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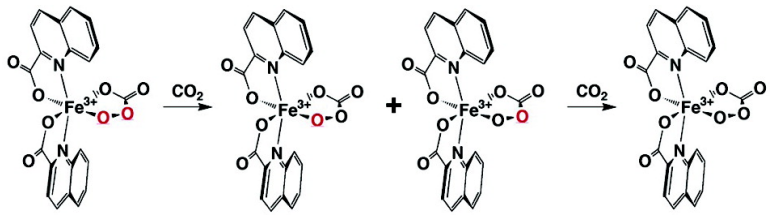
J. Am. Chem. Soc., **2005**, 127 (13), 4550-4551• DOI: 10.1021/ja0427202 • Publication Date (Web): 10 March 2005



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Reversible O−O Bond Cleavage and Formation of a Peroxo Moiety of a Peroxocarbonate Ligand Mediated by an Iron(III) Complex

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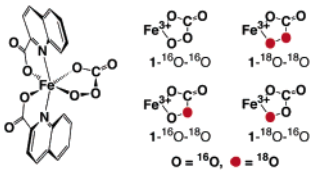
Mononuclear iron complexes having a peroxo group such as η^2-peroxide, η^1-hydroperoxide, alkylperoxide, or peroxocarbonate are of particular importance for understanding the reaction mechanisms in various oxidation reactions catalyzed by mononuclear iron enzymes and their functional models.[1,2] The O−O bond cleavage of the peroxo group is a key step of dioxygen activation by metal complexes. On the other hand, the O−O bond formation is also essential for the dioxygen formation by water oxidation. Reversible O−O bond cleavage and formation were first observed in the equilibrium between (μ-η^2:η^2-peroxo)Cu(II)$_2$ and bis(μ-oxo)Cu(III)$_2$ complexes by Tolman and co-workers[3] and more recently by others.[4] Recently, reversible O−X bond formation between Fe(IV)− or Mn(V)−(oxo)(porphyrin) complexes and X (X = Cl^-, Br^-, PhI) have also been reported.[5] Herein we report the first example of reversible O−O bond cleavage and formation of a peroxo group involving an iron(III) complex containing a peroxocarbonate ligand, $[Fe(qn)_2(O_2C(O)O)]^-$ (**1**) (qn = quinaldinate).[2]



Complex **1** is stable at −40 °C in acetonitrile and DMF under CO_2 for weeks. The resonance Raman spectrum of $[Fe(qn)_2(^{18}O-^{18}OC(O)O)]^-$ (**1**-^{18}O−^{18}O) in acetonitrile at −40 °C shows a ν(O−O) band at 842 cm^{-1} (Figure 1a). Upon warming the solution up to 20 °C, we observed that drastic spectral changes occurred to give new bands at 858, 868, and 884 cm^{-1} (spectra b−d and c′). By comparing the authentic sample (**1**-scrambled) prepared from ^{18}O-labeled H_2O_2 ($H_2{}^{16}O_2/H_2{}^{16}O{}^{18}O/H_2{}^{18}O_2$ = 25:50:25), we assigned these bands to the ν(O−O) vibrations of **1**-^{18}O−^{16}O, **1**-^{16}O−^{18}O, and **1**-^{16}O−^{16}O, respectively. These spectral changes clearly demonstrate the successive conversion from **1**-^{18}O−^{18}O through **1**-^{18}O−^{16}O and **1**-^{16}O−^{18}O to **1**-^{16}O−^{16}O, where the intensity ratio of **1**-^{18}O−^{16}O and **1**-^{16}O−^{18}O is the same as that observed for **1**-scrambled (cf. spectra c′ and e′), indicating that the formation rates of these two species are the same. The ESI-TOF/MS intensity changes of three isotopomers (**1**-^{18}O−^{18}O, **1**-^{18}O−^{16}O + **1**-^{16}O−^{18}O, and **1**-^{16}O−^{16}O) in DMF at 20 °C also showed the successive conversion from **1**-^{18}O−^{18}O (m/z = 480) through **1**-^{18}O−^{16}O + **1**-^{16}O−^{18}O (m/z = 478) to **1**-^{16}O−^{16}O (m/z = 476) together with the decomposition of **1** (Figure 2). In addition, the reverse

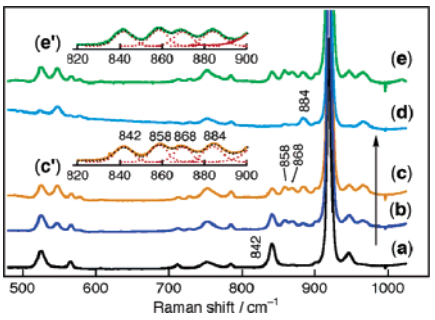


Figure 1. Raman spectra of **1**-^{18}O−^{18}O (a) at −40 °C, warming at 20 °C (b) for 5 min, (c) for 10 min, (d) for 30 min, and (e) that of **1**-scrambled in acetonitrile at −40 °C. Insets (c′ and e′) are Gaussian analyses of the ν(O−O) bands of (c) and (e).

