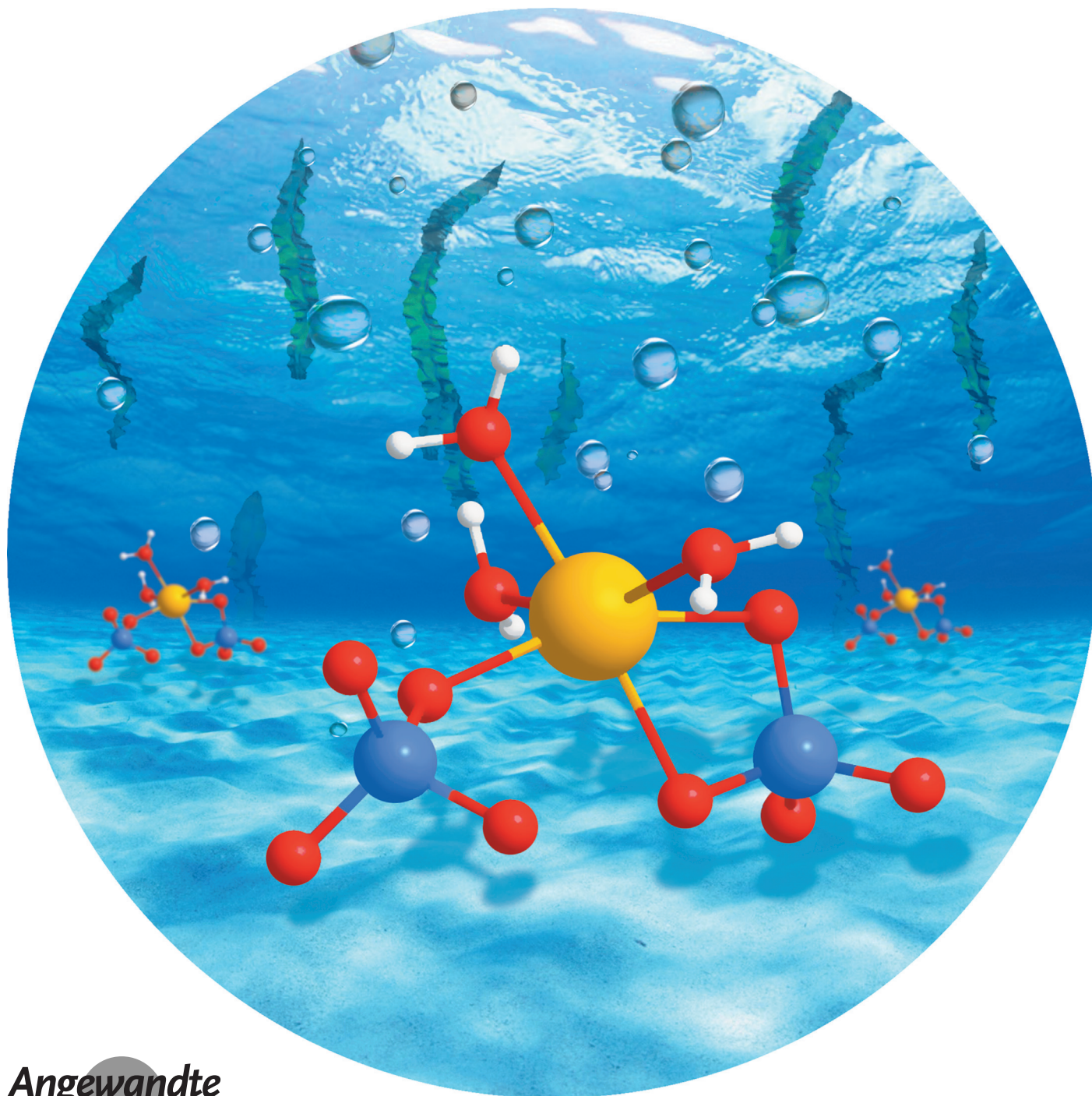


**O<sub>2</sub> Production** Hot PaperDeutsche Ausgabe: DOI: 10.1002/ange.201510156  
Internationale Ausgabe: DOI: 10.1002/anie.201510156

