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Direct evidence for catalase activity of $[\text{Ru}^{\text{V}}(\text{edta})(\text{O})]^{-\dagger}$

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Reported is the first example of a ruthenium(III) complex, $\text{Ru}^{\text{III}}(\text{edta})$ (edta^{4-} = ethylenediaminetetraacetate), that catalyzes the disproportion of H_2O_2 to O_2 and water in resemblance to catalase activity, and shedding light on the possible mechanism of action of the $[\text{Ru}^{\text{V}}(\text{edta})(\text{O})]^{-}$ formed in the reacting system.

In the biological system, hydrogen peroxide is known to effectively react with ferric states of heme-containing peroxidases and catalases in a two-electron redox reaction.^{1,2} We reported earlier that $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^{-}$ (edta^{4-} = ethylenediaminetetraacetate) reacts with ROOH ($\text{ROOH} = \text{H}_2\text{O}_2$,³ $t\text{-BuOOH}$,⁴ HSO_5^{-}) to produce a high-valent two-electron oxidized $[\text{Ru}^{\text{V}}(\text{edta})(\text{O})]^{-}$ intermediate (analogue of compound I) that mimics the heme-based peroxide-activating enzyme, peroxidase.^{1,2} For many years, $\text{Ru}^{\text{III}}(\text{edta})$ complexes have received much attention because of their high lability towards aqua-substitution reactions, and a range of accessible oxidation states making them attractive candidates for catalytic applications.⁵ Recently, we have shown that $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^{-}$ effectively catalyzes the oxidation of a wide range of biologically important molecules including cysteine,^{6a} thiourea,^{6b} thiocyanate,^{6c} thiosulfate,^{6d} hydroxyurea,^{7a} L-arginine,^{7b} azide^{7c} and azo-dyes⁸ in the presence of H_2O_2 .

It is noteworthy here that while studying the above referred to oxidation reactions, we noticed that gas bubbles were evolved in the reaction system when the $\text{Ru}^{\text{III}}(\text{edta})$ catalyst is added to a solution with a high H_2O_2 concentration in the absence of substrate. The evolved gas was identified as dioxygen (O_2) by gas chromatographic analysis. These observations indicated the possible role of $\text{Ru}^{\text{III}}(\text{edta})$

as a catalase^{9,10} mimic to promote the disproportionation of H_2O_2 into dioxygen and water, which prompted us to undertake the present investigation. In this communication, we report for the first time a kinetic and mechanistic evaluation of the catalase activity of the $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^{-}$ complex in the presence of H_2O_2 .

$\text{K}[\text{Ru}^{\text{III}}(\text{Hedta})\text{Cl}]\cdot 2\text{H}_2\text{O}$ was prepared by following the published procedure and characterized accordingly (see Section S1 in ESI†).¹¹ The $\text{K}[\text{Ru}^{\text{III}}(\text{Hedta})\text{Cl}]$ complex rapidly converts into the $[\text{Ru}^{\text{III}}(\text{Hedta})(\text{H}_2\text{O})]^{-}$ complex (Fig. 1) when dissolved in water.^{12,13} The sixth coordination site of the ruthenium complex is occupied either at low pH by a water molecule or at high pH by an hydroxide ion. The pK_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.^{12,13}

$[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^{-}$ revealed peroxidase activity while reacting with peroxides to generate the $[\text{Ru}^{\text{V}}(\text{edta})(\text{O})]^{-}$ (ruthenium equivalents of the much discussed compound I).^{3,4} Of particular interest is the reaction of $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^{-}$ with H_2O_2 wherein the formation of $[\text{Ru}^{\text{V}}(\text{edta})(\text{O})]^{-}$ was observed spectrophotometrically since the product solution exhibited the characteristic peak of the $[\text{Ru}^{\text{V}}(\text{edta})(\text{O})]^{-}$ species at 390 nm ($\epsilon_{\text{max}} = 8000 \pm 20 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁴ However, the kinetic traces reported in Fig. S1 (see ESI†) and Fig. 2 show that less $[\text{Ru}^{\text{V}}(\text{edta})(\text{O})]^{-}$, characterized by the absorbance at 390 nm, is formed at higher H_2O_2 concentrations. In this respect, the final absorbance reached at 390 nm as a function of H_2O_2 concentration is presented in Fig. 2c. Upon close scrutiny of the kinetic traces and the absorbance data as a function of H_2O_2

Fig. 1 Pictorial representation of the $[\text{Ru}^{\text{III}}(\text{Hedta})(\text{H}_2\text{O})]^{-}$ complex.

