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[Ru\textsuperscript{III}(EDTA)(H\textsubscript{2}O)]\textsuperscript{-} mediated oxidation of cellular thiols by HSO\textsubscript{5}\textsuperscript{-}

Papiya Sarkar, Amrita Saha and Debabrata Chatterjee*

Fig.S1 Time resolved spectral changes for the [Ru(EDTA)(H\textsubscript{2}O)]\textsuperscript{-} catalyzed oxidation of RSH with HSO\textsubscript{5}\textsuperscript{-} at 25 °C and pH = 6.2 (10 mM phosphate buffer), [Ru\textsuperscript{III}] = 0.1 mM, [RSH] = 0.5 mM, [HSO\textsubscript{5}\textsuperscript{-}] = 2.5 mM.  (a) RSH = Cysteine, (b) RSH = Glutathione and (c) RSH = Penicillamine.
**Figure S2A** Effect of HSO₅⁻ concentration on the kinetic traces for the [Ru<sup>III</sup>(EDTA)(H₂O)]<sup>-</sup> catalyzed oxidation of RSH with HSO₅⁻ at 25 °C and pH = 6.2 (10 mM phosphate buffer), [Ru<sup>III</sup>] = 0.1 mM, [RSH] = 0.5 mM. (a) RSH = Cysteine, (b) RSH = Glutathione and (c) RSH = N-Acetylcysteine.
Figure S2B  Plot of \( k_{\text{obs}} \) versus [HSO\(_5\)^-] for the [Ru^{III}(EDTA)(H\(_2\)O)]\(^-\) catalyzed oxidation of RSH with HSO\(_5\)^- at 25 \(^\circ\)C and pH = 6.2 (10 mM phosphate buffer),  (a) RSH = Cysteine, (b) RSH = Glutathione and (c) RSH = N-Acetylcysteine
Fig. S3 Spectral changes recorded (for extended period of time) for the [Ru(EDTA)(H$_2$O)]$^-$ catalyzed oxidation of RSH with HSO$_5^-$ (RSH = Glutathione) at 25 °C and pH = 6.2 (1 mM phosphate buffer). [Ru$^{III}$] = 0.1 mM, [RSH] = 1.0 mM, [HSO$_5^-$] = 5.0 mM

S4. We have carried the following preliminary experiments prior to the HPLC analysis for the product(s) of the catalytic reaction mixture. We did not notice any spectral changes by mixing the solutions of RSH and HSO$_5^-$ as seen in Fig. S4a.

Figure S4a Spectra of (—) aqueous solutions of cysteine (1.0 mM) and HSO$_5^-$ (10 mM) taken in the two compartments of a tandem cell, respectively and (—) after mixing the two solutions in the cell. pH 6.2 (phosphate buffer).
We performed HPLC analysis of the controlled solutions as well as reaction mixtures. HPLC analysis was carried out on a Waters HPLC (M 515 & PDA) coupled with a photodiode array detector and a symmetry C18 (5 mm, 100 A) column. Elutions were performed using an HPLC-grade water–acetonitrile mixture (70 : 30 v/v) as the mobile phase at a flow rate of 0.5 mL min$^{-1}$. HPLC parameters were calibrated with authentic samples of thiols (RSH = CySH, GSH, PSH and Na-AcCySH) and two of the disulfide products CysSSCys and GSSG.

Followings are the results:

**Figure S4b**  HPLC of 1mM solution of CySH (CySH = cysteine). RT (Retention time) = 3.836

**Figure S4c**  HPLC of 1mM solution of CySSCy. RT = 3.623
Figure S4d  HPLC of the reaction mixture containing CySH (1mM) and HSO₅⁻ (2.5 mM). The reaction mixture was subjected to HPLC analysis after 10 min of mixing. (CySH = cysteine). Peaks at 3.822 and 3.669 are assigned to the peaks of CySH and CySSCy, respectively. (Control experiment in absence of the ruthenium(III) catalyst complex)

Figure S4e  HPLC of the reaction mixture containing [RuIII(EDTA)(H₂O)]⁺ (0.1 mM), CySH (1mM) and HSO₅⁻ (2.5 mM). The reaction mixture was subjected to HPLC analysis after 1 min of reaction. (CySH = cysteine). Peaks at 3.891 and 3.666 are assigned to the peaks of CySH and CySSCy, respectively.
Figure S4f  HPLC of 1mM solution of GSH (where GSH = glutathione). RT = 4.434

Figure S4g  HPLC of 1mM solution of GSSG. RT = 3.835
**Figure S4h**  HPLC of the reaction mixture containing [Ru<sup>III</sup>(EDTA)(H<sub>2</sub>O)]<sup>-</sup> (0.1 mM), GSH (1mM) and HSO<sub>3</sub>- (2.5 mM). The reaction mixture was subjected to HPLC analysis after 1 min of reaction. (GSH = glutathione). Peaks at 4.363 and 3.842 are assigned to the peaks of GSH and GSSG, respectively.

**Figure S4i**  HPLC of 1mM solution of N-AcCySH (N-AcCySH = N-acetylcysteine). RT = 3.365
**Figure S4j**  HPLC of the reaction mixture containing \([\text{Ru}^{III}(\text{EDTA})(\text{H}_2\text{O})]^-\) (0.1 mM), N-AcCySH (1 mM) and HSO\(_4^−\) (2.5 mM). The reaction mixture was subjected to HPLC analysis after 10 min of reaction. (N-AcCySH = N-acetylcysteine). Peaks at 3.343 and 2.817 are assigned to the peaks of N-AcCySH and N-AcCySSCyAc-N, respectively.

**Figure S4k**  HPLC of 1 mM PSH (PSH = penicillamine) 1 mM) RT (PSH) = 2.772.
HPLC of the reaction mixture containing [Ru(EDTA)(H$_2$O)]$^{2+}$ (0.1 mM), PSH (1mM) and HSO$_5^-$ (2.5 mM). The reaction mixture was subjected to HPLC analysis after 10 min of reaction. (PSH = Penicillamine). Peaks at 2.764 and 2.486 are assigned to the peaks of PSH and PSSP, respectively.

In order to further support towards formation of the disulfido products (RSSR) for the oxidation N-acetylcysteine and penicillamine ESI-MS studies of the reaction mixture reaction mixture obtained at the end of the catalytic oxidation reaction were performed. Electrospray Ionization Mass Spectral (ESI-MS) measurements were performed on a Q-TOF MS (Waters, USA) with positive ion ESI mode. The applied capillary voltage was 3000 V.

**Figure S4m** ESI-MS spectra of the reaction mixture obtained at the end of the catalytic oxidation of (a) N-acetylcysteine and (b) penicillamine.
Figure S5 Plots of ln(k_{\text{ox}}/T) vs. 1/T for the [Ru^{III}(EDTA)(H_2O)]^+ catalyzed oxidation of thols, RSH by \text{HSO}_5^-. For (a) RSH = Cysteine, (b) RSH = Glutathione, (c) RSH = N-Acetylcysteine and (d) RSH = Penicillamine.