# Ca<sup>2+</sup>-Induced Oxygen Generation by FeO<sub>4</sub><sup>2-</sup> at pH 9–10

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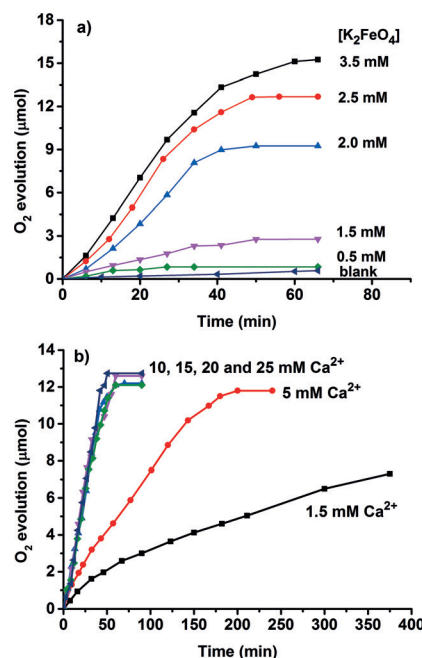
**Abstract:** Although  $\text{FeO}_4^{2-}$  (ferrate(IV)) is a very strong oxidant that readily oxidizes water in acidic medium, at pH 9–10 it is relatively stable (<2% decomposition after 1 h at 298 K). However,  $\text{FeO}_4^{2-}$  is readily activated by  $\text{Ca}^{2+}$  at pH 9–10 to generate  $\text{O}_2$ . The reaction has the following rate law:  $d[\text{O}_2]/dt = k_{\text{cat}}[\text{Ca}^{2+}][\text{FeO}_4^{2-}]^2$ .  $^{18}\text{O}$ -labeling experiments show that both O atoms in  $\text{O}_2$  come from  $\text{FeO}_4^{2-}$ . These results together with DFT calculations suggest that the function of  $\text{Ca}^{2+}$  is to facilitate O–O coupling between two  $\text{FeO}_4^{2-}$  ions by bridging them together. Similar activating effects are also observed with  $\text{Mg}^{2+}$  and  $\text{Sr}^{2+}$ .

**P**lants and cyanobacteria make use of a  $\text{Mn}_4\text{CaO}_5$  cluster located at the oxygen-evolving center (OEC) of photosystem II (PSII) to carry out water oxidation.<sup>[1–4]</sup> The protons and electrons obtained from water oxidation are ultimately used to reduce carbon dioxide to carbohydrates. Various multi-manganese complexes have been synthesized as structural models of the OEC.<sup>[5–10]</sup> Notably the recently reported  $\text{Mn}_3\text{CaO}_4$  cluster<sup>[7–9]</sup> and the  $\text{Mn}_4\text{CaO}_4$  cluster<sup>[10]</sup> are closely related to the cubane structure of the OEC. There are also a few studies on the effects of  $\text{Ca}^{2+}$  and other metal ions on the properties and reactivities of manganese oxo clusters and other model compounds of PSII. For example, the presence  $\text{Ca}^{2+}$  and other non-redox active metal aqua ions shift the reduction potentials ( $E^0$ ) of manganese oxo clusters and there is a linear correlation between  $E^0$  and  $\text{p}K_{\text{a}}$  of the metal ions.<sup>[11,12]</sup> The catalytic water-oxidation activity of manganese oxides is enhanced by the presence of  $\text{Ca}^{2+}$ .<sup>[13,14]</sup>  $\text{Ca}^{2+}$  is also found to induce the oxidative release of  $\text{O}_2$  from a non-heme iron peroxo complex, while other metal ions that are better Lewis acids than  $\text{Ca}^{2+}$  are not effective.<sup>[15]</sup>

We are interested to investigate the effects of  $\text{Ca}^{2+}$  and other Group 2 ions on water oxidation by simple, well-defined molecular metal oxo species, which would facilitate interpretation of kinetic and mechanistic data. Herein we report the effects of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Sr}^{2+}$  on water oxidation at pH 9–10 by  $\text{K}_2\text{FeO}_4$ , which is a very stable black solid at room temperature under moisture-free conditions. Potassium and other metal ferrates have received much attention in recent years because of their potential use as green oxidants in organic synthesis and water treatment.<sup>[16]</sup>

