanism of thiourea oxidation, which is quite complex because of the formation of various oxidation products with the oxidation state of sulfur ranging from -1 to +6,^{7,8} the physiological effects of thiourea oxides (products from the oxidation of thiourea) have drawn attention of researchers to look at the biofunction of these sulfur species.^{9,10}

The significance of thiourea oxidation has been well documented in a very recent review article,¹¹ however, the use of a metal complex as a catalyst in TU oxidation is scanty in the literature.¹²⁻¹⁴ It is noteworthy that no report on the use of a ruthenium complex as a catalyst in thiourea oxidation is

available in the literature, albeit there exists a report on the formation of urea *via* hydrolysis of [Ru(NH₃)₅(TU)]³⁺ in basic aqueous solution.¹⁵ In view of the above and considering the potential of the Ru^{III}-edta/H₂O₂ system towards effecting oxidation of various substrates,¹⁶ we have undertaken a detailed kinetic and mechanistic investigation of the oxidation of thiourea by the Ru^{III}(edta)/H₂O₂ system in aqueous solution. This is the first report on the oxidation of thiourea with H₂O₂ using a ruthenium complex. We report herein the results of kinetic studies of the oxidation of thiourea by the Ru^{III}(edta)/H₂O₂ system as a function of [TU] and [H₂O₂] at 25 °C and pH 4.9. The goal of the present work is to contribute to the mechanistic understanding of the catalytic oxidation process.

Experimental

Materials

K[Ru^{III}(Hedta)Cl]·2H₂O was prepared by following the published procedure.¹⁷ The micro-analysis and spectral data are in good agreement with those reported in the literature.¹⁷ Anal. calculated for K[Ru^{III}(Hedta)Cl]·2H₂O: C 24.0, H 3.42, N 5.59; Found. C 23.8, H 3.45, N 5.63. IR, ν/cm^{-1} : 1720 (free -COOH), 1650 (coordinated -COO⁻). UV-Vis in H₂O: $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{M}^{-1}\text{cm}^{-1}$): 283 (2800 ± 50), 350 sh (680 ± 10). All other chemicals used were of A.R grade. Doubly distilled H₂O was used throughout the experiments.

Instrumentation

A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical (C, H, N) data. The UV-Vis and IR (using KBr

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pellets) spectra were recorded on Varian Model Cary 100 Bio and Perkin Elmer Model Lambda 783 spectrophotometers, respectively. Kinetic measurements were performed in a reaction vessel using a Hellma 661.502-QX quartz suprasil immersion probe attached *via* optical cables to a 150 W Xe lamp and a multi-wavelength J&M detector, which records complete absorption spectra at constant time intervals. The reaction of $[\text{Ru}^{\text{III}}(\text{edta})(\text{TU})]^-$ with H_2O_2 was followed at 466 nm, whereas the reaction of $[\text{Ru}^{\text{III}}(\text{edta})(\text{OOH})]^{2-}$ and $[\text{Ru}^{\text{V}}(\text{edta})\text{O}]^-$ (produced in the reaction of $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ with H_2O_2) with TU was monitored at 425 and 390 nm, respectively. All the instruments were thermostated at the desired temperature (± 0.1 °C). The pH of the solutions was measured with a Mettler Delta 350 pH meter. Acetate and phosphate buffers were used to adjust the pH of the experimental solutions. Observed rate constants (k_{obs}) are presented as an average of several kinetic runs (at least 5–8) and were reproducible within $\pm 4\%$.

The analysis of the oxidation products of thiourea was performed using an HPLC system (Waters 600 pump and 600 controller with Waters 2487 dual absorbance detector) equipped with a C_{18} Nova-Pak column (Waters, 3.9×150 mm, bead size 4 μm) pre-equilibrated with 5% methanol. Elutions were performed using a mobile phase of an HPLC grade water-acetonitrile mixture (70:30 v/v) at a flow rate of 0.5 mL min^{-1} . Elution profiles of thiourea, $\text{Ru}(\text{edta})$ and H_2O_2 were obtained isocratically in the same solvent at a flow rate of 0.8 mL min^{-1} . Elution was followed at different wavelengths reported for thiourea and its corresponding oxidation products.²⁰ The retention times for thiourea (TU), hydrogen peroxide (H_2O_2) and formamidine disulfide (TU_2) at 236 nm were found to be 1.62, 2.1, and 2.6 min, respectively, under the selected conditions.

