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Oxidation Reactivity of a Structurally and Spectroscopically Well-defined Mononuclear Peroxocarbonato–Iron(III) Complex

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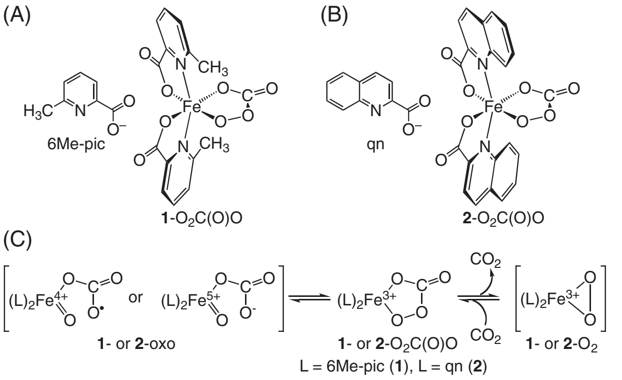
A mononuclear peroxocarbonato–iron(III) complex [Fe(6Me-pic)$_2$(O$_2$C(O)O)]$^-$ (**1**-O$_2$C(O)O) with bidentate ligands (6Me-pic), prepared by the reaction of a carbonato–iron(III) complex [Fe(6Me-pic)$_2$(CO$_3$)]$^-$ (**1**-CO$_3$) with H$_2$O$_2$, was fully characterized. **1**-O$_2$C(O)O showed reversible O–O bond cleavage and reformation of the peroxo group under CO$_2$ at 25 °C. **1**-O$_2$C(O)O is capable of not only oxidizing the C=C bond of cyclooctene but also the C–H bond of toluene. As for cyclooctene, epoxidation is favorable under CO$_2$ in the presence of H$_2$O, while *cis*-dihydroxylation precedes under N$_2$, indicating that the oxidation reactivity of **1**-O$_2$C(O)O toward cyclooctene can be tuned by changing the concentration of CO$_2$ and H$_2$O.

Peroxocarbonate (or peroxomonocarbonate, HCO$_4$$^-$) is a moderately reactive oxidant that can be classified as a peroxy acid, such as peracetic acid and *m*-chloroperbenzoic acid that are extensively utilized for the oxidation/oxygenation of organic compounds. HCO$_4$$^-$ generated from the reaction of H$_2$O$_2$ with HCO$_3$$^-$ in H$_2$O[1–5] has demonstrated its competence in the epoxidation of various olefins,[2] *N*-oxidation of tertiary amines,[3] and *S*-oxidation of organic sulfides[4] and thiols.[5] It has been shown that the epoxidation reaction with HCO$_4$$^-$ is significantly accelerated by the addition of some transition-metal (Mn, Fe, etc.) salts, whose activity is further enhanced by additives such as salicylic acid.[6] A putative peroxocarbonato–metal species has been proposed as a key intermediate in the epoxidation of olefins;[6] the active species is yet to be identified. Some peroxocarbonato–metal complexes have been prepared to date;[7–9] however, their oxidation abilities toward external substrates have not been studied in detail.[9a,9c–9f]

Previously, we reported the crystal structure of a mononuclear peroxocarbonato–iron(III) complex [Fe(qn)$_2$(O$_2$C(O)O)]$^-$ (**2**-O$_2$C(O)O)[8a] with a high-spin iron(III) center (Scheme 1B). Furthermore, **2**-O$_2$C(O)O showed reversible cleavage and reformation of the peroxo O–O bond of **2**-O$_2$C(O)O via the formation of a high-valent iron–oxo species (Fe^{IV}=O or Fe^{V}=O: **2**-oxo), in which an iron–peroxo species, (Fe^{III}(O$_2$): **2**-O$_2$), and CO$_2$ are under equilibrium conditions (Scheme 1C).[8b] Such iron(III)–peroxo and high-valent iron–oxo species are crucial intermediates that are responsible for alkane hydroxylation and arene dihydroxylation found in non-heme mononuclear iron enzymes[10] such as taurine/α-ketoglutarate dioxygenase (TauD)[10,11] and naphthalene dioxygenase (NDO).[10,12] However, the poor solubility of **2**-O$_2$C(O)O in conventional organic solvents prevented the investigating of its oxidation reactivity. We have improved its solubility by altering the bidentate ligand (6Me-pic instead of qn) in order to examine the oxidation reactivity of the peroxocarbonato–iron(III) species, whose peroxo moiety shows reversible O–O bond cleavage and reformation. We report the oxidation reactivity of a structurally and spectroscopically well-defined peroxocarbonato–iron(III) complex [Fe(6Me-pic)$_2$(O$_2$C(O)O)]$^-$ (**1**-O$_2$C(O)O)[13] (Scheme 1A) toward substrates including PPh$_3$, *cis*-cyclooctene, naphthalene, toluene, and cyclohexanecarboxaldehyde (CCA). We found interesting selectivity control of cyclooctene oxidation by **1**-O$_2$C(O)O due to the reversible release and uptake of CO$_2$ (Scheme 1C).