Although ferrate(VI) ( $\text{FeO}_4^{2-}$ ) is a strong oxidant ( $E^0 = 2.2$  V and 0.72 V at pH 0 and 14, respectively) that readily oxidizes water at low pH,<sup>[17]</sup> at pH 9–10 it is relatively stable at room temperature.<sup>[17]</sup> In our hands decomposition of a 1 mM solution is less than 2% in 1 h at pH 9–10 at 298 K, as monitored by UV/Vis spectrophotometry. At pH > 9 ferrate(VI) exists predominantly as the  $\text{FeO}_4^{2-}$  ion, since the  $\text{p}K_{\text{a}}$  of  $\text{HFeO}_4^-$  is 7.3.<sup>[16]</sup> However, upon adding a few equivalents of

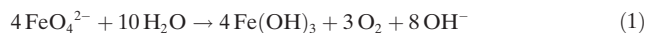
$\text{Ca}^{2+}$  to  $\text{K}_2\text{FeO}_4$  in water at pH 10 and 298 K,  $\text{O}_2$  evolution readily occurred, as monitored by a gas chromatography–thermal conductivity detector (GC–TCD; Figure 1, Table S1). The rate and the amount of  $\text{O}_2$  increase with increasing  $\text{FeO}_4^{2-}$  concentration (Figure 1a) and increasing  $\text{Ca}^{2+}$  concentration (Figure 1b), but saturation behavior occurs above



**Figure 1.** Plots of  $\text{O}_2$  evolution (determined by GC) versus time for  $\text{Ca}^{2+}$ -induced oxygen generation by  $\text{K}_2\text{FeO}_4$  at initial pH 10,  $T = 298$  K. a) Effects of  $[\text{K}_2\text{FeO}_4]$ ;  $[\text{Ca}(\text{OTf})_2] = 15$  mM. b) Effects of  $[\text{Ca}(\text{OTf})_2]$ ;  $[\text{K}_2\text{FeO}_4] = 2.5$  mM.

4 equivalents of  $\text{Ca}^{2+}$ . A maximum yield of 85% was obtained after 1 h. The yields were calculated based on Equation (1). An orange precipitate of  $\text{Fe}(\text{OH})_3$  was observed as the reaction proceeded. Similar yields and rates were obtained when the reaction was carried out at pH 9.0 (Table S1 and Figure S1 in the Supporting Information). In the absence of  $\text{Ca}^{2+}$  only a trace amount of  $\text{O}_2$  was observed after 1 h (<2%).  $\text{Mg}^{2+}$  and  $\text{Sr}^{2+}$  showed similar activating effects on oxygen generation by  $\text{FeO}_4^{2-}$  at pH 9–10, with maximum  $\text{O}_2$  yields of 73% and 90%, respectively (Table S1 and Figure S2–5).

According to Equation (1) the pH of the solution should



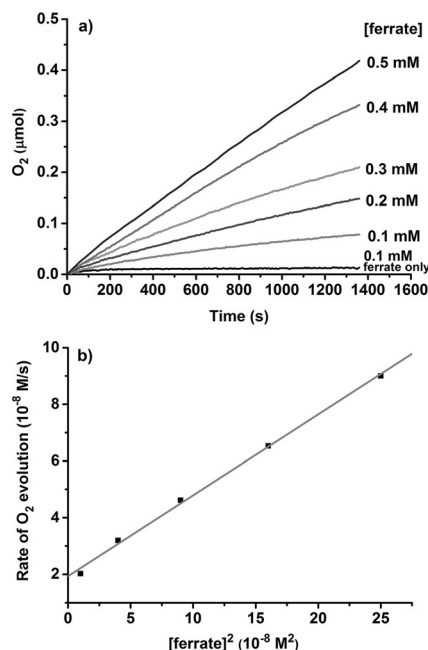
increase during water oxidation. Indeed when 2.5 mM of  $\text{K}_2\text{FeO}_4$  was mixed with 15 mM  $\text{Ca}^{2+}$  the pH of the solution increased from 10.0 to 11.6 after 1 h. To minimize pH changes which could affect the rate of the reaction, the kinetics of  $\text{M}^{2+}$ -induced water oxidation were also investigated at relatively low  $\text{FeO}_4^{2-}$  concentrations (0.1–0.5 mM); under these conditions the pH of the solutions increased by no more than 0.2. At such low  $\text{FeO}_4^{2-}$  concentrations the amount of  $\text{O}_2$  evolved could not be accurately determined by GC, instead  $\text{O}_2$  was continuously monitored by a Clark-type electrode.

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Supporting information for this article is available on the WWW  
under <http://dx.doi.org/10.1002/anie.201510156>.