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Fig. 2 Kinetic traces recorded for the reaction of $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ with H_2O_2 at 25 °C and pH 5.0 (10 mM acetate buffer). (a) $[\text{H}_2\text{O}_2] = 4.0$ mM, (b) $[\text{H}_2\text{O}_2] = 0.2$ M and (c) plot of absorbance at 390 nm at different $[\text{H}_2\text{O}_2]$. $[\text{Ru}^{\text{III}}] = 0.2$ mM.

concentration (Fig. S1, ESI† and Fig. 2), it is observed that the onset of the catalase activity is strongly governed by the H_2O_2 concentration. A lower concentration of $[\text{Ru}^{\text{V}}(\text{edta})(\text{O})]^-$ is required to initiate the catalase activity at higher H_2O_2 concentration. Once a steady-state concentration of $[\text{Ru}^{\text{V}}(\text{edta})(\text{O})]^-$ is attained, no appreciable spectral changes were further observed, but evolution of dioxygen (O_2) was clearly visible at the higher H_2O_2 concentration specified in Fig. 2.

The above described reaction was studied further by following the formation of dioxygen (O_2) gas chromatographically (see Fig. S2 in ESI†). The results of O_2 evolution studies at various H_2O_2 concentrations (see Fig. S3 and Table S1 in ESI†) are summarized in Table 1. It is clearly seen from Table 1 that an increase in H_2O_2 concentration increases the amount of O_2 generated in the reaction system. Furthermore, the amount of O_2 produced is close to the expected yield of 50% in terms of the amount of H_2O_2 used.

On the basis of the above observations, we further extended our studies by monitoring the time course of O_2 evolution as a function of H_2O_2 concentration at constant temperature (25 °C) and pH 5.0 (see Fig. S4 in ESI†). The initial rate of the reaction estimated from the maximum slope of the plots, increases linearly with increasing H_2O_2 concentration (see Fig. S5 in ESI†). Based on the above experimental facts and by analogy

Table 1 Results of O_2 evolution studies as a function of H_2O_2 concentration at 25 °C and pH = 5.0 (10.0 mM acetate buffer). $[\text{Ru}^{\text{III}}] = 2.0$ μmol

H_2O_2 (mmol)	O_2 produced (mmol) after 4 h
0.1	0.043
0.2	0.111
0.4	0.190
1.0	0.440
2.0	0.825

Scheme 1 Suggested mechanism for the catalytic disproportion of H_2O_2 by $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$.

with the reported mechanism for the disproportion of H_2O_2 into O_2 and H_2O , a working mechanism is proposed for the catalase activity of $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ as outlined in Scheme 1.

In the proposed reaction scheme, the reaction is initiated by binding of the oxidant H_2O_2 to the $\text{Ru}(\text{III})$ centre, producing a 'compound O' like species $[\text{Ru}^{\text{III}}(\text{edta})(\text{OOH})]^{2-}$. Heterolytic cleavage of the O–O bond in $[\text{Ru}^{\text{III}}(\text{edta})(\text{OOH})]^{2-}$ results in the formation of a 'compound I' like species $[\text{Ru}^{\text{V}}(\text{edta})(\text{O})]^-$ (step 2 in Scheme 1). In the subsequent rate-determining step, the $[\text{Ru}^{\text{V}}(\text{edta})(\text{O})]^-$ complex reacts with another molecule of H_2O_2 (in the presence of a high concentration of H_2O_2) to produce dioxygen and brings the $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ catalyst back into the catalytic cycle. Under turn-over conditions, the $[\text{Ru}^{\text{V}}(\text{edta})(\text{O})]^-$ species is immediately formed through the rapid reaction of $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ with H_2O_2 , and a steady state concentration of $[\text{Ru}^{\text{V}}(\text{edta})(\text{O})]^-$ is maintained as observed in Fig. 2a and b.