Scheme 1. (A) Bidentate ligand 6Me-pic and its peroxocarbonato–iron(III) complex **1**-O$_2$C(O)O. (B) Bidentate ligand qn and its peroxocarbonato–iron(III) complex **2**-O$_2$C(O)O. (C) Reversible cleavage and reformation of the peroxo O–O bond of **1**- or **2**-O$_2$C(O)O (left) and an equilibrium with **1**- or **2**-O$_2$C(O)O and **1**- or **2**-O$_2$ (right) under CO$_2$.

We have previously shown that **2**-O$_2$C(O)O was prepared by the reaction of a bis(μ-hydroxo)diiron(III) complex [Fe$_2$(qn)$_4$(μ-OH)$_2$] with ca. 10 equiv of H$_2$O$_2$ in the presence of DBU or (*n*-Bu$_4$N)(OAc) in DMF at −60 °C under CO$_2$.[8a] In contrast, it was found that the peroxocarbonato–iron(III) complex [Fe(6Me-pic)$_2$(O$_2$C(O)O)]$^-$ (**1**-O$_2$C(O)O) can be prepared by the reaction of a carbonato–iron(III) complex [Fe(6Me-pic)$_2$(CO$_3$)]$^-$ (**1**-CO$_3$) with only 1 equiv of H$_2$O$_2$ in acetonitrile at −40 °C under CO$_2$, which was confirmed by UV–vis and ESI-TOF/MS measurements (Figure S2, Supporting Information).[14]

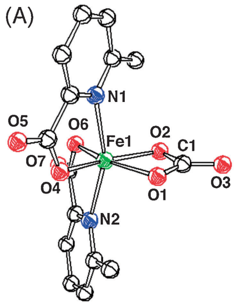
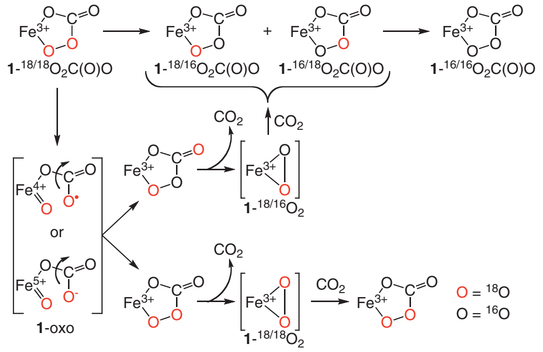


Figure 1. ORTEP views (50% probability) of complex anions of (A) $[Fe(6Me\text{-}pic)_2(CO_3)]^-$ (**1**-CO_3) and (B) $[Fe(6Me\text{-}pic)_2(O_2C(O)O)]^-$ (**1**-$O_2C(O)O$).