Figure 2 shows the effects of  $\text{FeO}_4^{2-}$  concentration on  $\text{Ca}^{2+}$ -induced oxygen generation by  $\text{FeO}_4^{2-}$  at pH 10. The experiments were carried out at nearly constant ionic strength using an excess of  $\text{Ca}^{2+}$  (20 mM). A plot of the initial rate vs.  $[\text{FeO}_4^{2-}]^2$  gives a straight line (Figure 2b). The effects of  $\text{Ca}^{2+}$

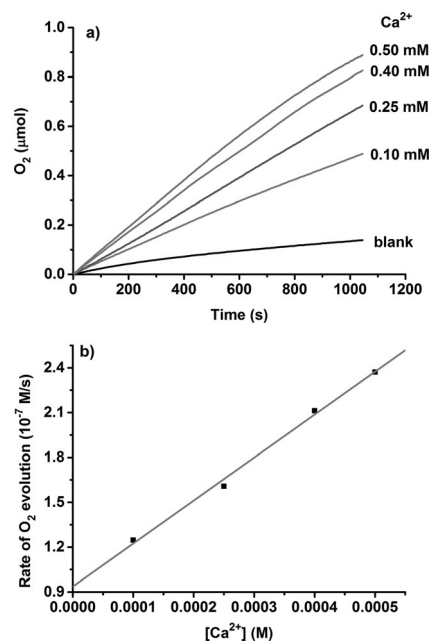


**Figure 2.** a) Effects of  $\text{FeO}_4^{2-}$  concentration on  $\text{Ca}^{2+}$ -induced oxygen generation ( $\text{O}_2$  determined by Clark electrode) by  $\text{K}_2\text{FeO}_4$  at pH 10 and 298 K.  $[\text{Ca}^{2+}] = 20$  mM. b) Plot of initial rate of  $\text{O}_2$  evolution versus  $[\text{FeO}_4^{2-}]^2$ . Slope = 0.29,  $y$ -intercept =  $1.93 \times 10^{-8}$ ,  $r^2 = 0.996$ .

concentration on oxygen generation under an excess of  $\text{FeO}_4^{2-}$  (2.5 mM) were also investigated (Figure 3a). A plot of initial rate versus  $\text{Ca}^{2+}$  concentration gives a straight line (Figure 3b). These results are in accordance with the rate law:  $d[\text{O}_2]/dt = k_{\text{Ca}}[\text{Ca}^{2+}][\text{FeO}_4^{2-}]^2$ . The same rate law was observed when  $\text{Mg}^{2+}$  or  $\text{Sr}^{2+}$  was used to activate  $\text{FeO}_4^{2-}$  (Figure S6–12). The rate constants ( $\text{M}^{-2}\text{s}^{-1}$ ) follow the order  $k_{\text{Mg}}(0.138 \pm 0.017) > k_{\text{Ca}}(0.129 \pm 0.014) > k_{\text{Sr}}(0.09 \pm 0.018)$ , this order is the same as that of their Lewis acidity ( $\text{p}K_{\text{a}}$  of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  are 11.2, 12.7, and 13.2, respectively).<sup>[18]</sup> However, the differences in the rate constants are rather small, despite a difference in two  $\text{p}K_{\text{a}}$  units among these metal ions. When  $\text{Ba}^{2+}$  ( $\text{p}K_{\text{a}}$  13.4) was added to  $\text{FeO}_4^{2-}$  at pH 9–10, a precipitate of  $\text{Ba}[\text{FeO}_4]$  was immediately formed, and no  $\text{O}_2$  evolution could be observed. Other  $\text{M}^{2+}$  aqua ions such as  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$  gave  $\text{M}(\text{OH})_2$  precipitates at pH 9–10.

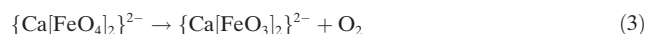
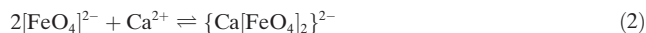
The effects of  $\text{Ca}^{2+}$  on  $\text{FeO}_4^{2-}$  in water has also been monitored by UV/Vis spectrophotometry (Figure S13). There is a gradual appearance of a broad absorption around 400 nm, consistent with the formation of  $\text{Fe}(\text{OH})_3$ . Similar changes were observed when  $\text{Sr}^{2+}$  or  $\text{Mg}^{2+}$  was used instead of  $\text{Ca}^{2+}$ .