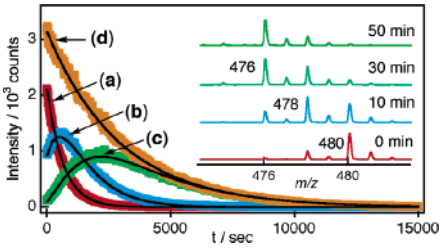


Figure 2. Time courses of ESI-TOF/MS intensity changes of **1** in DMF at 20 °C under CO_2 (bubbling for 3 min). Conversion profiles of (a) **1**-^{18}O−^{18}O (m/z = 480), (b) **1**-^{18}O−^{16}O + **1**-^{16}O−^{18}O (m/z = 478), (c) **1**-^{16}O−^{16}O (m/z = 476), and (d) decomposition profile of **1**. Solid lines are the fitting curves using eqs 2−4 with $k_c = 2.4 \times 10^{-3}$ s^{-1} and $k_d = 3.4 \times 10^{-4}$ s^{-1}. The inset is the ESI-TOF/MS spectral changes of **1** with time, where intensities of main signals are normalized for clarity.

conversion from $[Fe(qn)_2(^{16}O-^{16}OC(^{16}O)^{16}O)]^-$ to $[Fe(qn)_2(^{18}O-^{18}OC(^{18}O)^{18}O)]^-$ was observed by the reaction with $C^{18}O_2$ (Figure S1), indicating that oxygens of the peroxo moiety come from $C^{18}O_2$. It was also found that exchange of the CO_2 moiety (O−O−***C(═O)O***) and isotope exchange of the O−O moiety (***O−O***−C(═O)O) occur independently, and the former is much faster than the latter, and this was confirmed by the reactions with $^{13}CO_2$ and $C^{18}O_2$ by ESI-TOF/MS spectroscopy (Figures S1 and S2). The results indicate that, unlike $[RhCl(O-O-C(O)O)(PEt_2Ph)_3]$,[6] formation of peroxocarbonate in **1** does not involve O−O bond cleavage of the peroxide and there is a rapid equilibrium between **1** and $[Fe(qn)_2(O_2)]^-$ (eq 1). Although $[Fe(qn)_2(O_2)]^-$ has not been detected at present, side-on peroxo−iron(III) species have been well-established.[1g,7]

$$[Fe(qn)_2(O_2C(O)O)]^- \rightleftharpoons [Fe(qn)_2(O_2)]^- + CO_2 \quad (1)$$

The decomposition rate of **1** is highly dependent on the reaction conditions such as concentrations of CO_2 and H_2O (vide infra),

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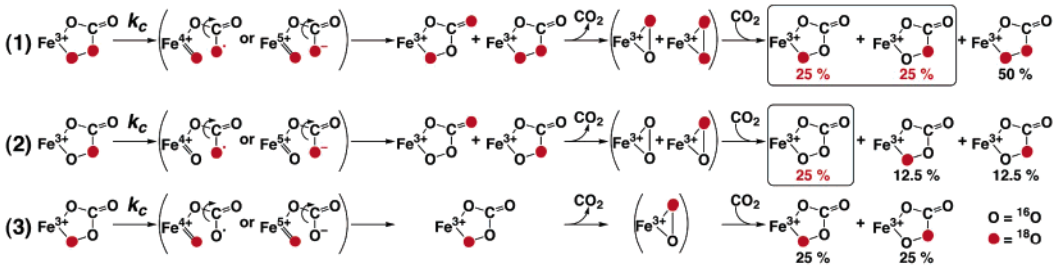
10.1021/ja0427202 CCC: $30.25