Results and discussion

The $[\text{Ru}^{\text{III}}(\text{Hedta})\text{Cl}]$ complex rapidly converts into the $[\text{Ru}^{\text{III}}(\text{Hedta})(\text{H}_2\text{O})]$ complex when dissolved in water.^{18,19} The sixth coordination site of the ruthenium complex is occupied either at low pH by a water molecule or at high pH by a hydroxide ion. The $\text{p}K_{\text{a}}$ values related to the acid-dissociation equilibria of the pendant carboxylic acid arm and the coordinated water molecule are 2.4 and 7.6, respectively at 25 °C.^{18,19}

The $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ complex rapidly reacts with TU to form a sulfur-bound red coloured complex $[\text{Ru}^{\text{III}}(\text{edta})(\text{TU})]^-$ ($\lambda_{\text{max}} = 466$ nm; $\epsilon_{\text{max}} = 1960 \pm 20$ $\text{M}^{-1} \text{cm}^{-1}$).¹⁹ The second-order rate constant for the formation of this complex is 2970 ± 50 $\text{M}^{-1} \text{s}^{-1}$ at 25 °C and pH 5.0.¹⁹ Addition of an excess of H_2O_2 to the red solution of $[\text{Ru}^{\text{III}}(\text{edta})(\text{TU})]^-$ resulted in a rapid decay of the band at 466 nm (Fig. 1). It is noteworthy that the kinetics of the spontaneous oxidation of thiourea by hydrogen peroxide was recently studied by Epstein *et al.*²⁰ A reversed-phase ion-pair HPLC technique was employed to monitor the course of the reaction, and quantitatively characterize the concentrations of a variety of sulfur-containing

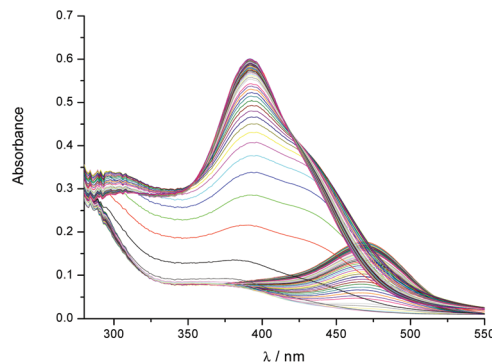


Fig. 1 UV-Vis spectral changes observed during the oxidation of $[\text{Ru}^{\text{III}}(\text{edta})(\text{TU})]^-$ (2.0×10^{-4} M) by H_2O_2 (2.0×10^{-2} M) at 25 °C and pH 4.9 (1 mM acetate buffer). Overall reaction time 120 s.

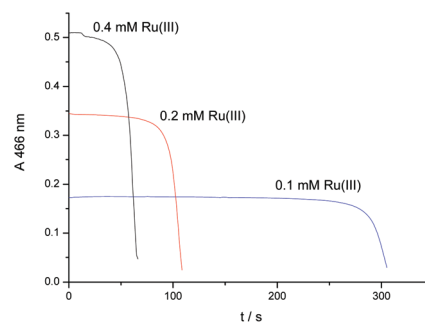


Fig. 2 Kinetic traces recorded at 466 nm for the $\text{Ru}(\text{edta})$ catalyzed oxidation of thiourea by H_2O_2 . $[\text{TU}] = 4 \times 10^{-4}$ M, $[\text{H}_2\text{O}_2] = 2 \times 10^{-2}$ M, 25 °C, pH 4.9 (1 mM acetate buffer).

species *viz.* formamidine disulfide (TU_2), thiourea dioxide (TUO_2), thiourea trioxide (TUO_3), sulfite and sulfate formed in the oxidation reaction. It was proposed that the oxidation of thiourea by H_2O_2 proceeds through the formation of a transient sufanyl acid ($\text{HOSC}(\text{NH})\text{NH}_2$) intermediate ($k_1 = 0.115$ $\text{M}^{-1} \text{s}^{-1}$ at 25 °C).²⁰ The sufanyl acid intermediate subsequently reacts with another molecule of thiourea to yield formamidine disulfide ($k_2 = 4.5$ $\text{M}^{-1} \text{s}^{-1}$ at 25 °C).²⁰ However, formamidine disulfide (TU_2) slowly converts into TUO_2 ($k_3 = 0.0058$ $\text{M}^{-1} \text{s}^{-1}$ at 25 °C). In our case, disappearance of the peak at 466 nm is attributed to the oxidation of the coordinated TU in $[\text{Ru}^{\text{III}}(\text{edta})(\text{TU})]^-$ by H_2O_2 under the specified conditions. After complete oxidation of thiourea, the reaction is followed by the formation of a band at 390 nm and a shoulder at 425 nm, characteristic for the formation of $[\text{Ru}^{\text{V}}(\text{edta})\text{O}]^-$ and $[\text{Ru}^{\text{III}}(\text{edta})(\text{OOH})]^{2-}$, respectively.²¹