To determine the source of O atoms in  $\text{O}_2$  evolved,  $^{18}\text{O}$ -labeling experiments were performed.  $\text{FeO}_4^{2-}$  exchanges its O atoms with  $\text{H}_2\text{O}$ , and a rate constant of  $1.37 \times 10^{-3} \text{ s}^{-1}$  at 273 K was reported.<sup>[17a]</sup> In our hands we obtained a first-order rate constant of  $(2.18 \pm 0.27) \times 10^{-3} \text{ s}^{-1}$  ( $t_{1/2} = 5.3$  min) at 298 K for



**Figure 3.** a) Effects of  $\text{Ca}^{2+}$  concentration on oxygen generation ( $\text{O}_2$  determined by Clark electrode) by  $\text{K}_2\text{FeO}_4$  at pH 10.  $[\text{FeO}_4^{2-}] = 2.5$  mM. b) Plot of initial rate of  $\text{O}_2$  evolution vs.  $[\text{Ca}^{2+}]$ . Slope =  $2.87 \times 10^{-4}$ ,  $y$ -intercept =  $9.37 \times 10^{-8}$ ,  $r^2 = 0.993$ .

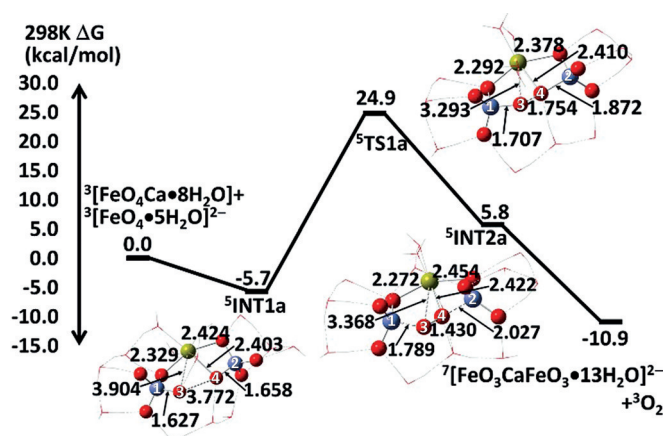
O-exchange between  $\text{K}_2\text{Fe}^{16}\text{O}_4$  and  $\text{H}_2^{18}\text{O}$ , using electrospray ionization mass spectrometry (ESI/MS; Table S2 and Figure S14,15). When  $\text{K}_2\text{Fe}^{18}\text{O}_4$  was dissolved in  $\text{H}_2^{16}\text{O}$  at pH 10 in the presence of 8 mol equivalents of  $\text{Ca}^{2+}$  at 298 K, the  $\text{O}_2$  evolved after 3 min consists of 27.7%  $^{16}\text{O}^{16}\text{O}$ , 19.2%  $^{16}\text{O}^{18}\text{O}$ , and 53.1%  $^{18}\text{O}^{18}\text{O}$ ; the relative amount of  $^{18}\text{O}^{18}\text{O}$  decreased with time as a result of O-exchange between  $\text{FeO}_4^{2-}$  and water (Table S3). On the other hand, when  $\text{K}_2\text{Fe}^{16}\text{O}_4/\text{Ca}^{2+}$  was dissolved in  $\text{H}_2^{18}\text{O}$ , the oxygen evolved after 3 min consists of 68.7%  $^{16}\text{O}^{16}\text{O}$ , 6.3%  $^{16}\text{O}^{18}\text{O}$ , and 25.0%  $^{18}\text{O}^{18}\text{O}$  (Table S4). As expected, the relative amount of  $^{18}\text{O}^{18}\text{O}$  increased with time in this case. These results unambiguously establish that both O atoms in the  $\text{O}_2$  evolved come from  $\text{FeO}_4^{2-}$  (after correcting for O-exchange between  $\text{FeO}_4^{2-}$  and  $\text{H}_2\text{O}$  during 3 min). The  $^{18}\text{O}$ -labeling results, together with the observed second-order dependence of the rate on  $\text{FeO}_4^{2-}$  concentration, are consistent with a  $\text{O}_2$  evolution mechanism that involves O–O coupling between two  $\text{FeO}_4^{2-}$  bound to a  $\text{Ca}^{2+}$  ion, as shown in Equations (2)–(3). The iron(IV) species formed after  $\text{O}_2$  evolution is expected to undergo rapid disproportionation to give  $\text{FeO}_4^{2-}$  and  $\text{Fe}(\text{OH})_3$ .<sup>[17]</sup>