Scheme 1. Possible Conversion Pathways from **1**-^{18}O−^{18}O through **1**-^{18}O−^{16}O and **1**-^{16}O−^{18}O to **1**-^{16}O−^{16}O



but the conversion profiles shown in Figure 2 are not significantly affected (Figures S3 and S4), suggesting that CO_2 and H_2O are not involved in the rate-determining step (vide infra). Possible conversion pathways are shown in Scheme 1. The first step is O−O bond cleavage of the peroxo moiety to generate a high-valent Fe^{IV}═O or Fe^{V}═O species as found for M(III)(peroxocarbonato)(porphyrin) (M = Mn and Fe),[8] which is assumed to be a rate-determining step in the conversion processes. Although such high-valent iron−oxo species have not been detected in this study, Fe^{IV}═O species have been well-established.[1g,9] Rotation around the O−C bond (O═Fe−***O***−***C***(O)O) and reformation of the O−O bond produce **1**-^{18}O−^{18}O and **1**-^{18}O−^{16}O in a 1:1 ratio. Then rapid equilibrium with **1**-^{18}O−^{16}O and CO_2 generates **1**-^{18}O−^{16}O (25%) and **1**-^{16}O−^{18}O (25%), where the overall conversion to **1**-^{18}O−^{16}O and **1**-^{16}O−^{18}O is 50% based on **1**-^{18}O−^{18}O (step 1 in Scheme 1). Conversion to **1**-^{16}O−^{16}O occurs only from **1**-^{16}O−^{18}O (step 2), but not from **1**-^{18}O−^{16}O (step 3), where the conversion from (**1**-^{18}O−^{16}O + **1**-^{16}O−^{18}O) to **1**-^{16}O−^{16}O is 25%. This proposed mechanism yields the following rate equations including the decomposition of **1**.

$$d[\mathbf{A}]/dt = -(k_c/2 + k_d)[\mathbf{A}] \quad (2)$$

$$d[\mathbf{B}]/dt = (k_c/2)[\mathbf{A}] - (k_c/4 + k_d)[\mathbf{B}] \quad (3)$$

$$d[\mathbf{C}]/dt = (k_c/4)[\mathbf{B}] - k_d[\mathbf{C}] \quad (4)$$

where k_c and k_d are the first-order rate constants for the O−O bond cleavage and the decomposition of **1**, respectively, **A** = **1**-^{18}O−^{18}O, **B** = (**1**-^{18}O−^{16}O + **1**-^{16}O−^{18}O), **C** = **1**-^{16}O−^{16}O. The conversion profiles of the above three isotopomers and decay of **1** can be reasonably fitted with $k_c = 2.4 \times 10^{-3}$ s^{-1} and $k_d = 3.4 \times 10^{-4}$ s^{-1} as shown in Figure 2 (solid lines).[10] In this mechanism, there is a possibility of direct exchange of the oxo group of putative Fe^{IV}═O or Fe^{V}═O species with water.[9b] However, addition of water (500 equiv) causes no change in the conversion rate ($k_c = 2.2 \times 10^{-3}$ s^{-1}), although the decomposition rate is much accelerated ($k_d = 1.4 \times 10^{-3}$ s^{-1}, see Figure S3). The same is true for the CO_2 concentration effect (see Figure S4).[11] Thus the results indicate that a direct exchange of the oxo group of putative Fe^{IV}═O or Fe^{V}═O species is not significant and the oxygens of the peroxo group come from the oxygens of CO_2 (see also Figure S1).

In summary, we have succeeded in the first observation of the reversible O−O bond cleavage and reformation of the peroxo group via the formation of a high-valent iron-oxo species such as Fe^{IV}═O or Fe^{V}═O, which binds its counterpart, carbonate radical or carbonate, in close proximity. This proximity effect may be responsible for the reformation of the O−O bond.

Acknowledgment. Financial support of this research by the Ministry of Education, Science, and Culture Grant-in-Aid for Scientific Research to H.F., M.S., T.K., and Y.W. is gratefully acknowledged.

Supporting Information Available: Experimental details of the kinetic studies and Figures S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) This k_d value is slightly larger than that obtained from the UV−vis measurements ($k_d = 2.6 \times 10^{-4}$ s^{-1}). This is due to the change in the reaction conditions; for ESI-TOF/MS experiments, a slightly lower CO_2 concentration was employed to suppress the occasional foaming of CO_2.

(11) In the absence of CO_2, the decomposition is significantly accelerated; $k_d = 1.4 \times 10^{-2}$ s^{-1} under N_2 and $k_d = 2.6 \times 10^{-4}$ s^{-1} under CO_2 were obtained from the UV−vis measurements (see Figure S5).

JA0427202