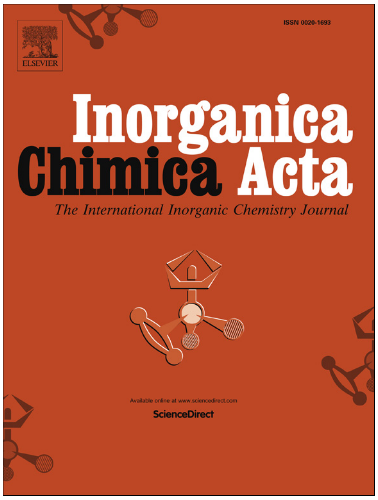

Research paper

A spectroscopic (stopped-flow UV-Vis and ^{1}H NMR Evans method) and DFT thermodynamic study of the comproportionation reaction of $[Os^{VIII}O_4(OH)_n]^{n-}$ (n = 1, 2) and $[Os^{VI}O_2(OH)_4]^{2-}$ †

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A spectroscopic (stopped-flow UV-Vis and ^{1}H NMR Evans method) and DFT thermodynamic study of the comproportionation reaction of $[Os^{VIII}O_4(OH)_n]^{n-}$ (n = 1, 2) and $[Os^{VI}O_2(OH)_4]^{2-}$ †

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From a mole ratio ^{1}H NMR Evans method experiment it is found that, in a 2.0 M NaOH aqueous matrix, diamagnetic $[Os^{VIII}O_4(OH)_n]^{n-}$ (n = 1, 2) (of d^0 electron configuration) and *trans*-$[Os^{VI}O_2(OH)_4]^{2-}$ species (d^2) react in a 1:1 mole ratio to form two paramagnetic Os^{VII} oxido/hydroxido product species (d^1). This result is further validated as the chemical reaction model that best fitted stopped-flow UV-Vis spectroscopy kinetic data is given by $[Os^{VIII}] + [Os^{VI}] \underset{k_{-COM}}{\overset{k_{COM}}{\rightleftharpoons}} 2\,[Os^{VII}]$. From non-linear least squares fits of stopped-flow UV-Vis spectroscopy kinetic traces the comproportionation reaction rate constants, activation energies (forward: $\Delta H^{\ddagger}_{(obs)}$, $\Delta S^{\ddagger}_{(obs)}$ and $\Delta G^{\ddagger}_{(obs)}$ are 10.3 ± 0.5 kcal mol^{-1}, -2.6 ± 1.6 cal mol^{-1} K^{-1} and 11.1 ± 0.9 kcal mol^{-1}, respectively; and reverse are -6.7 ± 1.0 kcal mol^{-1}, -63.6 ± 3.4 cal mol^{-1} K^{-1} and 12.2 ± 2.0 kcal mol^{-1} respectively) and standard reaction energies ($\Delta H^{\circ}_{rxn(obs)}$, $\Delta S^{\circ}_{rxn(obs)}$ and $\Delta G^{\circ}_{rxn(obs)}$ are 17.1 ± 1.2 kcal mol^{-1}, 61.0 ± 4.3 cal mol^{-1} K^{-1} and -1.1 ± 2.5 kcal mol^{-1}, respectively) at 298.15 K were determined. Stopped-flow kinetic isotope experiments provide evidence that these redox reactions coincide with the transfer of a proton. A systematic DFT speciation study of Os^{VI} and Os^{VII} oxido/hydroxido complexes in a simulated aqueous phase (COSMO) yield that the thermodynamically most stable Os^{VI} species is the singlet spin state *trans*-$[Os^{VI}O_2(OH)_4]^{2-}$ complex and the thermodynamically most stable paramagnetic Os^{VII} product species are a combination of *trans*-$[Os^{VII}O_3(OH)_2]^-$ and *mer*-$[Os^{VII}O_3(OH)_3]^{2-}$ species. Using the DFT results, the Os^{VI} & Os^{VIII} comproportionation reaction is now proposed to be $[Os^{VIII}O_4(OH)_2]^{2-}$ reacts with *trans*-$[Os^{VI}O_2(OH)_4]^{2-}$ to yield two *trans*-$[Os^{VII}O_3(OH)_2]^-$ species and two hydroxide anions. The

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†Electronic supplementary information (ESI) available: Supplementary UV-Vis spectra, figures, tables, numerical considerations regarding the stopped-flow experimental kinetic analyses and cartesian coordinates of all optimised structures. See DOI: