Electronic Supporting Information

Oxidation of thiocyanate with H_2O_2 catalyzed by $[Ru^{III}(edta)(H_2O)]^{-\dagger}$

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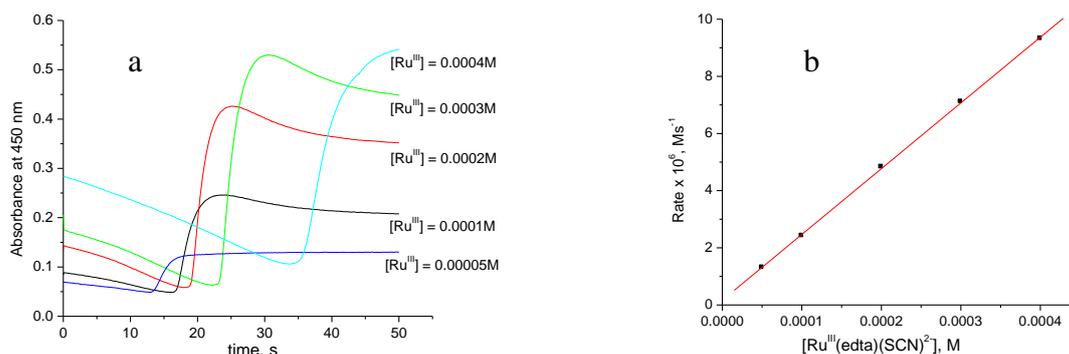
Figure S1. (a) Absorption vs. time trace for the oxidation of thiocyanate with H_2O_2 at varied $[Ru^{III}(edta)(SCN)]^{2-}$ concentration and (b) plot of rate vs. [Ru-complex] at, pH 4.3 (1 mM acetate buffer) and 25 °C. $[H_2O_2] = 20$ mM

Table S1 Rate data (used in **Figure S1b**) estimated from **Figure S1a** at varied $[Ru^{III}]$

$[Ru^{III}]$, M	10^6 Rate, Ms^{-1}
5×10^{-5} M	1.31 ± 0.02
1×10^{-4} M	2.42 ± 0.02
2×10^{-4} M	4.83 ± 0.04
3×10^{-4} M	7.11 ± 0.04
4×10^{-4} M	9.32 ± 0.05
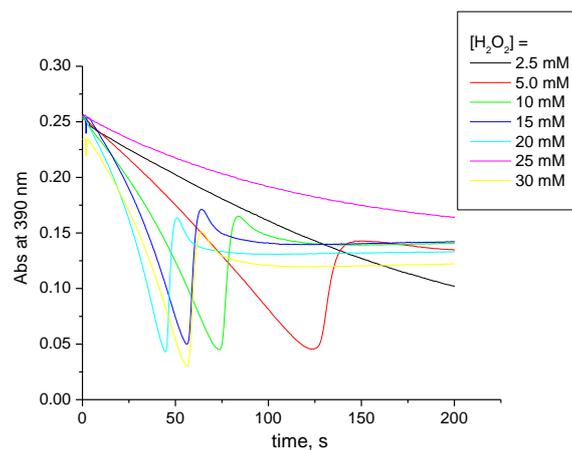
Figure S2. Time vs. absorption trace for the oxidation of thiocyanate with at varied [H_2O_2] at 25 °C. [Ru] = 2.5 x 10^{-4} M , [SCN^-] = 2.5 x 10^{-4} M, pH 4.3 (1 mM acetate buffer)

Table S2 Rate data (estimated from **Figure S2**) at various H_2O_2 concentration

[H_2O_2], M	Rate, M s^{-1}
2.5 x 10^{-3}	(0.24 ± 0.004) x 10^{-6}
5.0 x 10^{-3}	(0.67 ± 0.006) x 10^{-6}
1.0 x 10^{-2}	(2.19 ± 0.02) x 10^{-6}
1.5 x 10^{-2}	(3.73 ± 0.02) x 10^{-6}
2.0 x 10^{-2}	(5.19 ± 0.03) x 10^{-6}
2.5 x 10^{-2}	(7.11 ± 0.03) x 10^{-6}
3.0 x 10^{-2}	(8.61 ± 0.04) x 10^{-6}
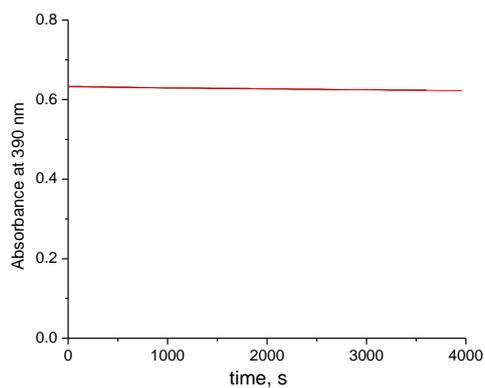
Figure S3. Time vs. absorption trace for the reaction of SCN^- (0.02M) with $[Ru^V(edta)O]^-$ (preformed by reacting $[Ru^{III}(edta)(H_2O)]^-$ and H_2O_2) at 25 °C and pH = 4.3. $[Ru^{III}] = 1.0 \times 10^{-4}$ M, $[H_2O_2] = 1.0 \times 10^{-4}$ M, $[SCN^-] = 0.02$ M.