The crystal structures of **1**-CO_3 and **1**-$O_2C(O)O$ showed that the complex anions have a distorted octahedral geometry around the iron atom with a *trans*-N_2O_4 donor set composed of a bidentate carbonate (for **1**-CO_3) or peroxocarbonate (for **1**-$O_2C(O)O$) and two bidentate 6Me-pic ligands (Figures 1 and S1).[15] The metric parameters of **1**-$O_2C(O)O$ (Table S2), including the peroxo O–O bond length (1.457(4) Å), were comparable to those of **2**-$O_2C(O)O$ (O–O, 1.455(5) Å).[8a]

The physicochemical properties (Figures S3–S9) of $[Fe(6Me\text{-}pic)_2(O_2C(O)O)]^-$ (**1**-$O_2C(O)O$) were quite similar to those of $[Fe(qn)_2(O_2C(O)O)]^-$ (**2**-$O_2C(O)O$),[8] except for a higher solubility in acetonitrile. Furthermore, **1**-$^{18/18}O_2C(O)O$ also showed reversible O–O bond cleavage and reformation of the peroxo group under CO_2 at 25 °C, as found for **2**-$^{18/18}O_2C(O)O$.[8b] The successive conversion from **1**-$^{18/18}O_2$-C(O)O (m/z 408) through **1**-$^{18/16}O_2C(O)O$ and **1**-$^{16/18}O_2$-C(O)O (m/z 406) to **1**-$^{16/16}O_2C(O)O$ (m/z 404) was confirmed by ESI-TOF/MS and rR measurements (Figures S7 and S8), where the oxygen atoms of the peroxo moiety are derived from CO_2.[8b] It should be noted that the ESI-TOF mass spectrum of **1**-$^{18/18}O_2C(O)O$ showed a mononuclear peroxo–iron(III) complex $[Fe(6Me\text{-}pic)_2(^{18}O_2)]^-$ (**1**-$^{18/18}O_2$: m/z 364)[16] together with a signal of **1**-$^{18/18}O_2C(O)O$ (Figure S8), whereas the corresponding analogue $[Fe(qn)_2(^{18}O_2)]^-$ (**2**-$^{18/18}O_2$) was not detected in the previous study.[8b] The successive conversion from **1**-$^{18/18}O_2$ (m/z 364) through **1**-$^{18/16}O$ and **1**-$^{16/18}O_2$ (m/z 362) to **1**-$^{16/16}O_2$ (m/z 360) was also observed, where the intensity ratios of these isotopomers are the same as those of the corresponding isotopomers of **1**-$O_2C(O)O$ (Figure S8). Thus, these observations strongly support the successive O–O bond conversion pathways of **1**-$O_2C(O)O$, involving a rapid exchange of the CO_2 moiety of **1**-$O_2C(O)O$ (Scheme 2),[8b] which was previously proposed for **2**-$O_2C(O)O$.