In order to substantiate the above mechanistic proposal (Scheme 1), we performed experiments wherein cysteine was used as a trap for the $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ complex. The $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ complex reacts rapidly with cysteine (CyS) to form a red coloured stable $[\text{Ru}^{\text{III}}(\text{edta})(\text{CyS})]^{2-}$ complex.^{6a} Addition of a large excess of cysteine to the greenish-yellow solution of $[\text{Ru}^{\text{V}}(\text{edta})(\text{O})]^-$ (freshly prepared by mixing solutions of $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ (0.2 mM) and H_2O_2 (0.06 M) in acetate buffer solution) immediately resulted in red coloration of the solution together with the appearance of the band at 510 nm (see Fig. 3a) characteristic for the formation of the $[\text{Ru}^{\text{III}}(\text{edta})(\text{CyS})]^{2-}$ complex. This essentially suggests the presence of free $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ in solution that rapidly reacts with cysteine to produce $[\text{Ru}^{\text{III}}(\text{edta})(\text{CyS})]^{2-}$ in the reaction system. The rapid-scan spectral measurements allowed us to further observe the decrease in absorbance at 390 nm characteristic of $[\text{Ru}^{\text{V}}(\text{edta})(\text{O})]^-$ species with time. Considering the fact that the reaction of $[\text{Ru}^{\text{V}}(\text{edta})(\text{O})]^-$ with cysteine is very slow (see Fig. S6 in ESI†),^{6a} the decrease in intensity of the peak at 390 nm (Fig. 3b) can be accounted for in terms of reactions (4) and (5).

Fig. 3 (a) UV-Vis spectral changes observed in the reaction of $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ (0.2 mM) with H_2O_2 (0.06 M) at 25 °C and pH 5.0 (10 mM acetate buffer) in the presence of cysteine (0.06 M). (b) Kinetic trace recorded for the reaction at 390 nm.

In presence of cysteine, the catalase activity of $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ is not observed anymore since $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ produced by the reaction of $[\text{Ru}^{\text{V}}(\text{edta})\text{O}]^-$ with H_2O_2 (eqn (4)) cannot participate in the catalytic cycle (Scheme 1) as it is rapidly trapped by the excess cysteine that results in the formation of $[\text{Ru}^{\text{III}}(\text{edta})(\text{Cys})]^{2-}$ (eqn (5)). No trace of gas bubbles related to the formation of O_2 was observed during the entire course of the reaction.

We have further assessed the catalase activity of $[\text{Ru}^{\text{V}}(\text{edta})\text{O}]^-$ by studying the reaction of $[\text{Ru}^{\text{V}}(\text{edta})\text{O}]^-$ (prepared independently by reacting $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ with KHSO_5) with H_2O_2 at high concentration. The reaction of $[\text{Ru}^{\text{V}}(\text{edta})\text{O}]^-$ (0.2 mM) with H_2O_2 (40 mM) produced 0.2 mmol of O_2 gas at the end of the reaction, supporting the fact that $[\text{Ru}^{\text{V}}(\text{edta})\text{O}]^-$ is responsible for the observed catalase activity.

Based on the above experimental observations the following rate-law can be derived on the basis of the rate-determining evolution of O_2 (eqn (3) in Scheme 1) monitored gas chromatographically.

$$\text{rate} = d[\text{O}_2]/dt = k_{\text{cat}}[\text{Ru}^{\text{V}}(\text{edta})\text{O}]^-[\text{H}_2\text{O}_2] \quad (6)$$

The linear dependence of the rate on $[\text{H}_2\text{O}_2]$ (see Fig. S5 in ESI†) in the presence of excess H_2O_2 ($[\text{H}_2\text{O}_2] \gg [\text{Ru}^{\text{III}}]$) is in line with the suggested mechanism. Since the steady-state concentration of $[\text{Ru}^{\text{V}}(\text{edta})\text{O}]^-$ changes with change in $[\text{H}_2\text{O}_2]$, the value of the second-order rate constant (k_{cat}) is estimated by using the slope of the plot of $\text{rate}/[\text{Ru}^{\text{V}}(\text{edta})\text{O}]^-$ versus $[\text{H}_2\text{O}_2]$ (see Fig. S7 in ESI†) to be $0.7 \pm 0.05 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C and pH 5.0.

