We believe that PAC has the characteristics to be a highly useful tool for studying interphases between optically transparent solid and liquid phases, provided that an appropriate reporter group with a suitable extinction coefficient can be localized in that environment.

Supplementary Material Available: Methodology for extracting pK_a's from the data generated in the PAC studies described in the paper (2 pages). Ordering information is given on any current masthead page.

Binuclear Non-Heme Iron Oxo Transfer Analogue Reaction System: Observations and Biological Implications

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Evidence from mechanistic studies on a variety of non-heme Fe metalloproteins suggests the intimate involvement of the [$Fe^{2+}O \leftrightarrow Fe^{4+}=O$] species as a source of reactive oxygen atom. This intermediate is involved in the proposed mechanisms of a wide variety of mononuclear non-heme Fe^{2+} monooxygenases such as the H_4biopterin-dependent hydroxylases,[1] the α-ketoglutarate-dependent hydroxylases,[2] isopenicillin-N synthase,[3] the bacterial iron hydroxylases,[4] and the aromatic dioxygenases.[5] More recently, a similar reactive oxygen species was postulated to play a key role in the μ-hydroxo-bridged binuclear iron center in soluble methane monooxygenase (MMO) isolated from *Methylococcus capsulatus* (Bath)[6a–h] and *Methylosinus trichosporium* OB3b.[6i–k] This enzyme is particularly interesting owing to its remarkably

broad substrate specficity, catalyzing not only the conversion of methane to methanol but also the incorporation of oxygen into the C–H bonds of a variety of alkanes, alkenes, ethers, and alicyclic, aromatic, and heterocyclic compounds.

Although various non-heme Fe model systems are proposed to involve iron–oxene species, the active oxygenating agents are not amenable to spectroscopic/structural characterization.[7–10] We are interested in evaluating (i) the ability of simple iron complexes to act as oxygen atom transfer catalysts and (ii) the kinetic, reactivity, and structural/electronic properties of the reactive intermediates. We disclose herein the ability of a binuclear non-heme Fe^{2+} coordination compound to catalytically decompose peracids in a heterolytic fashion and present evidence for the formation of an intermediate and its involvement in the transfer of an oxenoid equivalent to simple organic substrates.

Starting with 1,2-bis(2-hydroxybenzamido)benzene (H_4HBAB),[11] formation of the dilithium salt (LiOH, MeOH) followed by meticulous drying and reaction with an equimolar amount of *trans*-Fe^{2+}(N-MeIm)$_2$(Cl)$_2$(MeOH)$_2$[12] in anhydrous MeOH under anaerobic conditions gave binuclear [Fe^{2+}(H_2HBAB)(N-MeIm)]$_2$ (I) (80%) as a yellow microcrystalline product.[15a,16] The reaction of Li$_2$H$_2$HBAB with anhydrous

Table I. Products from the Fe^{2+} and Fe^{3+} Catalyzed Oxygen Atom Transfer Reactions of Organic Substrates (RH) by PhIO in CH_2Cl_2/1% DMF

substrate	catalyst[c]	% reacn efficiency[d]	products
cyclohexene[a]	I	35	cyclohexene epoxide (12.5%), cyclohexenol (25%), cyclohexenone (50%), cyclohexanone (12.5%)[f]
	II	NR[e]	PhI
	III	NR[e]	PhI
PhSMe[b]	I	30	PhS(O)Me (90%), PhS(O)$_2$Me (10%)[g]
PhS(O)Me[a]	I	80	PhS(O)$_2$Me[g]

[a] Ratio of catalyst:PhIO:substrate was 1:(2 × 10³):(1 × 10⁴), [catalyst] = 0.05 mM. Reactions were followed over a 6-h time period. Reported values were obtained at 6 h. [b] Ratio of I:PhIO:PhSMe was 1:200:1000, [I] = 0.05 mM. [c] I = [Fe^{2+}(H_2HBAB)(N-MeIm)]$_2$; II = [Fe^{3+}(H_2HBAB)]$_2$(NO_3)$_2$; III = [Fe^{3+}(H_2HBAB)]$_2$O. [d] 100% represents one substrate oxygenation per PhIO consumed in the reaction. [e] NR, less than 2% substrate reaction within 6 h. [f] Product quantization indicates a turnover number of ≈30. [g] Product quantization indicates a turnover number of 4.

