Cite this: Chem. Commun., 2011, 47, 4159-4161

www.rsc.org/chemcomm

COMMUNICATION

Oxygen evolution from BF₃/MnO₄^{-†}

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Received 3rd January 2011, Accepted 14th February 2011 DOI: 10.1039/c1cc00019e

 MnO_4^- is activated by BF₃ to undergo intramolecular coupling of two oxo ligands to generate O_2 . DFT calculations suggest that there should be a spin intercrossing between the singlet and triplet potential energy surfaces on going from the active intermediate $[MnO_2(OBF_3)_2]^-$ to the $O \cdots O$ coupling transition state.

O–O bond formation involving metal-oxo complexes is a crucial step in oxygen evolution in biological and chemical systems.¹ In general there are two basic mechanisms for O–O bond formation *via* metal-oxo species: (1) nucleophilic attack of water or hydroxide on metal-oxo species, (2) coupling of two metal-oxo groups.^{2,3} The water nucleophilic attack mechanism has been proposed for the oxygen evolving complex (OEC) of photosystem II.^{4–6} Nucleophilic attack of hydroxide on Mn(v)-oxo corrole species has recently been demonstrated.^{7,8} This mechanism has also been proposed for water oxidation by a number of ruthenium catalysts.^{3,9–11} Oxygen evolution *via* coupling of metal oxo groups has also been proposed for a number of systems.^{12–17} Recently, a ruthenium(II) dihydroxo complex was reported to undergo photochemical O···O coupling to generate HOOH.¹⁸

We report herein that in the presence of BF₃, MnO₄⁻ undergoes a novel intramolecular coupling of two oxo ligands in CH₃CN to generate O₂. Previously we have reported that the oxidation of alkanes by KMnO₄ in CH₃CN is greatly accelerated by BF₃.¹⁹ Kinetic and mechanistic studies suggest that at [BF₃] = $(0.1-3) \times 10^{-3}$ M and [MnO₄⁻] = $(0.5-1) \times 10^{-4}$ M in CH₃CN, a 1 : 1 adduct is formed, *i.e.* [BF₃·MnO₄]⁻, which is the active species responsible for the oxidation of C–H bonds. At higher concentrations of BF₃ $(>5 \times 10^{-2}$ M) and MnO₄⁻ $(>5 \times 10^{-3}$ M), there is evidence that the predominant species is [2BF₃·MnO₄]⁻. DFT calculations show that the energy barrier for the oxidation of CH₄ by [2BF₃·MnO₄]⁻ is lower than that of [BF₃·MnO₄]⁻ by about 6 kcal mol⁻¹.¹⁹ However, when BF₃ (>5 × 10^{-2} M in CH₃CN) was mixed with KMnO₄ (>5 × 10^{-3} M) at high concentrations in the absence of organic substrates, the purple color of MnO₄⁻ was still discharged rapidly, and gas bubbles could be seen, which was shown to be O₂ by GC and GC-MS analysis. The volume of O₂ evolved under various conditions was measured by a gas burette, and representative data are shown in Table 1.

The % yield of O_2 (calculated per mol of MnO_4^-) increases with [BF₃] (entries 1–4) and levels off to 66% (2.2 ml of O_2) at around 7 equiv. (0.088 M). The yield is not quantitative, presumably BF₃/MnO₄⁻ also oxidizes the solvent CH₃CN. Similar yields were obtained when "Bu₄N[MnO₄] (entry 5) or Ph₄P[MnO₄] (entry 10) was used instead of KMnO₄, while a higher yield of 77% was found for Me₄N[MnO₄] (entry 8). The use of other solvents such as ClCH₂CH₂Cl or CF₃C₆H₅ instead of CH₃CN resulted in much lower yields of O₂. The kinetics of O₂ evolution have been studied by measuring the volume of O₂ as a function of time. The rate of formation of O₂ follows clean first-order kinetics (Fig. 1). Representative kinetic data are shown in Table 2.

