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Chemical and Visible-Light-Driven Water Oxidation by Iron Complexes at pH 7–9: Evidence for Dual-Active Intermediates in Iron-Catalyzed Water Oxidation**

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In recent decades, tremendous efforts have been devoted by chemists to develop efficient, cost-effective catalytic methods for solar-driven water oxidation, which would provide an unlimited source of protons and electrons for the production of hydrogen and other renewable fuels.[1] However, to be economically viable, the catalysts for water oxidation should be made from earth-abundant materials;[2] so far only a few cobalt,[3] manganese,[4] iron,[5] and copper[6] water-oxidation catalysts (WOCs) have been developed. Among the first-row transition metals, iron is probably the most desirable to be used in WOCs because it is the most abundant and relatively nontoxic. Collins, Bernhard, and co-workers recently reported the use of an iron(III) complex bearing a tetraamido macrocyclic ligand (Fe^{III}-TAML) to catalyze water oxidation by Ce^{IV} at approximately pH 1 with a turnover number (TON) of 18 and turnover frequency (TOF) of greater than $1.3\ s^{-1}$.[5a] Subsequently, Fillol and Costas et al., also reported that a number of iron complexes bearing tetradentate N-donor ligands can catalyze water oxidation at low pH with TON > 350 and > 1000 using Ce^{IV} and IO_4^-, respectively.[5b] Herein, we report chemical and light-driven water oxidation catalyzed by a number of iron complexes and iron salts at pH 7–9 in borate buffer. We provide evidence that at this pH range, Fe_2O_3 particles are produced, which are the actual catalyst for water oxidation.

The catalytic activity of various iron complexes towards water oxidation at pH 7–9 was investigated by a chemical method using $[Ru(bpy)_3](ClO_4)_3$ (bpy = bipyridine) as the terminal oxidant (Table 1). $[Ru(bpy)_3]^{3+}$ is commonly used as an oxidant in this pH range because of its relative stability and high redox potential ($E^0 = 1.21$ V),[7] whereas Ce^{IV}, the other commonly used oxidant, is stable only at low pH values.

Table 1: Iron-catalyzed water oxidation by $[Ru(bpy)_3](ClO_4)_3$ at pH 8.5 in borate buffer.[a]

Entry	Catalysts	% Yield[b]	TOF [s^{-1}]	TON[c]
1	No catalyst	8	–	–
2	$Fe(mcp)Cl_2$	9	–	–
3	$[Fe(bpy)_2Cl_2]Cl$	49	3.6	95
4	$[Fe(tpy)_2]Cl_2$	16	1.5	19
5	$[Fe(cyclen)Cl_2]Cl$	54	4.4	108
6	$Fe(tmc)Br_2$	48	4.6	93
7	$Fe(ClO_4)_3$	71	9.6	147

[a] [Catalyst] = 0.8 μM, $[Ru(bpy)_3(ClO_4)_3]$ = 0.75 mM, in 15 mM borate buffer (pH 8.5) at 23 °C. Time = 120 s. [b] Determined by a Clark electrode. Yield = (mol of O_2)/(1/4×mol of $Ru(bpy)_3(ClO_4)_3$). The error is around 10%. [c] TON = (mol of O_2 after subtracting the blank)/(mol of catalyst).

Initially we investigated the complex *cis*-$Fe(mcp)Cl_2$ (mcp = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl)cyclohexane-1,2-diamine; Figure S1), because it was recently reported to be a highly active catalyst for water oxidation by Ce^{IV} or IO_4^- at low pH.[5b] In our hands, when we used this complex as a catalyst and $(NH_4)_2Ce(NO_3)_6$ as the oxidant in unbuffered water, we obtained a TON of 290 ± 15, in reasonable agreement with the value of 320 ± 15 reported in the literature.[5b] However, when we used $[Ru(bpy)_3](ClO_4)_3$ as the oxidant at pH 7–9 in borate buffer, no oxygen was produced (after subtracting the background signal) from this complex (Table 1, entry 2 and Figure S2). On the other hand, when other iron complexes such as $[Fe(bpy)_2Cl_2]Cl$, $[Fe(tpy)_2]Cl_2$, *cis*-$[Fe(cyclen)Cl_2]Cl$, and *trans*-$Fe(tmc)Br_2$ (where tpy = 2,2′:6′,2″-terpyridine, cyclen = 1,4,7,10-tetraazacyclodecane, and tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) were used as catalysts, oxygen evolution readily occurred, with TON ranging from 19 to 108 (Table 1, entries 3–6). Notably, simple iron salts such as $Fe(ClO_4)_3$ is even more active than the other iron complexes (Table 1, entry 7; Table S1 and Figure S3).