Fig. 2 shows typical kinetic traces recorded at 466 nm to demonstrate the effect of the catalyst concentration on the oxidation of coordinated TU in $[\text{Ru}^{\text{III}}(\text{edta})(\text{TU})]^-$. All traces show an initial induction period which increases with decreasing catalyst concentration (Fig. 2) and is ascribed to the rapid reformation of the $[\text{Ru}^{\text{III}}(\text{edta})(\text{TU})]^-$ complex in the presence of an excess of TU following the oxidation of the coordinated TU under the specified conditions. Following the induction

period, the reaction rate (slope of the trace) becomes slower on decreasing the $\text{Ru}^{\text{III}}(\text{edta})$ concentration.

On the basis of the observed spectral changes reported in Fig. 1, a series of experiments were performed in which the concentrations of Ru - edta , H_2O_2 and thiourea were systematically varied, while pH and temperature were kept constant in order to obtain time-resolved concentration dependences for the observed reaction steps. Some typical absorbance-time traces at 466 nm as a function of $[\text{TU}]$ and $[\text{H}_2\text{O}_2]$ are shown in Fig. 3 and 4, respectively. The kinetic traces in Fig. 3 and 4 all exhibit the mentioned induction period due to the rapid reformation of $[\text{Ru}^{\text{III}}(\text{edta})(\text{TU})]^-$ by the reaction of TU (excess over $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ catalyst complex) following the oxidation of coordinated TU in $[\text{Ru}^{\text{III}}(\text{edta})(\text{TU})]^-$ (band at 466 nm). The induction period increases with increasing $[\text{TU}]$ (Fig. 3) as a result of the reformation of $[\text{Ru}^{\text{III}}(\text{edta})(\text{TU})]^-$ that will continue for a longer time in the presence of a larger excess of TU, *i.e.* a longer recycling of the catalyst, $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$. Following the induction period, the rate of the reaction becomes slightly slower on increasing the TU concentration (Fig. 3).

Representative kinetic traces (recorded at 466 nm) for the oxidation of coordinate TU in $[\text{Ru}^{\text{III}}(\text{edta})(\text{TU})]^-$ as a function of $[\text{H}_2\text{O}_2]$ are shown in Fig. 4. The induction period clearly shortens on increasing the H_2O_2 concentration as seen in Fig. 4. Under the specified conditions, the rate of the oxidation

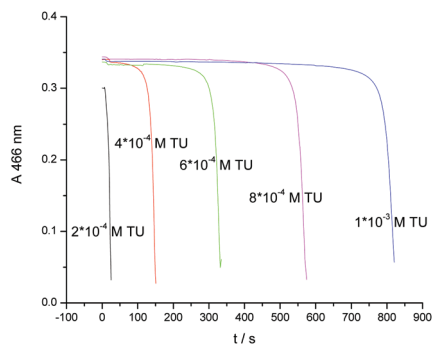


Fig. 3 Kinetic traces recorded at 466 nm for the $\text{Ru}(\text{edta})$ catalyzed oxidation of thiourea by H_2O_2 . $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^- = 2 \times 10^{-4} \text{ M}$, $[\text{H}_2\text{O}_2] = 2 \times 10^{-2} \text{ M}$, $[\text{TU}] = (2\text{--}10) \times 10^{-4} \text{ M}$, 25°C , pH 4.9 (1 mM acetate buffer).