The first-order rate constant k_{O_2} is independent of [KMnO₄] $(1 \times 10^{-3}$ -8 $\times 10^{-3}$ M) and [BF₃] $(3 \times 10^{-2}$ -1.2 $\times 10^{-1}$ M). This is consistent with the mechanism shown in eqn (1) and (2), with saturation kinetics being reached under the relatively high [BF₃] used, and the observed first-order kinetics is due to unimolecular decomposition of [2BF₃·MnO₄]⁻. Unfortunately attempts to study the kinetics at lower [BF₃] were unsuccessful,

Table 1 % Yield of O_2 obtained by BF_3/MnO_4^- under various conditions $^{\it a}$

Entry	Complex	BF ₃ [equiv.]	Solvent	Yield of O ₂ [%]
1	K[MnO ₄]	1.8	CH ₃ CN	25 ± 5
2	K[MnO ₄]	3.6	CH ₃ CN	54 ± 5
3	K[MnO ₄]	7.2	CH ₃ CN	66 ± 5
4	K[MnO ₄]	14.4	CH ₃ CN	65 ± 5
5	ⁿ Bu ₄ N[MnO ₄]	8.0	CH ₃ CN	58 ± 5
6	ⁿ Bu ₄ N[MnO ₄]	8.0	CF ₃ C ₆ H ₅	33 ± 5
7	$^{n}Bu_{4}N[MnO_{4}]$	8.0	ClCH ₂ CH ₂ Cl	15 ± 5
8	$Me_4N[MnO_4]$	8.0	CH ₃ CN	77 ± 5
9	$Me_4N[MnO_4]$	8.0	ClCH ₂ CH ₂ Cl	7 ± 5
10	Ph ₄ P[MnO ₄]	8.0	CH ₃ CN	64 ± 5
11	Ph ₄ P[MnO ₄]	8.0	ClCH ₂ CH ₂ Cl	4 ± 5

^{*a*} KMnO₄, 12.6 mM; solvent, 10 ml; BF₃·CH₃CN, 1 ml; $T = 20 \pm 1$ °C; time = 10–15 min. % Yield = (mole of O₂ produced/mole of [MnO₄]⁻ used) × 100%.

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[†] Electronic supplementary information (ESI) available: Experimental details and DFT calculations. See DOI: 10.1039/c1cc00019e



Fig. 1 Plot of O₂ production *versus* time for the reaction between $KMnO_4$ (7.6 × 10⁻³ M) and $BF_3 \cdot CH_3 CN$ (1.2 × 10⁻¹ M) in $CH_3 CN$ at 20 ± 1 °C. The black line represents the best fit line.

Table 2 Representative first-order rate constants for O_2 production from BF_3/KMnO4 at 20 \pm 1 $^\circ C$ in CH_3CN

[KMnO ₄]/M	[BF ₃]/M	$k_{O_2}{}^{a}/\mathrm{s}^{-1}$
7.6×10^{-3}	1.2×10^{-1}	$(9.8 \pm 0.9) \times 10^{-3}$
7.6×10^{-3}	6.2×10^{-2}	$(1.0 \pm 0.1) \times 10^{-2}$
7.6×10^{-3}	3.1×10^{-2}	$(9.8 \pm 0.7) \times 10^{-3}$
3.8×10^{-3}	1.2×10^{-1}	$(9.9 \pm 0.8) \times 10^{-3}$
1.9×10^{-3}	$1.2 imes 10^{-1}$	$(1.1 \pm 0.1) \times 10^{-2}$
^{<i>a</i>} Values of k	are the average of at least three	successive runs

since the yields of O_2 became much lower and the volumes were too small to be measured accurately.

$$2BF_3 + MnO_4^- \stackrel{K_2}{\longleftrightarrow} [2BF_3 \cdot MnO_4]^-$$
(1)

$$[2BF_3 \cdot MnO_4]^- \xrightarrow{K_{O_2}} O_2 + Mn \text{ product}$$
(2)