The maximum TOF of $9.6\ s^{-1}$ is higher than those of other earth-abundant artificial catalysts such as $[Co_4(H_2O)_2(\alpha\text{-}PW_9O_{34})_2]^{10-}$ ($5\ s^{-1}$)[3c] and Fe^{III}-TAML ($1.3\ s^{-1}$).[5a] In the absence of an iron catalyst, 8% yield of oxygen was also detected (Table 1, entry 1), which comes from background oxidation of water by $[Ru(bpy)_3]^{3+}$.[8] No oxygen could be detected when the reaction was carried out in phosphate buffer (Table S1, entry 8), which is attributed to the formation of the very insoluble $FePO_4$ ($K_{sp} = 9.92 \times 10^{-29}$). On the other

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hand, a less than or equal to 2 mM solution of an iron salt in 15 mM borate buffer remains clear, which is attributed to the much more soluble iron borate complex.[9]

The catalytic activity of the iron complexes and salts for visible-light-driven water oxidation was also investigated using $[Ru(bpy)_3]Cl_2$ as the photosensitizer (PS) and $Na_2S_2O_8$ as the sacrificial oxidant, at pH 7.5–9 in borate buffer (Table 2; Table S2, Figures S4, S5).[10] $Na_2S_2O_8$ has been used as a sacrificial oxidant in cobalt- and ruthenium-catalyzed water oxidation.[3b,11] The photochemical generation of the $[Ru(bpy)_3]^{3+}$ oxidant occurs according to Equations (1) and (2). The overall reaction is shown in Equation (3).

Table 2: Visible-light-driven water oxidation by iron catalysts.[a]

Entry	Catalysts	O_2 [µmol]	% Yield[b]	TON[c]
1	No catalyst	0.4	5	–
2	$Fe(mcp)Cl_2$	2.0	24	194
3	$[Fe(bpy)_2Cl_2]Cl$	1.7	21	157
4	$[Fe(tpy)_2]Cl_2$	3.5	42	376
5	$[Fe(cyclen)Cl_2]Cl$	3.8	46	412
6	$Fe(tmc)Br_2$	3.4	41	364
7	$Fe(ClO_4)_3$	4.0	48	436

[a] [Catalyst] = 1.0 µM, $[Ru(bpy)_3Cl_2]$ = 0.2 mM, $[Na_2S_2O_8]$ = 2 mM in 15 mM borate buffer (pH 8.5) at 23 °C, $\lambda > 420$ nm. [b] Determined by GC, yield = (mol of O_2)/(1/2×mol of $Na_2S_2O_8$). [c] TON = (mol of O_2 after subtracting the blank)/(mol of catalyst). The error is around 10%.

$$[Ru(bpy)_3]^{2+} + S_2O_8^{2-} \xrightarrow{h\nu} [Ru(bpy)_3]^{3+} + SO_4^{\bullet -} + SO_4^{2-} \quad (1)$$

$$[Ru(bpy)_3]^{2+} + SO_4^{\bullet -} \rightarrow [Ru(bpy)_3]^{3+} + SO_4^{2-} \quad (2)$$

$$2\,H_2O + 2\,Na_2S_2O_8 \rightarrow O_2 + 4\,H^+ + 4\,Na^+ + 4\,SO_4^{2-} \quad (3)$$