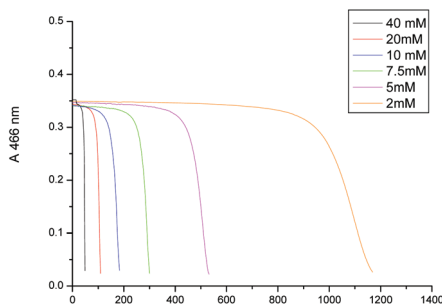


Fig. 4 Kinetic traces recorded at 466 nm for the $\text{Ru}(\text{edta})$ catalyzed oxidation of thiourea by H_2O_2 . $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^- = 2 \times 10^{-4} \text{ M}$, $[\text{TU}] = 4 \times 10^{-4} \text{ M}$, $[\text{H}_2\text{O}_2] = (2\text{--}40) \times 10^{-3} \text{ M}$, 25°C , pH 4.9 (1 mM acetate buffer).

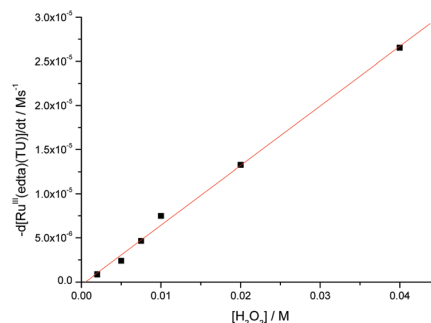


Fig. 5 Plot of the rate of disappearance of the red $[\text{Ru}^{\text{III}}(\text{edta})(\text{TU})]^-$ complex versus $[\text{H}_2\text{O}_2]$ at 25°C , pH 4.9 (1 mM acetate buffer), $[\text{Ru}^{\text{III}}] = 2 \times 10^{-4} \text{ M}$.

reaction estimated by the maximum slope reached following the induction period, increases linearly with increasing H_2O_2 concentration (Fig. 5).

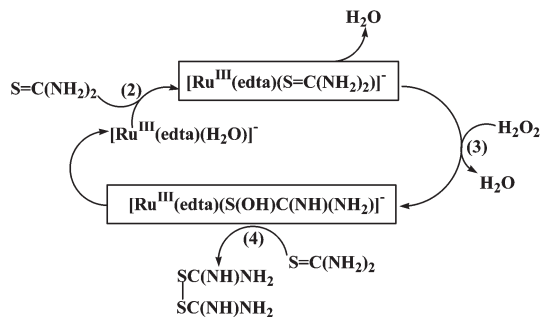
The observed reaction of $[\text{Ru}^{\text{III}}(\text{edta})(\text{TU})]^-$ with H_2O_2 under the specified conditions can be accounted for in terms of the rate-law expressed in eqn (1)

$$-d[\text{Ru}^{\text{III}}(\text{edta})(\text{TU})^-]/dt = k[\text{Ru}^{\text{III}}(\text{edta})(\text{TU})^-][\text{H}_2\text{O}_2] \quad (1)$$

The value of the second-order rate constant (k) estimated from the slope of the plot in Fig. 5 is $3.4 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C . This rate constant for the $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ mediated oxidation of thiourea is approximately thirty times faster than the spontaneous oxidation of thiourea by H_2O_2 .²⁰ The kinetic data, therefore, signify the catalytic role of the $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ complex towards effecting oxidation of thiourea under the specified experimental conditions.

Very recently we have reported on the reactivity of the catalytically active intermediate species $[\text{Ru}^{\text{III}}(\text{edta})(\text{OOH})]^{2-}$ and $[\text{Ru}^{\text{V}}(\text{edta})\text{O}]^-$ that are formed in the reaction of $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ with H_2O_2 (at higher concentrations up to 50 mM) and effect substrate oxidation.¹⁶ These intermediates are ruthenium equivalents of Compounds 0 and I much discussed in biomimetic oxidation processes.^{22,23} Since $[\text{Ru}^{\text{V}}(\text{edta})\text{O}]^-$ species are known to effect the oxidation of organic substrates,²⁴ we have also examined the reaction of $[\text{Ru}^{\text{V}}(\text{edta})\text{O}]^-$ (preformed by reacting $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ with H_2O_2 in a 1 : 1 ratio) with TU (in high excess), and found no immediate spectral changes (see Fig. S1 in ESI†) demonstrating the inability of $[\text{Ru}^{\text{V}}(\text{edta})\text{O}]^-$ to effect the oxidation of TU. Similarly, the spectral studies observed (see Fig. S2 in ESI†) for the reaction of $[\text{Ru}^{\text{III}}(\text{edta})(\text{OOH})]^{2-}$ with TU revealed that the decay of the shoulder at 425 nm signifying the conversion of $[\text{Ru}^{\text{III}}(\text{edta})(\text{OOH})]^{2-}$ to $[\text{Ru}^{\text{V}}(\text{edta})\text{O}]^-$ is not affected by the presence of TU even in excess. This necessarily suggests the non-involvement of $[\text{Ru}^{\text{III}}(\text{edta})(\text{OOH})]^{2-}$ species in the oxidation of TU under the specified conditions.