¹⁸O-labeling experiments have been performed by using 91% ¹⁸O-labeled KMn¹⁸O₄. KMn¹⁸O₄ does not exchange its O atoms with water for at least 24 h at room temperature. When 1.1×10^{-2} M of 91% ¹⁸O-labeled KMn¹⁸O₄ was reacted with 1.8×10^{-1} M BF₃ in CH₃CN, the gas produced consisted of $66\% {}^{36}O_2$, $34\% {}^{34}O_2$ and $0\% {}^{32}O_2$ (±5%). For unimolecular decomposition of [2BF₃·MnO₄]⁻, the oxygen evolved should contain around 83% 36O2, 16% 34O2 and 1% 32O2. The observed lower ³⁶O₂% probably arises from exchange of $[2BF_3 \cdot MnO_4]^-$ with trace amount of H₂O present in CH₃CN (although freshly distilled from CaH₂). In another experiment 1.1×10^{-2} M of unlabeled KMnO₄ was reacted with 1.8 × 10^{-1} M BF₃ in CH₃CN in the presence of 8.8×10^{-2} M H₂¹⁸O (97% ¹⁸O-enriched), in this case the gas produced consisted of $32\% {}^{32}O_2$, $47\% {}^{34}O_2$ and $21\% {}^{36}O_2$ (±5%), again suggesting exchange of KMnO₄ with H₂O. Although KMnO₄ does not exchange with water at room temperature, it is not unreasonable for $[2BF_3 \cdot MnO_4]^-$ to exchange rapidly with water since it is expected to be much more susceptible to nucleophilic attack by water at the manganese centre. The observed first-order kinetics for O₂ evolution is also consistent with a mechanism that involves nucleophilic attack of H₂O in CH₃CN on Mn=O. However if this is the case, then the predominant product using $KMn^{18}O_4$ should be ${}^{34}O_2$ (eqn (3)). Moreover, if oxygen exchange occurs between KMn¹⁸O₄ and H₂O before water nucleophilic attack, then ³²O₂ and ³⁴O₂ should be the



Fig. 2 ESI-MS of the reaction mixture of $KMnO_4$ and BF_3 in CH_3CN at 20 °C.

predominant products, and the amount of ${}^{36}O_2$ should be much less than that observed.

$$[2BF_{3} \cdot Mn^{18}O_{4}]^{-} + H_{2}^{16}O \rightarrow {}^{16}O^{18}O$$
(3)

In the oxidation of alkanes by BF_3/MnO_4^- , the manganese product is MnO_2 .¹⁹ However in O₂ evolution from $BF_3/MnO_4^$ in the absence of the organic substrate, no solid or colloidal MnO_2 was observed. The reactant solutions turned from purple to pink and then colorless. Analysis of the product solution by ESI/MS (Fig. 2) shows predominantly the Mn(II) fluoro species $[MnF_3]^- \cdot 2BF_3$ and $[MnF_3]^- \cdot 3BF_3$ at m/z 248.1 and 316.0, respectively. There is also a minor peak at m/z291.0, which can be assigned to the Mn(III) species $[Mn(OBF_2)_2F_2]^- \cdot BF_3$. These results are consistent with unimolecular four-electron decomposition of $[MnO_4 \cdot 2BF_3]^$ to give O₂ and $[Mn(OBF_2)_2F_2]^-$, the Mn(III) species is unstable and is further reduced to Mn(II).

DFT calculations have been performed to gain insight into the mechanism of the BF₃-activated O₂ evolution from MnO_4^- . The singlet ground state of MnO_4^- (T_d symmetry) has four identical oxygen atoms and only one BF₃-coordinated intermediate (¹AIM1) of [MnO₂(OBF₃)₂]⁻ is identified. However, the triplet MnO_4^- (C_{2v} symmetry) can form three BF₃-coordinated intermediates (³AIM1, ³BIM1 and ³CIM1) for [MnO₂(OBF₃)₂]⁻ (Fig. S1, ESI⁺).