We and others have previously reported that  $\text{Fe}_2\text{O}_3/\text{Fe}(\text{OH})_3$  nanoparticles, either directly used or generated from iron complexes and salts, can catalyze visible-light induced water oxidation by  $[\text{Ru}(\text{bpy})_3]^{2+}/\text{S}_2\text{O}_8^{2-}$  at pH 7–9.<sup>[19]</sup> However, the active intermediate should not be  $\text{FeO}_4^{2-}$  since in the absence of  $\text{Ca}^{2+}$  it oxidizes water very slowly in this pH range. Also  $\text{Ca}^{2+}$  ions did not have any effects on catalytic water

oxidation by this system (Figure S16).

To obtain more insights into the mechanism of  $\text{Ca}^{2+}$ -induced oxygen generation by  $\text{FeO}_4^{2-}$ , density functional theory (DFT) calculations have been performed on the reaction between  $\text{FeO}_4\text{Ca}$  and  $\text{FeO}_4^{2-}$ . As the evolution of  $\text{O}_2$  from  $\text{FeO}_4^{2-}/\text{Ca}^{2+}$  occurs in aqueous medium, the solvent effect was treated by a hybrid model which consists of an explicit solvent effect of 13 water molecules surrounding  $\text{FeO}_4\text{Ca}$  and  $\text{FeO}_4^{2-}$  and an implicit solvent effect by polarizable continuum model (PCM).<sup>[20]</sup> The  $^3[\text{FeO}_4]^{2-}$  and  $^3[\text{FeO}_4\text{Ca}]$  species first couple to form a stable quintet intermediate,  $^5[\text{FeO}_4\text{CaFeO}_4 \cdot 13\text{H}_2\text{O}]^{2-}$  (**<sup>5</sup>INT1a**) (Scheme 1).



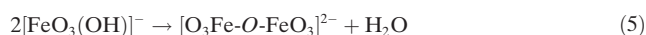
**Scheme 1.** Quintet potential energy surface for the  $\text{O}_2$  evolution from  $[\text{FeO}_4\text{Ca} \cdot 8\text{H}_2\text{O}] + [\text{FeO}_4 \cdot 5\text{H}_2\text{O}]^{2-}$  at the B3LYP level using LanL2TZ(f) basis set (Fe) and 6-311++G(d,p) basis set (H, O, and Ca). Relative 298 K Gibbs free energies in water are given in  $\text{kcal mol}^{-1}$  and selected bond lengths are in Å. O: red, Fe: purple, Ca: green.

In **<sup>5</sup>INT1a**, the  $\text{Ca}^{2+}$  has an octahedral coordination environment; it is bonded to three water molecules, two oxo ligands of one  $\text{FeO}_4^{2-}$  and one oxo ligand of the other  $\text{FeO}_4^{2-}$ . The electron spin density on each  $\text{FeO}_4^{2-}$  is fairly even; the Fe metal bears approximately 1.4 electrons and the oxo ligand has approximately 0.2 electrons. This suggests that the **<sup>5</sup>INT1a** is formed by a direct coupling of  $^3[\text{FeO}_4 \cdot 5\text{H}_2\text{O}]^{2-}$  and  $^3[\text{FeO}_4\text{Ca} \cdot 8\text{H}_2\text{O}]$  without any significant change in electronic distribution. There is no significant change in Fe–O distances before and after binding to  $\text{Ca}^{2+}$  (Table S5–7). The **<sup>5</sup>INT1a** then undergoes O–O coupling between a non- $\text{Ca}^{2+}$  bound oxo ligand of one  $\text{FeO}_4^{2-}$  and a  $\text{Ca}^{2+}$ -bound oxo ligand of the other  $\text{FeO}_4^{2-}$  (i.e. between O3 and O4) via **<sup>5</sup>TS1a** to form **<sup>5</sup>INT2a**. The O3–O4 distance is significantly shortened from 3.772 Å to 1.754 Å whereas the Fe1–O3/Fe2–O4 bond lengths are slightly elongated by 0.08–0.21 Å in **<sup>5</sup>TS1a**. The free-energy barrier height ( $\Delta G_{298}^\ddagger$ ) of **<sup>5</sup>TS1a** is 24.9  $\text{kcal mol}^{-1}$ . In **<sup>5</sup>INT2a**, the O3–O4 bond length of 1.430 Å is consistent with a peroxo bond. The **<sup>5</sup>INT2a** then decomposes into  $^3\text{O}_2$  and  $^7[\text{FeO}_3\text{CaFeO}_3 \cdot 13\text{H}_2\text{O}]^{2-}$  with  $\Delta G = -16.7 \text{ kcal mol}^{-1}$ ; and the electron spin on O3 and O4 become  $-1.0$  while the electron spin on Fe1 and Fe2 are about  $+2.0$ . Each of the remaining oxo group bears approximately 0.2 electrons. The **<sup>5</sup>INT2a** is adiabatically correlated with  $^7[\text{FeO}_3\text{CaFeO}_3 \cdot 13\text{H}_2\text{O}]^{2-}$  and  $^3\text{O}_2$ .