As mentioned above, there is a rapid equilibrium between **1**-$O_2C(O)O$ and **1**-O_2 + CO_2.[17] Thus, the reactivity of **1**-$O_2C(O)O$ both under CO_2 and N_2 was investigated in electrophilic, nucleophilic, and C–H bond oxidation reactions with several substrates such as PPh_3, *cis*-cyclooctene, naphthalene, toluene, and CCA in acetonitrile at 25 °C (details are given in the Supporting Information). The oxidation products determined by GC-MS are listed in Table S3. In the reaction of **1**-$O_2C(O)O$ with an excess amount (50 equiv) of PPh_3, **1**-$O_2C(O)O$ acted as an oxo-transfer reagent to produce $O{=}PPh_3$ (ca. 95%) either under CO_2 or N_2, as found for the peroxocarbonato–metal complexes.[9a,9c–9f] The reaction of **1**-$O_2C(O)O$ with a 1000-fold excess of *cis*-cyclooctene afforded cyclooctene oxide (ca. 10%) and *cis*-1,2-cyclooctanediol (ca. 10%) together with a trace amount of 2-cycloocten-1-one (ca. 1%) under CO_2,[18] whereas **1**-$O_2C(O)O$ under N_2 afforded the epoxide and *cis*-diol in respective yields of ca. 3% and ca. 28% with a trace amount of 2-cycloocten-1-one.[19] The results are in contrast to those of the selective epoxidation observed for HCO_4^-/transition-metal salts[6] and the related peracetato–iron(III) complex $[Fe(6Me_2\text{-}BPP)(CH_3C(O)O_2)]^+$.[20] It should be noted that the *cis*-diol (D)/epoxide (E) product ratio (D/E ratio, hereafter) dramatically changes from 1/1 under CO_2 to 10/1 under N_2, resulting in a 10-fold change in the selectivity of cyclooctene oxidation from epoxidation to *cis*-dihydroxylation. This result indicates that the D/E selectivity by **1**-$O_2C(O)O$ toward cyclooctene is dominated by the concentration of CO_2, although the oxidation ability of **1**-$O_2C(O)O$ is modest. The observed *cis*-dihydroxylation is important and closely relevant to naphthalene *cis*-dihydroxylation catalyzed by NDO;[10,12] however, only a limited number of examples of *cis*-dihydroxylation by iron complexes are known so far.[21,22] Similar high D/E selectivity has also been achieved for catalytic cyclooctene oxidation by iron(II) complexes with tetradentate N4 ligands having 6-methyl-2-pyridylmethyl side arm(s), where the D/E ratios are 7.0/1 ($[Fe(6Me_3\text{-}TPA)(CH_3CN)_2]^{2+}$),[21] 5.0/1 ($[Fe(6Me_2\text{-}BPMEN)(OTf)_2]$),[21a] and 5.5/1 ($[Fe(^{Me,Me}Py\text{-}tacn)(OTf)_2]$).[22] Que et al. have proposed that a putative high-spin η^2-Fe^{III}–OOH species or the corresponding O–O bond cleaved HO–$Fe^V{=}O$ species is responsible for the *cis*-dihydroxylation of olefin catalyzed by $[Fe(6Me_3\text{-}TPA)(CH_3CN)_2]^{2+}$.[21] Thus, in the present system, a similar η^2-Fe^{III}–OOH species formed by the protonation of **1**-O_2, derived from **1**-$O_2C(O)O$, appears to be dominant for *cis*-dihydroxylation, whereas a putative high-valent iron–oxo species ($Fe^{IV}{=}O$ or $Fe^V{=}O$: **1**-oxo) or **1**-$O_2C(O)O$ seems to give rise to the epoxide. Although **1**-$O_2C(O)O$ under N_2 strongly favors *cis*-dihydroxylation, no oxidation products of naphthalene were observed. Furthermore, unlike other well-defined non-heme η^2-peroxo–iron(III) complexes,[23] **1**-$O_2C(O)O$ under N_2 showed no nucleophilic oxidative reaction toward CCA.



Scheme 2. Possible conversion pathways from **1**-$^{18/18}O_2C(O)O$ through **1**-$^{18/16}O_2C(O)O$ and **1**-$^{16/18}O_2C(O)O$ to **1**-$^{16/16}O_2C(O)O$. The following reactions to **1**-$^{16/16}O_2C(O)O$ proceed in the same way.

A noteworthy fact is that the addition of 1000 equiv of water into the reaction mixtures significantly improved the epoxidation selectivity of **1**-$O_2C(O)O$ under CO_2 (D/E ratio from 1/1 to 1/8.5) and N_2 (D/E ratio from 10/1 to 1/1.5) (Table S3). These results then indicate that the oxidation reactivity of **1**-$O_2C(O)O$ toward cyclooctene can be tuned by regulating the concentration of not only CO_2 but also H_2O, where a 83-fold change in the D/E ratio is observed on going from the condition under $CO_2 + H_2O$ (D/E = 1/8.3) to under N_2 (D/E = 10/1). Although the influence of water on the epoxidation is uncertain at the present time, the presence of water may affect the nature of the active oxidizing species.