Ru, JYOTIRMOY.   I.I.C.B KOLKATA

DB45 21 (0.221) Sm (Mn, 2x1.00); Sb (1,70.00); Cm (1:22)

(a)

364.98
380.97
206.97
202.98
211.95
413.81 435.82
516.74

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                                                                      12:50:41
                                                                      TOF MS ES+
                                                                      189

(b)

164.86
148.97
180.84
144.88
176.81
137.08
206.95
95.05
102.09
87.91
121.86
158.85 160.86
134.88
207.96
222.98
105.03
125.87
149.97
166.86
182.84 196.80
224.97 244.98 248.82
112.86
211.93
238.79
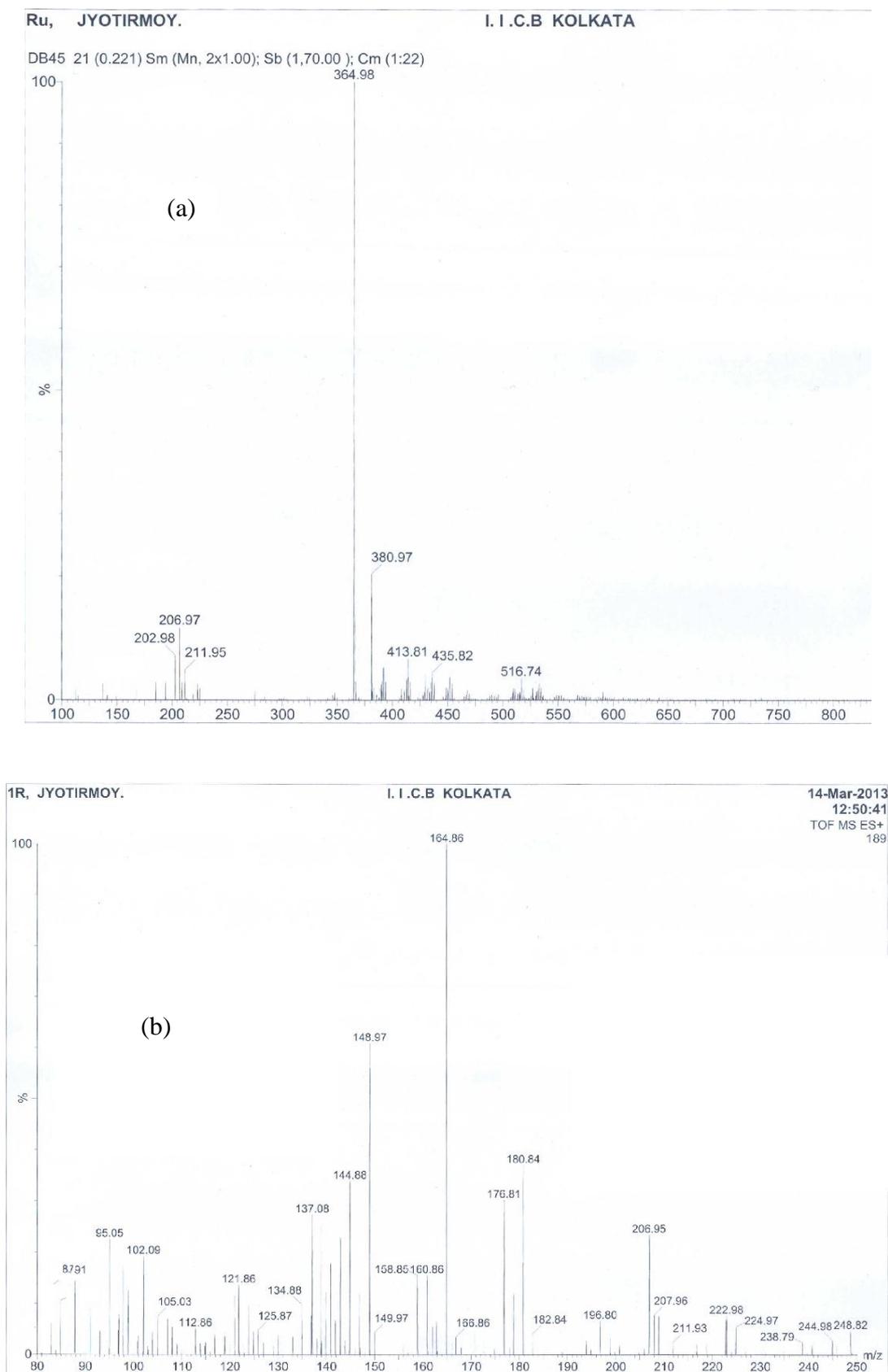
Figure S4. Results of ESI-MS studies for the oxidation of SCN$^-$ by the Ru(edta)/H$_2$O$_2$ system. (a) Reaction mixture was analyzed just after disappearance of the red colour (after 200 sec) and b) after 1 h. [Ru(edta)(H$_2$O)$^-$] = 2.0 x 10^{-4} M, [SCN$^-$] = 2 x 10^{-3} M, [H$_2$O$_2$] = 2 x 10^{-2} M, pH = 4.3 adjusted by (NaOH/HClO$_4$).