We have also calculated the potential energy surface for O–O coupling through the  $^3[\text{FeO}_4\text{CaFeO}_4 \cdot 13\text{H}_2\text{O}]^{2-}$  (**<sup>3</sup>INT1a**) intermediate (Scheme S1), however in this case the barrier is much higher (46.1  $\text{kcal mol}^{-1}$ ).

The reaction mechanisms for  $\text{O}_2$  evolution from  $\text{FeO}_4\text{Mg} + \text{FeO}_4^{2-}$  and  $\text{FeO}_4\text{Sr} + \text{FeO}_4^{2-}$  are similar to that of  $\text{FeO}_4\text{Ca} + \text{FeO}_4^{2-}$ . The  $\Delta G_{298}^\ddagger$  ( $\text{kcal mol}^{-1}$ ) for  $\text{O}_2$  evolution from the three metal ions follow the order  $\text{Mg}^{2+}(20.4) < \text{Ca}^{2+}(24.9) < \text{Sr}^{2+}(28.7)$ , which is the same as the experimentally determined order.

In conclusion, we have demonstrated that the Group 2 metal aqua ions  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Sr}^{2+}$  readily activate the  $\text{FeO}_4^{2-}$  ion at pH 9–10 to generate  $\text{O}_2$ . Experimental and DFT calculations suggest that the reaction goes through a  $[\text{M}[\text{FeO}_4]_2]^{2-}$  intermediate in which the two  $\text{FeO}_4^{2-}$  ions are bridged by  $\text{M}^{2+}$ . The  $\text{M}^{2+}$  appears to play mainly a structural role that brings the two  $\text{FeO}_4^{2-}$  ions together to facilitate O–O coupling between them (I2M mechanism<sup>[21]</sup>) to generate a peroxo species. The observed similar rate constants and calculated  $\Delta G_{298}^\ddagger$  for water oxidation activated by the three different metal ions suggests that there is little electronic effect of the  $\text{M}^{2+}$  ions. The Fe–O distances in free and  $\text{M}^{2+}$ -bound  $\text{FeO}_4^{2-}$  are also very similar. The proposed mechanism is similar to oxygen generation by  $\text{FeO}_4^{2-}$  in acidic medium, in which the  $\text{FeO}_4^{2-}$  is first protonated followed by spontaneous condensation to give an oxo-bridged diferrate, which then undergoes O–O coupling.<sup>[17b]</sup> Oxygen generation by ferrate(V) at pH around 5–8 may be represented by Equations (4)–(6). At lower pH ferrate(VI) may undergo di- and tri-protonation followed by condensation ( $\text{H}_3\text{Fe}^{\text{VI}}\text{O}_4$ ,  $\text{p}K_1 = 1.5$ ,  $\text{p}K_2 = 3.5$ ,  $\text{p}K_3 = 7.2$ ).<sup>[16b]</sup> At pH > 9  $\mu$ -oxo species cannot form. However, we show in this work that the Group 2 ions can also bring the two ferrates together to facilitate O–O coupling.



## Acknowledgements

This work was supported by Hong Kong University Grants Committee (AoE/P-03-08) and the Research Grants Council of Hong Kong (CityU 101612 and CityU 11301514).

**Keywords:** calcium · dioxygen generation · iron(VI) · Lewis acid

**How to cite:** *Angew. Chem. Int. Ed.* **2016**, 55, 3012–3016  
*Angew. Chem.* **2016**, 128, 3064–3068

- [1] J. P. McEvoy, G. W. Brudvig, *Chem. Rev.* **2006**, 106, 4455–4483.
- [2] J. Barber, *Chem. Soc. Rev.* **2009**, 38, 185–196.
- [3] Y. Umena, K. Kawakami, J. R. Shen, N. Kamiya, *Nature* **2011**, 473, 55–60.
- [4] J. Yano, V. Yachandra, *Chem. Rev.* **2014**, 114, 4175–4205.