The temperature dependence of k_{cat} was investigated at pH 5.0, and the values of k_{cat} so estimated from the plots of $\text{rate}/[\text{Ru}^{\text{V}}(\text{edta})\text{O}]^-$ versus H_2O_2 concentration (see Fig. S7 in ESI†)

are 0.42 ± 0.02 , 0.57 ± 0.03 , $0.70 \pm 0.05 \text{ M}^{-1} \text{ s}^{-1}$ and $1.1 \pm 0.3 \text{ M}^{-1} \text{ s}^{-1}$ at 15, 20, 25 and 30 °C, respectively. The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ determined from the Eyring plot (see Fig. S8 in ESI†) are $50 \pm 5 \text{ kJ mol}^{-1}$ and $-78 \pm 13 \text{ J mol}^{-1} \text{ deg}^{-1}$, respectively. The values of activation parameters are comparable to those reported for the reduction of $[\text{Ru}^{\text{V}}(\text{edta})\text{O}]^-$ by ascorbate.¹⁵ and consistent with the outer-sphere electron transfer reaction between a negatively charged ($[\text{Ru}^{\text{V}}(\text{edta})\text{O}]^-$) and electrically neutral (H_2O_2) reactant molecules.

The lack of an ionic strength effect in the present reaction is in agreement with the proposed rate-determining step (eqn (3) in Scheme 1) in regard to the Bronsted equation¹⁶ for a reaction between a charged and a neutral reactant. However, the increase in the O_2 evolution on going from Li^+ to Na^+ to K^+ (see Fig. S9 in ESI†) essentially provides an evidence for the operation of an outer-sphere electron transfer process.^{17,18} It is suggested that the cation (M^+) acts as a means of bringing a negatively charged $[\text{Ru}^{\text{V}}(\text{edta})\text{O}]^-$ and neutral H_2O_2 close enough to lead to the formation of an intermediate (see Fig. S10 in ESI†), in which electron transfer through the solvent takes place in an outer-sphere manner. Considering the size of the hydrated cations which is in the order: $\text{Li}^+ > \text{Na}^+ > \text{K}^+$, the K^+ would be more effective than Na^+ or Li^+ in bringing the reacting species close enough, and thus facilitating the electron transfer process. It is noteworthy here that the initial rate of O_2 evolution did not change appreciably when the reaction was performed in a mixture of H_2O and D_2O (1 : 1 v/v ratio).

We have further examined the effect of pH on the catalase type activity of the $\text{Ru}(\text{edta})$ complex, and found a decrease in the O_2 evolution rate at pH higher than 6.0 (see Fig. S11 in ESI†). This is due to the fact that $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ (that exists predominantly in the pH range 4–6) is much more labile to react with H_2O_2 leading to formation of $[\text{Ru}^{\text{III}}(\text{edta})(\text{OOH})]^{2-}$ species (which governs the efficiency of the catalytic process by producing the catalytically active $[\text{Ru}^{\text{V}}(\text{edta})\text{O}]^-$ species) than its corresponding hydroxo species, $[\text{Ru}^{\text{III}}(\text{edta})(\text{OH})]^{2-}$.

Although it is difficult to compare quantitatively this catalytic system to others as the experimental conditions vary widely from one system to another, the efficacy of the present catalytic system in terms of the initial rate of O_2 evolution is indicated in Table 2. The results show that the $\text{Ru}^{\text{III}}(\text{edta})$ system shows significant catalytic activity that is only surpassed by the $\text{Fe}^{\text{III}}(\text{TAML})$ system.

In summary, we report the first example of a $\text{Ru}(\text{III})$ complex capable of exhibiting catalase type activity with the production

Table 2 Rate constant data at 25 °C for O_2 evolution during H_2O_2 decomposition induced by some mono-nuclear transition metal complexes in aqueous solution

Catalyst	k	Ref.
$\text{Cu}(\text{II})$ -bipy complex	$6.8 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$	19
$\text{Mn}(\text{II})$ -bpy complex	$3.2 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$	20
$\text{Mn}(\text{III})$ -Schiff base complex	$0.34 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$	21
$\text{Fe}(\text{III})$ -PTS complex	$0.2 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$	22
$\text{Fe}(\text{III})$ -TAML complex	$1.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	23
$\text{Co}(\text{III})$ -hematoporphyrin	$6.76 \times 10^{-2} \text{ s}^{-1}$	24
$\text{Ru}(\text{III})$ -edta complex	$0.7 \text{ M}^{-1} \text{ s}^{-1}$	This work

of dioxygen under ambient conditions. Considering that $[\text{Ru}^{\text{V}}(\text{edta})(\text{O})]^-$ is the catalytically active species responsible for H_2O_2 disproportionation, the catalytic turn-over number (TON) achieved is 1400 under optimal catalytic conditions. The results of the present investigation indicates future prospects of ruthenium(III) complexes in catalase mimicking activity. Research pertinent to the above issues is in progress.

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