Electronic Supporting Information (ESI)

$[Ru^{III}(edta)(H_2O)]^-$ mediated oxidation of hydroxyurea with H_2O_2. Kinetic and mechanistic investigation

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Experimental

Materials. $K[Ru^{III}(Hedta)Cl].2H_2O$ was prepared by following the published procedure,[30] and characterized by elemental analysis and spectral data which were in agreement with data reported in the literature. Anal. Calculated for $K[Ru^{III}(Hedta)Cl].2H_2O$: 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 H_2O: λ_{max}/nm ($\varepsilon_{max}/M^{-1} cm^{-1}$): 283 (2800 ± 50), 350 sh (680 ± 10). The complex rapidly hydrolyses to the aqua complex when dissolved in water, and thus exists predominantly in its most labile form $[Ru^{III}(edta)(H_2O)]^-$ (**1**) in the pH range 4 to 6. Hydrogen peroxide solutions were prepared by dilution of reagent-grade 35 % (Fluka) hydrogen peroxide and stored at 4 °C prior to use. The concentration of hydrogen peroxide was periodically determined by titration with potassium permanganate. All other chemicals used were of AR grade, and doubly distilled H_2O was used to prepare all solutions.

Instrumentation. UV-visible spectra were collected as a function of time by the use of a rapid-scanning, dual beam spectrophotometer (Specord S 600) coupled with Alalytikjena temperature controller. The measurements were made in tandem quartz cuvettes. Either a SF-61SX2 (HI-TECH) stopped-flow spectrophotometer coupled to a (KinetaScan) rapid scan spectral attachment or an Applied Photophysics SX 18.MV stopped-flow instrument coupled to an J&M rapid scan detector, and on-line data acquisition systems were used for all kinetic measurements. Kinetic measurements at high pressure were carried out using a homemade, high pressure stopped-flow system. Kinetic traces were analyzed with the OLIS KINFIT program (Bogart, GA). 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. Acetic acid-acetate buffer was used to adjust the pH of the
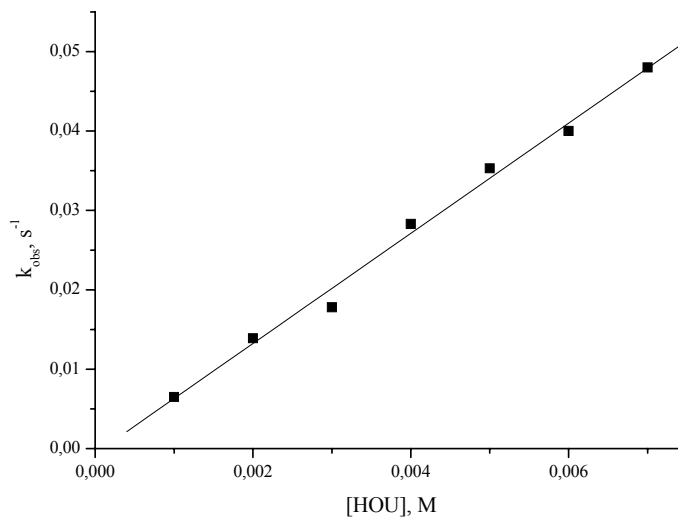
experimental solutions. Observed pseudo-first order rate constants (k_{obs}) are presented as an average of several kinetic runs (at least 10 to 12) and were reproducible within $\pm$ 4%. Estimation of nitrite and nitrate was performed on a Dionex DX 120 chromatograph. The release of NO resulting form addition of H_2O_2 to a solution of Ru-edta and HU was monitored with isolated nitric oxide meter (WP Instruments, model ISO-NO Mark II).

A.   Typical kinetic traces recorded at 370 nm for the reaction between $[Ru(edta)H_2O]^-$ (1.0 x 10^{-4} M) and HOU at 25 °C, pH = 5.0 (acetate buffer), [HOU] = 2.0 x 10^{-3} M (A), [HOU] = 4.0 x 10^{-3} M (B), [HOU] = 5.0 x 10^{-3} M (C) and [HOU] = 6.0 x 10^{-3} M (D).
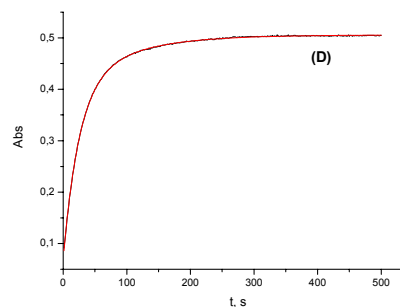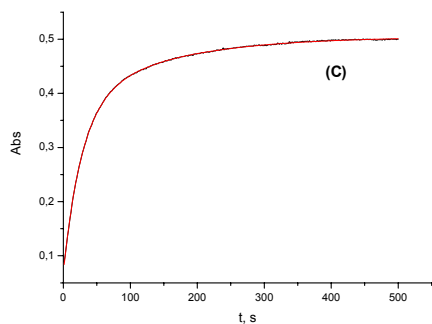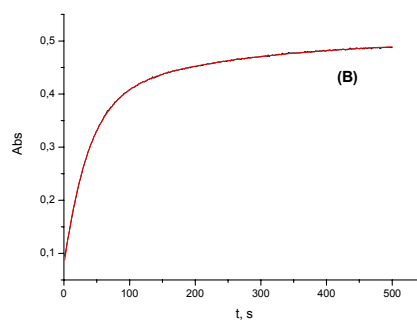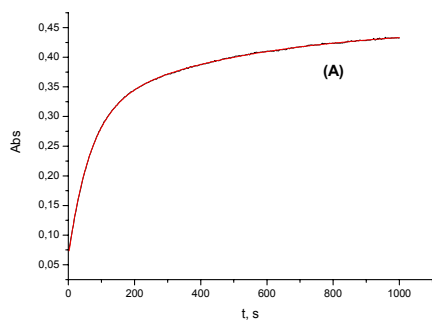
B.   Effect of [HOU] on the observed rate constant for the reaction of 1×10^{-4} M $[Ru^{III}(edta)(H_2O)]^-$ with HOU at 25 °C and pH = 5.0.

