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# **Graphical Abstract**

# **Ru(EDTA)** mediated partial reduction of O<sub>2</sub> by H<sub>2</sub>S

## Debabrata Chatterjee\* Namita Jaiswal and Papyia Sarkar



# **Ru(EDTA)** mediated partial reduction of $O_2$ by $H_2S^{\dagger}$

Debabrata Chatterjee\* Namita Jaiswal and Papyia Sarkar

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An effective procedure for selective reduction of  $O_2$  to  $H_2O_2$  exploring the use of hydrogen sulfide, an obnoxious industrial pollutant as reductant is reported herein. The reduction of [Ru<sup>III</sup>(EDTA)pz]  $(EDTA^4 = ethylenediaminetetraacetate; pz = pyrazine)$  by hydrogen sulfide resulting in the formation of a red  $[Ru^{II}(EDTA)pz]^{2-}$  complex ( $\lambda_{max} = 462$  nm) has been studied spectrophotometrically and 10 kinetically using both rapid scan and stopped-flow techniques. The time course of the reaction was followed as a function of [HS<sup>-</sup>]<sub>i</sub>, pH (5.5 - 8.5), and temperature. Alkali metal ions were found to have a positive influence ( $K^+ > Na^+ > Li^+$ ) on the reaction rate. Kinetic data and activation parameters are interpreted in terms of a mechanism (admittedly speculative) involving outer-sphere electron transfer between the reaction partners. Reaction of red  $[Ru^{II}(EDTA)pz]^{2-}$  complex with molecular oxygen 15 regenerates the [Ru<sup>III</sup>(EDTA)pz]<sup>-</sup> species in the reacting system along with the formation of H<sub>2</sub>O<sub>2</sub>, a

partially reduced product of dioxygen  $(O_2)$  reduction. A detailed reaction mechanism in agreement with the spectral and kinetic data is presented.

### Introduction

Development of metal complexes as catalyst for the oxygen <sup>20</sup> reduction reaction (ORR) is of continued interest <sup>1</sup> in its own right and in the context of life processes such as biological respiration, 55 and various beneficial effects of H<sub>2</sub>S in our bodies have recently and in energy converting systems such as fuel cells. In this regard use of H<sub>2</sub>S, an obnoxious industrial pollutant as an effective reducing agent was exemplified long back by the Claus process' in 25 which O<sub>2</sub> is reduced directly to H<sub>2</sub>O by undergoing 4-electron

reduction.<sup>2</sup>



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Fig. 1 Pictorial representation of the [Ru<sup>III</sup>(HEDTA)(H<sub>2</sub>O)] complex

- 40 In recent past we have shown that Ru(EDTA) complex could act as an efficient electron transfer and O-atom transfer agent for effecting oxidation of biologically important thiols (cysteine, glutathione).<sup>3</sup> The Ru(EDTA) complexes have been proposed as alternatives to Pt(II) anti-tumour agents, as reported in several 75
- 45 reviews.<sup>4</sup> Electron transfer reaction leading to the reduction of Ru(III) to Ru(II) assumes immense importance as tumour cell metabolism favours the presence of Ru(II) relative to Ru(III), thus increasing the selective tumour toxicity.<sup>5a</sup> Furthermore, metabolic conditions such as hypoxia in tumour cells provide a more 80 <sup>50</sup> reductive environment than is found in normal tissue.<sup>5b</sup> In the

present studies we have explored the possibility of using the hydrogen sulfide in the catalytic scheme on the selective reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>. It is noteworthy, hydrogen sulfide, the smallest thiol is now believed to be an important redox-signaling molecule, been recognized.6

In the present work, we have undertaken a detailed kinetic and mechanistic investigation of the reduction of [Ru<sup>III</sup>(EDTA)pz]<sup>-</sup> to [Ru<sup>II</sup>(EDTA)pz]<sup>2-</sup> with hydrogen sulfide, and reoxidation of  $_{60}$  [Ru<sup>II</sup>(EDTA)pz]<sup>2-</sup> by molecular oxygen, O<sub>2</sub>. The reason for choosing [Ru<sup>III</sup>(EDTA)pz] complex for the present investigation is the substantial spectral difference between Ru(III)- and Ru(II)species affording an amenable way for the kinetic studies. The results of these studies together allow rationalization of the 65 Ru(EDTA) mediated catalysis of dioxygen (O<sub>2</sub>) reduction to hydrogen peroxide  $(H_2O_2)$  using hydrogen sulfide  $(H_2S)$  as reducing agent.