Based on the above experimental observations, the oxidation of thiourea by the $\text{Ru}(\text{edta})/\text{H}_2\text{O}_2$ system can be accounted for in terms of the suggested reaction mechanism outlined in Scheme 1.



Scheme 1 Suggested mechanism for the Ru(edta) catalyzed oxidation of TU with H₂O₂. Reactions (2), (3) and (4) represent the different reaction steps in the overall catalytic process.

As proposed in Scheme 1, oxidation of TU predominantly takes place through substrate activation and not by peroxide activation. The coordinated edta ligand plays a key-role as it imparts high lability in [Ru^{III}(edta)(H₂O)]⁻ towards water substitution through which TU can bind to ruthenium directly through the S-donor atom, resulting in the formation of a red coloured complex (characteristic of sulfur to ruthenium charge transfer) in a kinetically preferred pathway. Coordination of TU through the S atom causes activation of the S=C bond of TU, and makes it vulnerable towards direct oxidation by H₂O₂. In the proposed scheme, reaction (3) is responsible for the oxidation of coordinated thiourea and is the rate-determining step. Under turnover conditions of excess thiourea (excess over ruthenium catalyst), [Ru^{III}(edta)S(OH)C(NH)(NH₂)]⁻ subsequently reacts rapidly with another molecule of thiourea in reaction (4) to form formamidine disulfide {(NH₂)(NH)C(SSC(NH)(NH₂))} selectively. [Ru^{III}(edta)H₂O]⁻ regenerated *via* reaction (4) in turn rapidly binds free TU through reaction (2) to mediate its further oxidation *via* reaction (3). Evidence for the complete consumption of TU and formation of formamidine disulfide (TU₂), an oxidation product of TU *via* reaction (4), came from HPLC studies carried out immediately following the disappearance of the red colour (see Fig. S3a in ESI[†]). It has been reported in the literature²⁰ that the reaction of S-hydroxylated thiourea {(HO)SC(NH)(NH₂)} and thiourea results in the formation of the oxidation product TU₂ in a kinetically preferred manner. In the presence of excess H₂O₂, TU₂ can undergo further slow oxidation to yield different species such as TUO₂.²⁰ In the present study we have also noticed complete depletion of TU₂ with concomitant formation of TUO₂ in the HPLC analysis of the sample of the reaction mixture taken after 1 h (see Fig. S3b in ESI[†]).

It is noteworthy that the rate of formation of the [Ru^{III}(edta)(TU)]⁻ complex in the reaction of [Ru^{III}(edta)H₂O]⁻ with TU governs the efficiency of the overall catalytic process. A much longer induction period was observed at pH 1.6 as compared to that observed at pH 4.9. A similar kinetic behaviour was also observed at higher pH 9.2 (see Fig. S4 in ESI[†]). These findings are consistent with the fact that the rate of the reaction of [Ru^{III}(edta)H₂O]⁻ with TU reaches a maximum in the pH range

4–6, and the much slower reactions at lower (pH 1–2) or higher pH (pH 8.5–9.5)¹⁹ substantiate the above arguments.

Conclusions

In conclusion, we report the first example of a Ru(III) complex capable of mediating the oxidation of thiourea using H₂O₂ as an oxidant under ambient conditions. The results of the present study strongly implicate the direct attack of the oxidant, H₂O₂ to the coordinated TU in the [Ru^{III}(edta)(TU)]⁻ complex resulting in the formation a [Ru^{III}(edta)S(OH)C(NH)(NH₂)]⁻ intermediate species, which further reacts with another molecule of TU to yield formamidine disulfide {(NH₂)(NH)C(SSC(NH)(NH₂))} as an immediate oxidation product. However, formamidine disulfide undergoes further slow oxidation during the prolonged reaction with H₂O₂.

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