Supporting information

**Oxygen Evolution from BF$_3$/MnO$_4$\(^-\)**

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Materials. **CAUTION:** Care should be taken in handling BF$_3$/MnO$_4^-$ in organic solvents, since the system is very reactive. Although we have not encountered any problems so far, the amount of MnO$_4^-$ used each time should be less than 50 mg. Potassium permanganate (Aldrich, 97%) was recrystallized from water.$^1$ $^{n}$Bu$_4$N[MnO$_4$]$^2$ and $^{18}$O-labeled K[MnO$_4$]$^3$ were prepared according to literature methods. Boron trifluoride–acetonitrile solution (BF$_3$·CH$_3$CN) (Fluka, 15.2 – 16.8%) was stored at -20 °C and used without further purification. The concentration was determined to be 16% by hydrolysis to H$_3$BO$_3$ and HF followed by titration with standard NaOH solution. H$_2^{18}$O (98 atom % $^{18}$O) was purchased from Medical Isotopes and used as received. Acetonitrile (Labscan, HPLC grade) was purified by Pure Solv$^\text{TM}$ Solvent Purification Systems (Innovative Technology, Inc.).

Instrumentation. Electrospray ionization mass spectra (ESI/MS) were obtained on a PE SCIEX API 365 mass spectrometer. The analyte solution was continuously infused with a syringe pump at a constant flow rate of 5 µL min$^{-1}$ into the pneumatically assisted electrospray probe with nitrogen as the nebulising gas. The declustering potential was typically set at 10-20 V. GC-MS measurements were carried out on a HP 6890 gas chromatograph equipped with a HP-5MS column (30 m × 0.25 mm i.d.) and interfaced to a HP 5975 mass-selective detector.

Kinetic and product analysis. The gas evolved during the experiment was determined as followed. In a typical reaction, a deaerated solution of MnO$_4^-$ (0.139 mmol) in CH$_3$CN (10 mL) was placed in a two neck round bottom flask (~16 mL) under argon at 293 K. One neck of the flask was connected to a gas burette and the other was sealed with a septum. A solution of deaerated BF$_3$·CH$_3$CN (1.26 mmol, 1 mL) was added through the septum into the MnO$_4^-$ solution with vigorous stirring. The volume of gas evolved was recorded at different time interval. The first-order rate constants, $k_{O_2}$, were obtained by nonlinear least-squares fits of $Y_t$ versus $t$ according to
the equation \( Y_t = Y_\infty + (Y_0 - Y_\infty) \exp(-k_{O_2}t) \), where \( Y_0 \) and \( Y_\infty \) are the initial and final \( O_2 \) produced (mmol), respectively. The gas was also analyzed by GC-MS.

**Determination of \( O_2 \) isotopic composition by GC-MS.**

In a typical reaction, a deaerated solution of 91\% \(^{18}\)O-labeled KMnO\(_4\) (0.08 mmol) in CH\(_3\)CN (6 mL) was placed in a vessel (~8 mL) sealed with a septum under argon at 293 K. A solution of BF\(_3\)-CH\(_3\)CN (1.29 mmol, 1 mL) was added into the solution using a gastight syringe. 50 \( \mu \)L gas in the headspace was withdrawn after 20 min and analyzed by GC-MS.

**DFT Calculations**

DFT calculations were carried out using Gaussian 03 program.\(^4\) The Becke's three-parameter nonlocal exchange functional\(^5\) and the Lee, Yang, and Parr nonlocal correlation functional (B3LYP)\(^6\) were utilized, with standard LANL2DZ basis set and relativistic effective core potential (ECP)\(^7\) for Mn, and the 6-31+G(d) basis set for all non-metal atoms. The geometries of all species were fully optimized and the harmonic vibration frequencies were calculated to obtain the zero-point energies (ZPE) and to verify nature [minimum or a transition state (TS)] of stationary points on the potential energy surfaces.

The calculated singlet-triplet splitting (17.3 kcal/mol) of MnO\(_4^\cdot\) at B3LYP/LAN2DZ/6-31+G(d) level is in good agreement with the value (22.8 kcal/mol) obtained at CCSD(T)/LAN2DZ/6-31+G(d) level.
References:


Supplementary Material (ESI) for Chemical Communications
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Fig. S1 Possible singlet and triplet decomposition pathways of 1:2 adduct [MnO₄⁺:₂BF₃].
Fig. S2 The potential energy profiles of the singlet and triplet reaction pathways of 1:2 adduct [MnO$_4^-$·2BF$_3$]. The relative energies are the electronic energy with zero-point energy and thermal corrections at 298 K in normal font while relative 298 K Gibb’s free energies are in the parentheses.
Fig. S3 Possible singlet and triplet decomposition pathways of 1:1 adduct

\[ \text{[MnO}_4^{−}\cdot\text{BF}_3] \].
Fig. S4 The potential energy profiles of the singlet and triplet reaction pathways of 1:1 adduct [MnO$_4$$^-$$\cdot$BF$_3$]. The relative energies are the electronic energy with zero-point energy and thermal corrections at 298 K in normal font while relative 298 K Gibb’s free energies are in the parentheses.
**Fig. S5** Optimized structures of the species involved in the triplet and singlet decomposition reactions of 1:2 adduct $[\text{MnO}_4^- \cdot 2\text{BF}_3]$. The bond distances are in angstroms and bond angles in degrees.

Fig. S5 (Continued)
Fig. S6 Optimized structures of the species involved in the triplet and singlet decomposition reactions of 1:1 adduct [MnO₄⁻·BF₃]. The bond distances are in angstroms and bond angles in degrees.