Control experiments showed that all three components, that is, the iron catalyst, the PS, and the sacrificial oxidant are required for oxygen evolution. The iron complexes and salts that are active catalysts in chemical oxidation are also active in photochemical water oxidation. Notably $Fe(mcp)Cl_2$, which is inactive in chemical oxidation, also produces oxygen under photochemical conditions. The evolved oxygen comes exclusively from water as shown by using ^{18}O-enriched water (46.4%; Figure S6). The observed O_2 yields of less than 50% can be attributed to non-O_2 productive decomposition reactions between $Na_2S_2O_8$ and $[Ru(bpy)_3]^{2+}$.[12]

In catalytic water oxidation, metal complexes often function only as precatalysts that decompose under oxidizing conditions to metal oxides, which are the real catalysts.[13] Hence, dynamic light scattering (DLS) was used to monitor any particles formed during the catalytic process. Upon irradiation of a solution of $Fe(ClO_4)_3$ with $Ru(bpy)_3^{2+}$ and $S_2O_8^{2-}$ at pH 8.5, particles began to appear after one minute (Figure 1 A). The particle size was found to increase with irradiation time to around 500–1200 nm, when oxygen evolution stopped (Figure 1 B). Similar particle formation was also observed in photochemical oxidation, and with all iron complexes listed in Table 2 (Figures S7–S13).

The particles formed after photocatalytic water oxidation were isolated and found to be Fe_2O_3 using various techniques, including energy-dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy (XPS; Figures S14–S17). Among the various types of Fe_2O_3, α-Fe_2O_3 has been extensively used as a photoelectrode for water splitting.[14] Hence α-Fe_2O_3 nanoparticles were prepared (15–70 nm, Figure S18) according to a published method[15] and their efficiency as photochemical and chemical water-oxidation catalysts was investigated. A TON of 58 was obtained for photochemical water oxidation, which is close to the value of 57 for $Fe(ClO_4)_3$ under the same conditions ([catalyst] = 10 µM; Table S2, entry 25). For chemical water oxidation a TON of 152 was obtained using α-Fe_2O_3 nanoparticles, which is the same as that of $Fe(ClO_4)_3$ ([catalyst] = 0.8 µM). These results strongly suggest that under oxidative conditions Fe^{3+}(aq) is converted to α-Fe_2O_3 nanoparticles, which are the actual catalyst for water oxidation. The catalytic activity of Fe_2O_3 decreases as the particle size increases. The Fe_2O_3 particles isolated at the end of the catalytic water oxidation were of micrometer size, and they were catalytically inactive. However, upon sonication in water for one hour, the particles were broken down to 40–130 nm size, and around 87% of the catalytic activity was restored (Figures S19, S20). Although α-Fe_2O_3 has been widely used in photoelectrochemical water splitting owing to its abundance, stability, and low band gap (1.9–2.2 eV), its photoactivity is generally low because of its short excited-state lifetime and small hole-diffusion length.[16] Photocatalytic water oxidation with α-Fe_2O_3 nanoparticles using $AgNO_3$ as the sacrificial donor gives an O_2 evolution rate of 1072 µmol h^{-1} g^{-1} and a TON of only 1.13,[17] whereas in the present case of $[Ru(bpy)_3]^{2+}$ as the PS and $Na_2S_2O_8$ as the sacrificial oxidant, the rate is much faster and a much higher TON of 1115 can be achieved.

We then tried to investigate how Fe_2O_3 is formed when the iron complexes are used as catalysts. We studied the stability of the iron complexes in aqueous solutions at pH 7–9 by ESI/MS. For $[Fe(cyclen)Cl_2]Cl$, $Fe(tmc)Br_2$, and $[Fe(bpy)_2Cl_2]Cl$, substantial amounts of free cyclen, tmc, or bpy ligand were formed in solution within one minute (Figures S21–S23). This