## Experimental

#### Materials

70 K[Ru<sup>III</sup>(HEDTA)Cl].2H<sub>2</sub>O was synthesized according to the published procedure.<sup>7</sup> Anal. calculated for K[Ru<sup>III</sup>(HEDTA)Cl]. 2H<sub>2</sub>O: C 24.0, H 3.42, N 5.59; Found. C 23.8, H 3.45, N 5.63. IR, v/cm<sup>-1</sup>: 1720 (free -COOH), 1650 (coordinated -COO<sup>-</sup>). UV-Vis in H<sub>2</sub>O:  $\lambda_{max}/nm (\epsilon_{max}/M^{-1} \text{ cm}^{-1})$ : 283 (2800 ± 50), 350 sh (680 ± 10). The K[Ru<sup>III</sup>(HEDTA)Cl] complex rapidly converts into the [Ru<sup>III</sup>(HEDTA)(H<sub>2</sub>O)] complex when dissolved in water.<sup>8,9</sup> The sixth coordination site of the ruthenium complex is occupied either at low pH by a water molecule (Fig. 1) or at high pH by a hydroxide ion. The pK<sub>a</sub> 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.<sup>8,9</sup> The  $[Ru^{III}(EDTA)pz]$  complex can very easily be prepared by mixing on the kinetic profile (time versus absorbance traces at 462 nm) is equimolar amounts of [Ru<sup>III</sup>(EDTA)(H<sub>2</sub>O)]<sup>-</sup> and pyrazine (pz) 55 typically displayed in Fig. 2b. through a very rapid and straightforward water substitution

- reaction ( $k = 2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C).<sup>8</sup> Details of the spectral and s electrochemical properties of [Ru<sup>III/II</sup>(EDTA)(pz)])<sup>-/2-</sup> complexes were reported in the earlier papers.<sup>8</sup> The absorption spectrum of  $_{60}$ the ruthenium(III) species is almost featureless above 390 nm, whereas the ruthenium(II) complex exhibits a strong characteristic metal-to-ligand charge transfer band in the visible region ( $\lambda_{max}$  =
- $10 462 \text{ nm}, \varepsilon_{\text{max}} = 11,000 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>8</sup> All other chemicals used were 65 maxof A.R grade and of the highest purity available. Experimental solutions of sodium bisulfide (Sigma Aldrich) were prepared by using argon saturated doubly distilled water, and their concentration was determined by iodometric titration.<sup>10 70</sup> 15 Concentration of bisulfide is expressed as initial concentration of bisulfide ([HS<sup>-</sup>]<sub>i</sub>). Considering pKa values (pKa<sub>1</sub> = 7.02 and  $pKa_2 \sim 17.1$ )<sup>11,12</sup> of related to the proton dissociation equilibria of \_\_\_\_\_  $H_2S$ , it is presumed that at pH > 8.0 presence of  $H_2S$  and  $S^{2-}$  in the solution is insignificant, whereas, at  $pH < 6.0 H_2S$  is the most 20 predominant reacting species. Gas-tight Hamilton syringes were used to transfer these solutions throughout our studies. 80

#### Instrumentation

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UV-vis absorption spectra were recorded on a Varian Model Cary 100 spectrophotometer using 1 cm path standard quartz cells. 85 25 Stopped-flow experiments were carried out with a Hi-Tech SF-61 SX2 (TgK Scientific Ltd.) spectrophotometer using a 1 cm optical path length. The reaction of [Ru<sup>III</sup>(EDTA)(pz)] with hydrogen sulfide was followed at 462 nm. Single wavelength kinetic profiles were collected in the photomultiplier mode by following the <sup>30</sup> appearance of  $[Ru^{II}(EDTA)pz]^{2-}$  at 462 nm, and data were processed using Hi-Tech KinetAsyst 3 software. Time-resolved UV-vis spectra were recorded with a Hi-Tech SF-61 SX2 (TgK 95 Scientific Ltd.) spectrophotometer equipped with a rapid scan diode array spectral attachment (KinetaScan). The solution 35 temperature was regulated with a thermostat water bath (JEIO TECH RW-1025G) within ±0.1 °C. The pH of the solutions was measured with a Mettler Delta 350 pH meter. Acetate, phosphate<sup>100</sup> and borate buffers were used to control the pH of the experimental solutions. NaCl was used to control the ionic strength. LiCl and

40 KCl were used to investigate the effect of varying the alkali metal cations. Kinetic data are presented as an average of several kinetic runs (at least 3-5) and were reproducible within  $\pm 4$  %.