- [5] C. S. Mullins, V. L. Pecoraro, *Coord. Chem. Rev.* **2008**, 252, 416–443.
- [6] G. C. Dismukes, R. Brimblecombe, G. A. N. Felton, R. S. Pryadun, J. E. Sheats, L. Spiccia, G. F. Swiegers, *Acc. Chem. Res.* **2009**, 42, 1935–1943.
- [7] J. S. Kanady, E. Y. Tsui, M. W. Day, T. Agapie, *Science* **2011**, 333, 733–736.
- [8] S. Mukherjee, J. A. Stull, J. Yano, T. C. Stamatatos, K. Pringouri, T. A. Stich, K. A. Abboud, R. D. Britt, V. K. Yachandra, G. Christou, A. Affiliations, *Proc. Natl. Acad. Sci. USA* **2012**, 109, 2257–2262.
- [9] J. S. Kanady, P. H. Lin, K. M. Carsch, R. J. Nielsen, M. K. Takase, W. A. Goddard III, T. Agapie, *J. Am. Chem. Soc.* **2014**, 136, 14373–14376.
- [10] C. X. Zhang, C. H. Chen, H. X. Dong, J. R. Shen, H. Dau, J. Q. Zhao, *Science* **2015**, 348, 690–693.
- [11] E. Y. Tsui, R. Tran, J. Yano, T. Agapie, *Nat. Chem.* **2013**, 5, 293–299.
- [12] E. Y. Tsui, T. Agapie, *Proc. Natl. Acad. Sci. USA* **2013**, 110, 10084–10088.
- [13] M. M. Najafpour, T. Ehrenberg, M. Wiechen, P. Kurz, *Angew. Chem. Int. Ed.* **2010**, 49, 2233–2237; *Angew. Chem.* **2010**, 122, 2281–2285.
- [14] M. Wiechen, I. Zaharieva, H. Dau, P. Kurz, *Chem. Sci.* **2012**, 3, 2330–2339.
- [15] S. Bang, Y. M. Lee, S. Hong, K. B. Cho, Y. Nishida, M. S. Seo, R. Sarangi, S. Fukuzumi, W. Nam, *Nat. Chem.* **2014**, 6, 934–940.
- [16] a) V. K. Sharma, R. Zboril, R. S. Varma, *Acc. Chem. Res.* **2015**, 48, 182–191; b) V. K. Sharma, *Coord. Chem. Rev.* **2013**, 257, 495–510; c) V. K. Sharma, *J. Environ. Manage.* **2011**, 92, 1051–1073.
- [17] a) H. Goff, R. K. Murmann, *J. Am. Chem. Soc.* **1971**, 93, 6058–6065; b) R. Sarma, A. M. Angeles-Boza, D. W. Brinkley, J. P. Roth, *J. Am. Chem. Soc.* **2012**, 134, 15371–15386; c) Y. Lee, R. Kissner, U. Gunten, *Environ. Sci. Technol.* **2014**, 48, 5154–5162.
- [18] S. J. Hawkes, *J. Chem. Educ.* **1996**, 73, 516–517.
- [19] a) G. Chen, L. J. Chen, S. M. Ng, W. L. Man, T. C. Lau, *Angew. Chem. Int. Ed.* **2013**, 52, 1789–1791; *Angew. Chem.* **2013**, 125, 1833–1835; b) D. Hong, S. Mandal, Y. Yamada, Y. M. Lee, W. Nam, A. Llobet, S. Fukuzumi, *Inorg. Chem.* **2013**, 52, 9522–9531; c) Q. J. Xiang, G. Chen, T. C. Lau, *RSC Adv.* **2015**, 5, 52210–52216.
- [20] a) S. Miertuš, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, 55, 117–129; b) S. Miertuš, J. Tomasi, *Chem. Phys.* **1982**, 65, 239–245.
- [21] X. Sala, S. Maji, R. Bofill, J. García-Antón, L. Escriche, A. Llobet, *Acc. Chem. Res.* **2014**, 47, 504–516.

Received: November 1, 2015

Published online: January 22, 2016