A	12.03268	0.47478
B	-4939.49045	140.23592

R	SD	N	P
-0.99919	0.01757	4	8.05062E-4

Y-axis: ln(k/T)

X-axis: 1/T
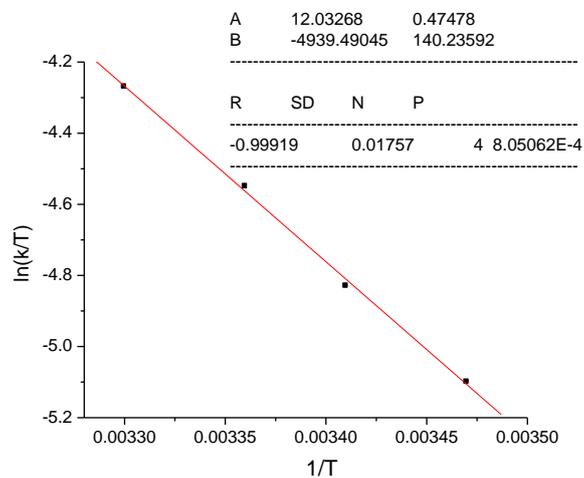
Figure S5. Eyring plot for the oxidation of SCN⁻ by the Ru(edta)/H_2O_2 system for at pH 4.3.

Table S3 Rate data (for **Figure S5**) at various temperature

Temp / °C	k, $M^{-1}s^{-1}$
15	1.78 ± 0.02
20	2.33 ± 0.03
25	3.11 ± 0.04
30	4.23 ± 0.04
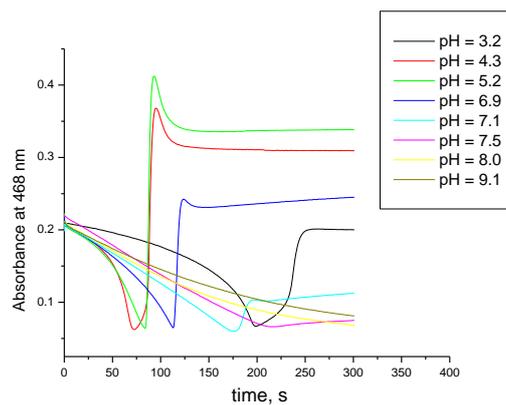
Figure S6. Effect of pH on the time vs. absorption trace for the oxidation of thiocyanate with at 25 °C. [Ru] = 2.5 x 10^{-4} M, [SCN$^-$] = 5 x 10^{-4} M, [H_2O_2] = 20 mM

Table S4   Rate data (estimated from **Figure S6**) at various pH

pH	Rate x 10^6, M s^{-1}
3.4	1.12 ± 0.04
4.3	3.71 ± 0.05
5.2	3.68 ± 0.06
5.6	3.24 ± 0.06
6.2	2.47 ± 0.05
6.7	1.44 ± 0.04
7.1	0.85 ± 0.03
7.5	0.74 ± 0.03
8.1	0.46 ± 0.02