We have also investigated the reactivity of **1**-$O_2C(O)O$ toward toluene (1000 equiv). **1**-$O_2C(O)O$ showed C–H bond oxidation ability toward toluene either under CO_2 or N_2 to give benzyl alcohol (ca. 2%) and benzaldehyde (ca. 10%) together with 1,2-diphenylethane (ca. 2%), although their yields were poor (Table S3). However, unlike cyclooctene, the reaction conditions have only a small influence on the product ratio of **1**-$O_2C(O)O$ toward toluene. The formation of 1,2-diphenylethane indicates the involvement of a benzyl radical that exist long enough to form the coupling dimer.[24]

In summary, we have succeeded in the structural and spectroscopic characterization of a new peroxocarbonato–iron(III) complex **1**-$O_2C(O)O$, whose peroxo moiety shows a reversible O–O bond cleavage and reformation. The oxidation abilities of **1**-$O_2C(O)O$ toward external substrates have also been explored and **1**-$O_2C(O)O$ is capable of not only oxidizing the C=C bond of cyclooctene but also the C–H bond of toluene. As for cyclooctene, selective epoxidation and *cis*-dihydroxylation by **1**-$O_2C(O)O$ were achieved by controlling the reaction conditions. Studies on the oxidation reactivity of **1**-$O_2C(O)O$ toward other olefins are in progress.

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Supporting Information is available electronically on J-STAGE.

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13 Abbreviations used: qn, quinaldinate; 6Me-pic, 6-methylpicolinate; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; $6Me_2$-BPP, *N*,*N*-bis(6-methyl-2-pyridylmethyl)-3-aminopropionate; $6Me_3$-TPA, tris(6-methyl-2-pyridylmethyl)amine; ^{Me,Me}Pytacn, *N*,*N′*-dimethyl-*N″*-(6-methyl-2-pyridylmethyl)triazacyclononane; $6Me_2$-BPMEN, *N*,*N′*-bis(6-methyl-2-pyridylmethyl)-*N*,*N′*-dimethyl-1,2-diaminoethane.

14 We also attempted to prepare $[Mn(6Me\text{-}pic)_2(O_2C(O)O)]^-$ (**3**-$O_2C(O)O$) because manganese salts show the highest activity among epoxidation of olefins by combination of HCO_4^- with transition-metal salts.[6b] ESI-TOF/MS study revealed that, unlike **1**-CO_3, the reaction of $[Mn(6Me\text{-}pic)_2(CO_3)]^-$ (**3**-CO_3)[15] with 1 equiv of H_2O_2 in acetonitrile at −40 °C under CO_2 did not generate the peroxocarbonate species **3**-$O_2C(O)O$, whereas a peroxo species $[Mn(6Me\text{-}pic)_2(O_2)]^-$ (**3**-O_2) was detected upon addition of 20 equiv of H_2O_2 to the solution of **3**-CO_3 (Figure S10). This reactivity is in contrast to that of **1**-CO_3. Thus, it is obvious that the metal ion plays a critical role in the formation of peroxocarbonate species in this system, although the origin of such a difference remains unclear. Unfortunately, **3**-O_2 was not isolated at −40 °C in this study.

15 The crystal structure of **3**-CO_3 was also determined by X-ray crystallography (Figure S1).

16 Peroxo–iron(III) species $[Fe(6Me\text{-}pic)_2(O_2)]^-$ (**1**-O_2) has been detected only under ESI-TOF/MS spectrometry conditions.

17 Thermal stability of **1**-$O_2C(O)O$ in acetonitrile at 25 °C is highly dependent on the reaction conditions as found for **2**-$O_2C(O)O$ in DMF; **1**-$O_2C(O)O$ decayed for 55 h under CO_2 and for 3 h under N_2 in acetonitrile at 25 °C (Figure S9).

18 Oxidation of *cis*-cyclooctene by **1**-CO_3 or **3**-CO_3 with 1 equiv of H_2O_2 under similar conditions was also carried out (Table S4).

19 Analogous reactions run under $CO_2 + O_2$ or O_2 showed smaller D/E ratios (1:15 under $CO_2 + O_2$ and 1.1:1 under O_2) because a larger amount of epoxide was formed to some extent via O_2 trapping of carbon centered radical intermediate derived from H-atom abstruction of cyclooctene, where the yields of 2-cycloocten-1-one were increased (ca. 6%).

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24 The higher yields of benzaldehyde (ca. 20%) were obtained in analogous reactions run under $CO_2 + O_2$ or O_2, indicating that benzaldehyde was formed to some extent via O_2 trapping of longer lived benzyl radical derived from H-atom abstruction of toluene.