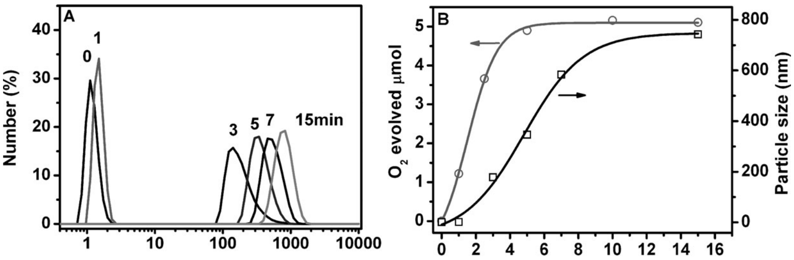

Figure 1. A) Particle size distribution at various irradiation times determined by DLS measurements. $[Fe(ClO_4)_3]$ = 10 µM, $[Ru(bpy)_3Cl_2]$ = 0.2 mM, $[Na_2S_2O_8]$ = 2 mM, pH 8.5. B) Plot of oxygen evolved (○) and size of particles formed (□) versus time during photochemical water oxidation. The two sets of data were obtained from two separate experiments under the same conditions.

suggests that the observed catalytic activity of these complexes arises from Fe^{3+}(aq) ions generated in solution prior to oxidation. On the other hand, the MS of Fe(mcp)Cl_2 in borate buffer shows only the presence of $[Fe(mcp)(OH)_2]^+$ and $[Fe(mcp)(OH)(BO_3H_2)]^+$ at $m/z = 414$ and $m/z = 458$, respectively; and no free mcp ligand was observed (Figure S25). This is probably the reason for the complete lack of catalytic activity of Fe(mcp)Cl_2 in chemical oxidation. Although Fe(mcp)Cl_2 is a highly active WOC at low pH values using Ce^{IV} ($E^0 = 1.75$ V)[7] or IO_4^- (E^0 $IO_4^-/IO_3^- = 1.60$ V)[7] as the oxidant, at high pH values, when $[Ru(bpy)_3]^{3+}$ ($E^0 = 1.21$ V)[7] is used as the oxidant, it may not be able to oxidize $[Fe(mcp)(OH)_2]^+$ to a high-valent iron-active species; in fact, the same $[Fe(mcp)(OH)_2]^+$ and $[Fe(mcp)(OH)(BO_3H_2)]^+$ species are present in solution before and after adding $[Ru(bpy)_3]^{3+}$, as monitored by MS (Figure S26). However, Fe(mcp)Cl_2 is an active visible-light-driven WOC in the presence of $[Ru(bpy)_3]^{2+}$ and $Na_2S_2O_8$. Irradiation of a solution of Fe(mcp)Cl_2 alone did not produce any free mcp ligand. We propose that in this case the strongly oxidizing $SO_4^{\bullet -}$ radical ($E^0 = 2.4$ V)[7] generated under photochemical conditions is involved in the oxidation of $[Fe(mcp)(OH)_2]^+$ to a high-valent iron oxo species. This species is stable in an acidic medium and is the active species for water oxidation, as proposed by Fillol, Costas, et al.[5b] On the other hand, we propose that this iron oxo species is unstable at high pH values, and it undergoes hydrolysis and reduction to generate Fe_2O_3, which is the real catalyst for water oxidation.

Our results and those of Fillol, Costas, et al.,[5b] suggest that the active iron catalysts for water oxidation at low and high pH values are different. At low pH values, water oxidation by iron complexes bearing multidentate N-donor ligands appears to go through a molecular iron oxo active intermediate, with no evidence for the formation iron oxide nanoparticles. Thermodynamically, at low pH values $[Fe(OH_2)_6]^{3+}$ is the stable Fe^{III} species rather than Fe_2O_3, but $[Fe(OH_2)_6]^{3+}$ does not catalyze water oxidation by Ce^{IV} or IO_4^-.[5b] FeO_4^{2-} is a well-known strong oxidant (E^0 $FeO_4^{2-}/Fe^{3+} = 2.2$ V) that readily oxidizes water,[18] however Ce^{IV} and IO_4^- are not capable of oxidizing Fe^{3+} to FeO_4^{2-}. Intermediate iron(IV) and iron(V) aquaoxo species are probably stronger oxidants than FeO_4^{2-}.[19] This means that at low pH values, even if some ligand dissociation occurs from an iron complex, the resulting $[Fe(OH_2)_6]^{3+}$ ion will not be able to catalyze water oxidation. On the other hand, at high pH values there is definitive evidence that ligand dissociation occurs before or after oxidation of the iron complex to generate Fe_2O_3 nanoparticles which is the actual catalyst for water oxidation.[20]

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