

Accepted Manuscript

Research paper

A spectroscopic (stopped-flow UV-Vis and ^1H NMR Evans method) and DFT thermodynamic study of the comproportionation reaction of $[\text{Os}^{\text{VIII}}\text{O}_4(\text{OH})_n]^{n-}$ ($n = 1, 2$) and $[\text{Os}^{\text{VI}}\text{O}_2(\text{OH})_4]^{2-}$ †

Daniel M.E. van Niekerk, Wilhelmus J. Gerber

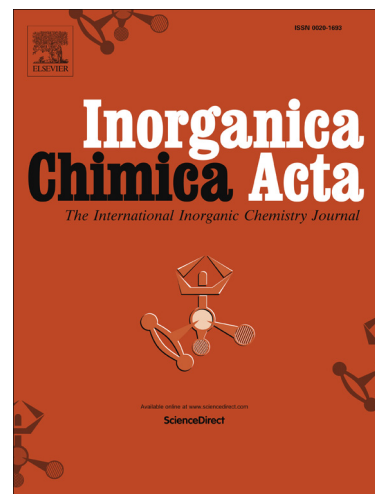
PII: S0020-1693(16)30720-4
DOI: <http://dx.doi.org/10.1016/j.ica.2016.10.022>
Reference: ICA 17315

To appear in: *Inorganica Chimica Acta*

Received Date: 4 August 2016
Revised Date: 17 October 2016
Accepted Date: 18 October 2016

Please cite this article as: D.M.E. van Niekerk, W.J. Gerber, A spectroscopic (stopped-flow UV-Vis and ^1H NMR Evans method) and DFT thermodynamic study of the comproportionation reaction of $[\text{Os}^{\text{VIII}}\text{O}_4(\text{OH})_n]^{n-}$ ($n = 1, 2$) and $[\text{Os}^{\text{VI}}\text{O}_2(\text{OH})_4]^{2-}$ †, *Inorganica Chimica Acta* (2016), doi: <http://dx.doi.org/10.1016/j.ica.2016.10.022>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



A spectroscopic (stopped-flow UV-Vis and ^1H NMR Evans method) and DFT thermodynamic study of the comproportionation reaction of $[\text{Os}^{\text{VIII}}\text{O}_4(\text{OH})_n]^{n-}$ ($n = 1, 2$) and $[\text{Os}^{\text{VI}}\text{O}_2(\text{OH})_4]^{2-}$ †

Daniel M. E. van Niekerk and Wilhelmus J. Gerber*

From a mole ratio ^1H NMR Evans method experiment it is found that, in a 2.0 M NaOH aqueous matrix, diamagnetic $[\text{Os}^{\text{VIII}}\text{O}_4(\text{OH})_n]^{n-}$ ($n = 1, 2$) (of d^0 electron configuration) and *trans*- $[\text{Os}^{\text{VI}}\text{O}_2(\text{OH})_4]^{2-}$ 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 $[\text{Os}^{\text{VIII}}] + [\text{Os}^{\text{VI}}] \xrightleftharpoons[k_{\text{COM}}]{k_{\text{COM}}} 2 [\text{Os}^{\text{VII}}]$. From non-linear least squares fits of stopped-flow UV-Vis spectroscopy kinetic traces the comproportionation reaction rate constants, activation energies (forward: $\Delta H_{(\text{obs})}^\ddagger$, $\Delta S_{(\text{obs})}^\ddagger$ and $\Delta G_{(\text{obs})}^\ddagger$ are $10.3 \pm 0.5 \text{ kcal mol}^{-1}$, $-2.6 \pm 1.6 \text{ cal mol}^{-1} \text{ K}^{-1}$ and $11.1 \pm 0.9 \text{ kcal mol}^{-1}$, respectively; and reverse are $-6.7 \pm 1.0 \text{ kcal mol}^{-1}$, $-63.6 \pm 3.4 \text{ cal mol}^{-1} \text{ K}^{-1}$ and $12.2 \pm 2.0 \text{ kcal mol}^{-1}$ respectively) and standard reaction energies ($\Delta H_{\text{rxn}(\text{obs})}^\circ$, $\Delta S_{\text{rxn}(\text{obs})}^\circ$ and $\Delta G_{\text{rxn}(\text{obs})}^\circ$ are $17.1 \pm 1.2 \text{ kcal mol}^{-1}$, $61.0 \pm 4.3 \text{ cal mol}^{-1} \text{ K}^{-1}$ and $-1.1 \pm 2.5 \text{ kcal mol}^{-1}$, 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*- $[\text{Os}^{\text{VI}}\text{O}_2(\text{OH})_4]^{2-}$ complex and the thermodynamically most stable paramagnetic Os^{VII} product species are a combination of *trans*- $[\text{Os}^{\text{VII}}\text{O}_3(\text{OH})_2]^-$ and *mer*- $[\text{Os}^{\text{VII}}\text{O}_3(\text{OH})_3]^{2-}$ species. Using the DFT results, the Os^{VI} & Os^{VIII} comproportionation reaction is now proposed to be $[\text{Os}^{\text{VIII}}\text{O}_4(\text{OH})_2]^{2-}$ reacts with *trans*- $[\text{Os}^{\text{VI}}\text{O}_2(\text{OH})_4]^{2-}$ to yield two *trans*- $[\text{Os}^{\text{VII}}\text{O}_3(\text{OH})_2]^-$ species and two hydroxide anions. The

Department of Chemistry and Polymer Science, Stellenbosch University, Private Bag X1, Stellenbosch 7602, Western Cape, South Africa. E-mail: wgerber@sun.ac.za; Fax: +27 21 808 3342; Tel: +27 21 808 2699

†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:

Download English Version:

<https://daneshyari.com/en/article/5152043>

Download Persian Version:

<https://daneshyari.com/article/5152043>

[Daneshyari.com](https://daneshyari.com)