## Results and discussion

Reaction of [Ru<sup>III</sup>(EDTA)pz]<sup>-</sup> with hydrogen sulfide was 45 carried out strictly under argon atmosphere. Addition of argon purged solution of NaHS to the pale-yellow solution of [Ru<sup>III</sup>(EDTA)pz]<sup>-</sup> (prepared by mixing the argon purged solutions of [Ru<sup>III</sup>(EDTA)(H<sub>2</sub>O)] and pyrazine in an equimolar ratio) at pH 8.5 (phosphate buffer) resulted in rapid changes of the spectral 50 features as shown typically in Fig. 2a. The observed spectral changes are ascribed to the formation of  $[Ru^{II}(EDTA)pz]^{2}$  via reduction of  $[Ru^{II}(EDTA)pz]^{-}$  by HS<sup>-</sup> under the specified <sup>105</sup> Fig. 3 Effect of [HS<sup>-</sup>]<sub>i</sub> on the rate of formation of  $[Ru^{II}(EDTA)(pz)]^{2-}$  at 25 conditions. The effect of concentration of bisulfide concentration



Fig. 2 (a) UV-Vis spectral changes for the reaction of [Ru<sup>III</sup>(EDTA)(pz)]<sup>-</sup> (0.2 mM) with HS (2.0 mM), (b) kinetic traces (recorded at 462 nm) at various [HS<sup>-</sup>]<sub>i</sub> at 25 °C, [Ru<sup>III</sup>] = 0.2 mM, pH 8.5 (phorphate buffer)

At a constant pH of 8.5 the rate of reduction estimated from the maximum slope of the kinetic traces (Fig. 2b), increases linearly (Fig. 3) with increasing initial concentration of bisulfide ([HS]<sub>i</sub>). Based on the above experimental observations, and considering that HS is the dominant reacting species at pH 8.5 a working mechanism is proposed in Scheme 1 for the reduction of [Ru<sup>III</sup>(EDTA)(pz)]<sup>-</sup> with HS<sup>-</sup>.



The rate determining step (1) proposed in the above mechanism involves one-electron transfer from HS to ruthenium(III) complex in an outer-sphere manner to yield the  $_{55}$  41  $\pm$  2, 50  $\pm$  2, and 70  $\pm$  2 M<sup>-1</sup> s<sup>-1</sup> at 15, 20, 25 and 30 °C, ruthenium(II) complex and the HS<sup>•</sup> radical. Reduction of another 5 molecule of ruthenium(III) complex by HS<sup>•</sup> radical occurred in a subsequent rapid and kinetically inconsequential step as outlined in Eq 2. Formation of colloidal sulfur in the reacting system was visible at the end of the reaction.

 $[Ru^{III}(EDTA)pz]^{-} + HS^{-} \xrightarrow{k_{red}} [Ru^{II}(EDTA)(pz)]^{2-} + HS^{\bullet}$ 

 $[Ru^{III}(EDTA)pz]^{-} + HS^{\bullet} \longrightarrow [Ru^{II}(EDTA)(pz)]^{2-} + S + H^{+}$ 