[HOU], M	k_{obs}, s^{-1}	k, M^{-1} s^{-1}
1×10^{-3}	0.0065	
2×10^{-3}	0.014	
3×10^{-3}	0.018	
4×10^{-3}	0.028	6.8 ± 0.4
5×10^{-3}	0.035	
6×10^{-3}	0.040	
7×10^{-2}	0.048	

C.   Effect of temperature on the second-order rate constant for the reaction of 1 x 10^{-4} M [Ru^{III}(edta)(H$_2$O]$^-$ with HOU at pH = 5.0.
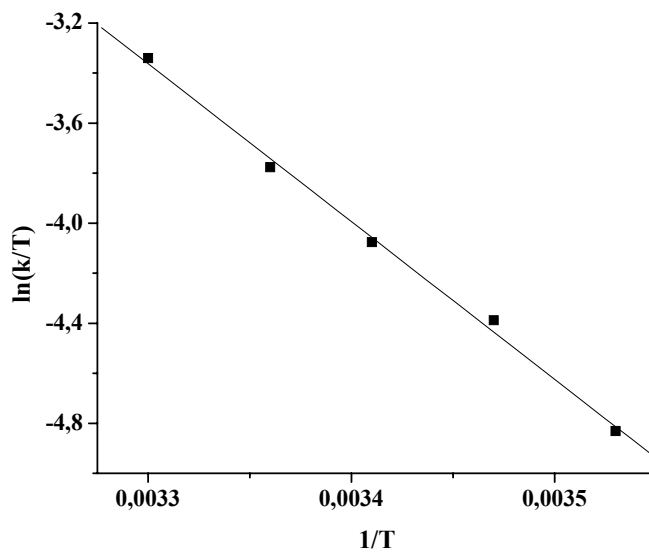
$$\Delta H^{\neq} = 52 \pm 2 \text{ kJ mol}^{-1}$$
$$\Delta S^{\neq} = -53 \pm 6 \text{ J K}^{-1} \text{mol}^{-1}$$

D.   Effect of pressure on the second-order rate constant for the reaction of 1×10^{-4} M $[Ru^{III}(edta)(H_2O)]^-$ with HOU at 25 °C and pH = 5.0.
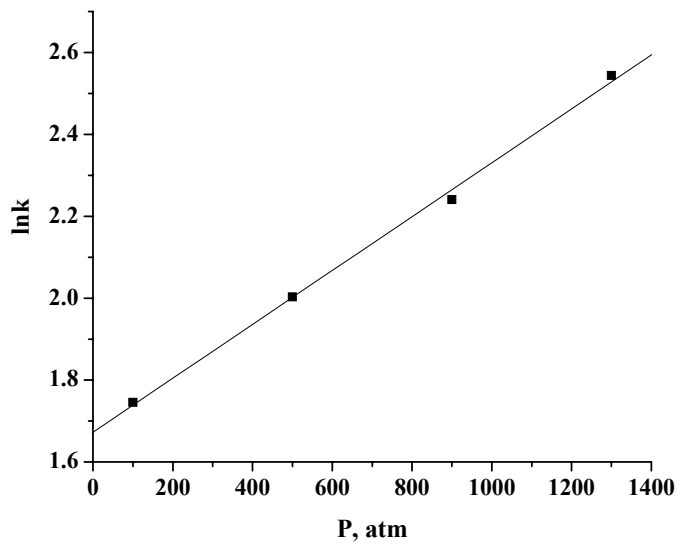
$$\Delta V^{\neq} = -16.0 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$$

E. Spectral changes that occur during the reaction of $[Ru^{III}(edta)(OU)]^{2-}$ with H_2O_2 in the presence of an excess of HOU.