In Fig. 3, the PESs for the singlet and triplet decomposition pathways **A** of $[2BF_3 \cdot MnO_4]^-$, which give the most stable products, are depicted. The PESs for triplet decomposition pathways **B** and **C** are given in ESI.† Both the singlet and triplet decomposition pathways **A** are similar, except that: (i) the overall reaction barrier (59.7 kcal mol⁻¹ relative to the reactant intermediate) of the singlet pathway is larger than that (16.6 kcal mol⁻¹) of the triplet pathway; (ii) the products of the singlet pathway are ${}^{3}O_{2}$ and ${}^{5}[MnF_{2}(OBF_{2})_{2}]^{-}$ while those of the singlet pathway are ${}^{3}O_{2}$ and ${}^{3}[MnF_{2}(OBF_{2})_{2}]^{-}$; (iii) the triplet pathway is more exothermic than the singlet pathway.

The theoretical calculations indicate that there is a spin intercrossing between the triplet and singlet PESs going from the adduct intermediates to $O \cdots O$ coupling TSs. The singlet MnO_4^- first attracts two BF₃ molecules to form the intermediate ¹AIM1. Through spin intercrossing, the $Mn-O_{a/b}$ bonds of ¹AIM1 are lengthened to form a triplet Mn(v) peroxo intermediate ³AIM2 *via* ³ATS. During this process, the



Fig. 3 The potential energy profiles of the singlet and triplet decomposition pathways A of the 1 : 2 adduct $[2BF_3 \cdot MnO_4]^-$. The relative energies are the electronic energy with zero-point energy and thermal corrections at 298 K.

 O_a -Mn- O_b angle decreases from 109.4° to 46.7° and the Mn- $O_{a/b}$ bond lengths increase by ~ 0.2 Å whereas the distance between O_a and O_b contracts to form a peroxo O–O bond (1.412 Å). For this decomposition reaction involving intercrossing of PESs, the activation barrier height (E_a) of ³ATS is -3.0 kcal mol⁻¹ (barrierless relative to free reactants) or 31.1 kcal mol^{-1} (relative to ¹AIM1) at the B3LYP/6-31 + G(d) level. ΔG^{\ddagger} and ΔS^{\ddagger} (relative to ¹AIM1) are 33.3 kcal mol⁻¹ and -7.6 cal mol⁻¹ K⁻¹. respectively. The ³ATS has an imaginary frequency of 471i cm⁻¹, which corresponds to the scissoring motion of O_a -Mn- O_b . With the continued elongation of Mn- $O_{a/b}$ bonds, the peroxo intermediate ³AIM2 converts into the intermediate ³AIM3 with an energy lowering of 35.7 kcal mol⁻¹. Finally, a ground-state O₂ molecule is dissociated from ³AIM3, with the manganese product being [MnF2(OBF2)2]-, which was experimentally observed by ESI/MS. We have also studied the decomposition channels of MnO₄⁻ without BF₃ and a 1:1 adduct [BF₃·MnO₄]⁻ (ESI[†]). Our computational studies show that the energy barrier for O_2 evolution follows the order $[MnO_4]^- \gg [MnO_4 \cdot BF_3]^- > [MnO_4 \cdot 2BF_3]^-.$

In summary, we have shown that MnO_4^- reacts with excess BF_3 to give $[MnO_2(OBF_3)_2]^-$ which decomposes to give O_2 *via* a novel intramolecular $O \cdots O$ coupling mechanism. It is worth mentioning that the FeO_4^{2-} ion can be readily activated by Brønsted acids to liberate O_2^{20} Our results should provide insights for the design of water oxidation catalysts based on metal-oxo species, it also raises the possibility that the role of the Ca^{2+} ion in photosystem II is to activate the manganese oxo intermediate.

The work described in this communication was supported by the Hong Kong University Grants Committee Area of Excellence Scheme (AoE/P-03-08) and General Research Fund (CityU 101408). We thank one of the reviewers for very helpful comments.

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