#### 10 Scheme 1 Mechanism for the reduction of [Ru<sup>III</sup>(EDTA)(pz)]<sup>-</sup> by HS<sup>-</sup>

Electron transfer reaction involving [Ru<sup>III</sup>(EDTA)(pz)]<sup>-</sup> complex generally occurs in an outersphere manner.<sup>3a,13,14</sup> In order to substantiate the occurrence of outersphere electron transfer 15 reaction in the present case we have examined the role of alkali cations on the rate of reduction of [Ru<sup>III</sup>(EDTA)pz]<sup>-</sup> by HS<sup>-</sup> at pH 8.5. The positive effect of alkali metal cations on the electron transfer rate for a reaction of two negatively charged reacting species occurring through an outer-sphere manner is well 20 documented in the literature.<sup>15-18</sup> It had been reported that the so cation acts as a bridge or as a means of allowing two negatively charged reacting ions close enough to form a triple ion, and thus facilitating the electron transfer process.<sup>15-18</sup> In the present case, the observed increase in the reaction rate on going from Li<sup>+</sup> to Na<sup>+</sup>  $_{25}$  to K<sup>+</sup> (see Fig.S1 in ESI) essentially support the argument in  $_{85}$  resulted in a gradual drop of the spectral features (Fig. 5a) favour of the outersphere electron transfer reaction. Considering the size of hydrated cations which is in the order:  $Li^+ > Na^+ > K^+$ , the K<sup>+</sup> would be more effective than Na<sup>+</sup> or Li<sup>+</sup> in bringing the reacting species close enough in forming the triplet-ion species 30 ([Ru<sup>III</sup>(EDTA)(pz)]<sup>-</sup>--M<sup>+</sup>--HS<sup>-</sup>), and thus facilitating the electron of transfer reaction as typically revealed by the increase in the

reaction rate in the present studies (see Fig.S1 in ESI).

Considering two molecules of [Ru<sup>III</sup>(EDTA)(pz)]<sup>2-</sup> is produced by one HS<sup>-</sup> as outlined in Scheme 1, the following rate-35 law can be derived on the basis of the rate-determining appearance of the [Ru<sup>III</sup>(EDTA)(pz)]<sup>2-</sup> complex monitored at 462 nm.

> rate =2  $k_{red} [Ru^{III}(edta)(pz)^{-}][HS^{-}]$ (3)

The linear dependence of the rate on [HS<sup>-</sup>] (Fig. 3) is in line with the suggested mechanism. The value of the second-order rate constant (k<sub>red</sub>) estimated using the slope of the plot of rate versus  $_{45}$  [HS<sup>-</sup>] (as shown in Fig. 3) is 50 ± 1 M<sup>-1</sup> s<sup>-1</sup> at 25 °C and pH 8.5. However, at lower pH (5.5) the rate of the reduction of 105 [Ru<sup>III</sup>(EDTA)(pz)]<sup>-</sup> by hydrogen sulfide was found to be considerably slower as revealed by the time versus absorbance trace (see Fig.S2). The observed decrease in reaction rate at lower

50 pH, is understandable by the fact that the reducing ability of  $H_2S$ , 110 which is the major reacting species at pH 5.5 ( $pK_1$  of  $H_2S$  is  $(7.02)^{11}$  appreciably lesser from that of its conjugate base HS<sup>-19</sup>

The temperature dependence of k<sub>red</sub> was investigated from 15 to 30 °C at pH 8.5, and the values of  $k_{red}$  so estimated are 29 ± 1, respectively. The values of  $\Delta H^{\neq}$  and  $\Delta S^{\neq}$  determined from the Evring plot (Fig.4) are  $39 \pm 2$  kJ mol<sup>-1</sup> and  $-60 \pm 6$  J mol<sup>-1</sup> deg<sup>-1</sup>. respectively are quite comparable with the  $\Delta H^{\neq}$  and  $\Delta S^{\neq}$  values reported for the reduction of [Ru<sup>III</sup>(EDTA)(pz)]<sup>-</sup> by negatively 60 charged reductants,<sup>13,14</sup> and consistent with the proposed rate law.



Fig. 4 Eyring plot for the reduction of [Ru<sup>III</sup>(EDTA)(pz)]<sup>-</sup> with HS<sup>-</sup> at pH 8.5 (phosphate buffer).

The  $[Ru^{II}(EDTA)(pz)]^{2-}$  complex was found to be unstable when exposed to the oxygen atmosphere. Addition of oxygen saturated solution of acetate buffer (1mM) to the red solution of [Ru<sup>II</sup>(EDTA)(pz)]<sup>2-</sup> (prepared by mixing the solutions of  $[Ru^{III}(EDTA)(pz)]^{-}$  and NaHS in an equimolar ratio at pH 5.5) characteristic of the [Ru<sup>III</sup>(EDTA)(pz)]<sup>2-</sup> complex.



Fig. 5 (a) Spectral changes for the oxidation of [Ru<sup>II</sup>(EDTA)(pz)]<sup>-</sup> (0.05 mM) with O<sub>2</sub>, (b) kinetic traces (recorded at 462 nm) at different [HS<sup>-</sup>]<sub>i</sub> at 25 °C, pH 5.5 (acetate buffer).

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The observed spectral changes (Fig. 5a) are attributed to the oxidation the  $[Ru^{II}(EDTA)(pz)]^{2}$ complex of to [Ru<sup>III</sup>(EDTA)(pz)]<sup>-</sup> by O<sub>2</sub> under the specified conditions. Absorbance-time traces shown in Fig. 5b exhibit an initial s induction period at higher hydrogen sulfide concentration which could be explicable in terms of the reformation of the [Ru<sup>II</sup>(EDTA)(pz)]<sup>2-</sup> complex in the presence of excess of HS<sup>-</sup> 55 DC is thankful to Dr. P Pal Roy, Director of the Central under the specified conditions. Appearance of the induction period as a result of the continued reformation of [Ru<sup>II</sup>(EDTA)(pz)]<sup>2-</sup>

10 indicating recycling of the catalyst complex at higher hydrogen sulfide concentration. Above observations clearly indicate the occurrence of a catalytic process (Scheme 2) in the reduction of dioxygen (O<sub>2</sub>) by H<sub>2</sub>S in presence of [Ru<sup>III</sup>(edta)(pz)]<sup>-</sup> as catalyst.



Scheme 2 Mechanism for the reduction of O<sub>2</sub> by H<sub>2</sub>S mediated by of 20 [Ru<sup>III</sup>(EDTA)(pz)]<sup>-</sup>.

While elemental sulfur, a two-electron oxidation product of 75 H<sub>2</sub>S visibly appeared in the reacting system at the end of the reaction, formation of H<sub>2</sub>O<sub>2</sub>, a two-electron reduction product of  $_{\rm 25}~O_2$  was confirmed by permanganate titration.  $^{20}~No~H_2O_2$  was detected in absence of Ru(EDTA) complex in the reacting system. However, formation of H2O2 with 88% yield (0.22 mM) was evidenced when 0.25 mM of NaHS was used as reductant in presence of Ru(EDTA) catalyst (0.05mM). Above results establish 30 the fact that the studied reaction is catalytic in nature. Considering

- $[Ru^{II}(EDTA)(pz)]^{2-}$  complex is the catalytic active species responsible for H<sub>2</sub>O<sub>2</sub> production, the catalytic turn-over number (TON) achieved is 4.2 under the employed conditions (as specified 90 6. under Fig.5b). Addition of L-ascorbic acid (a stronger reducing
- 35 agent) to the resultant solution immediately recovered the spectral features of the [Ru<sup>II</sup>(EDTA)(pz)]<sup>2-</sup> complex almost quantitatively which supports the fact that the Ru(EDTA) catalyst is not degraded 95 under turn-over conditions.

# Conclusions

- <sup>40</sup> In the present study, we have conclusively demonstrated that the [Ru<sup>III</sup>(EDTA)(pz)]<sup>-</sup> complex can effectively and readily be reduced to the corresponding ruthenium(II) complex by hydrogen sulfide. <sup>2543.</sup> D. Chatterjee, J. Chem. Soc., Dalton Trans., 1996, 4389 The proposed outersphere mechanism is admittedly speculative as other mechanisms with the evidence presented herein cannot be
- Reoxidation of  $[Ru^{II}(EDTA)(pz)]^{2-}$  complex 45 ruled out. accompanied with the formation H2O2 and ruthenium(III) analogue110 could be achieved by molecular oxygen  $(O_2)$ . In summary, the present redox studies of Ru(EDTA) complexes containing the aromatic N-heterocyclic ligand pyrazine is definitely an instructive
- 50 beginning toward the development of more efficient ruthenium<sup>115</sup> 20.

based catalysts for the selective reduction of O2 via two oneelectron outersphere reductions to produce H<sub>2</sub>O<sub>2</sub>, which is a promising candidate for a renewable energy source.

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## Notes and references

60 Chemistry and Biomimetics Group, CSIR-Central Mechanical Engineering Research Institute, MG Avenue, Durgapur-713209, India, Fax: 91-343-2546745; Tel: 91-343-2546828; E-mail: dchat57@hotmail.com

<sup>†</sup>Electronic supplementary information (ESI) available: kinetic traces.

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