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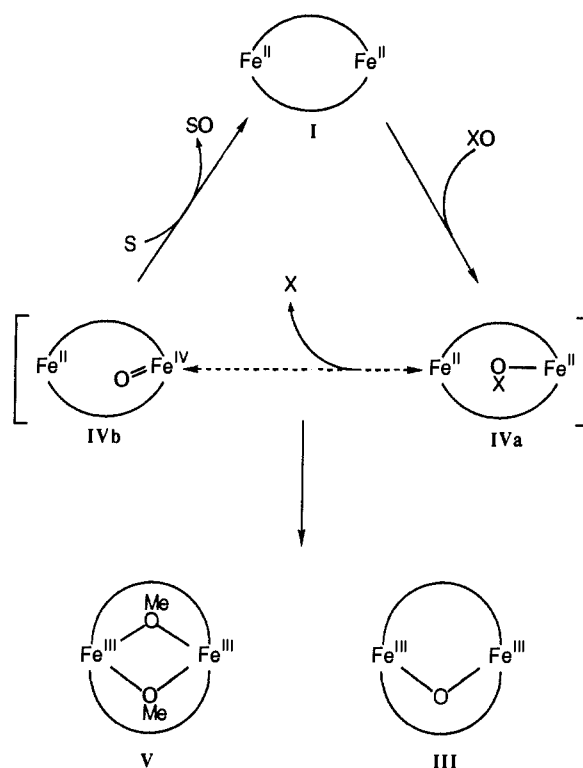
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Communications to the Editor

$Fe(NO_3)_3$ in CH_3CN gives an instant precipitate, which after further washing with CH_3CN affords purple microcrystalline $[Fe^{3+}(H_2HBAB)]_2(NO_3)_2$ (II) (70%).[15b] The μ-oxo-bridged $Fe^{3+}(H_2HBAB)$ dimer (III) was generated by the addition of 2-4 equiv of Et_3N and 1 equiv of H_2O to a solution of II. Overnight stirring afforded III isolated as orange microcrystals.[15c]

The decomposition of two peracids (*m*-chloroperbenzoic acid, *m*CPBA; phenylperacetic acid, PPAA) by I and II were followed by UV/vis spectroscopy using 2,4,6-tri-*tert*-butylphenol (TBPH), which along with solvent (MeOH) acts as a trapping reagent for the reactive Fe intermediate.[18,19] For I, the increase in absorption at both 400 and 630 nm indicated 15-20 turnovers, while for II, 6-10 turnovers were observed. This result was independent of the peracid used. Upon completion of the reaction (4 h), $\leq 10\%$ active oxygen remained in the reaction mixtures.[20] In all cases, analysis of the solutions showed the presence of HCHO in quantities expected for oxygen mass balance.[21] The appropriate control reactions indicate negligible background reactions ($\leq 10\%$) in the absence of I or II.

The mechanism of catalytic O-O decomposition (homolytic vs heterolytic) was probed by using PPAA as substrate.[22] Parallel reactions, followed by UV/vis and GC analysis, indicated different mechanisms for the Fe^{2+} and Fe^{3+} compounds.[23] GC characterization of the catalytic reaction of I with PPAA indicated the quantitative presence of phenylacetic acid, which is produced solely from the heterolytic decomposition of PPAA.[24,25] The catalytic reaction of II with PPAA only produced products expected from decarboxylation of the unstable phenylacetic radical ($PhCH_2CO_2\bullet$). The observation that phenylacetic acid is stable in the presence of II precludes the possibility of heterolytic peracid decomposition followed by radical formation.[25] This result clearly indicates that the reaction of I with PPAA proceeds via heterolytic cleavage of the percarboxylic O-O bond while II follows a homolytic pathway.

Catalytic atom transfer reactions were investigated by using PhIO as oxygen atom donor molecule and either cyclohexene, methyl phenyl sulfide, or methyl phenyl sulfoxide as substrate

(15) (a) $[Fe^{2+}(H_2HBAB)(N\text{-}MeIm)]_2\cdot MeOH$ (I). Anal. Calcd for $C_{49}H_{44}N_8O_9Fe_2$: C, 58.80; H, 4.43; N, 11.20; Fe, 11.18. Found: C, 59.34; H, 4.16; N, 11.50; Fe, 10.80. Isothermal distillation determination of molecular weight (Signer method):[17] MW 1000, dimer. UV/vis: λ_{max} (ϵ_M) = 312 (sh, 30000) nm ($CH_2Cl_2/1\%$ DMF). IR: $\nu_{amideNH}$ = 3450 cm^{-1}, $\nu_{amideCO}$ = 1640 cm^{-1}. (b) $[Fe^{3+}(H_2HBAB)]_2(NO_3)_2\cdot(DMF)_2\cdot Et_2O$ (II). Anal. Calcd for $C_{50}H_{52}N_8O_{17}Fe_2$: C, 52.28; H, 4.53; N, 9.76; Fe, 9.7. Found: C, 52.54; H, 4.56; N, 9.49; Fe, 8.99. UV/vis: λ_{max} (ϵ_M) = 306 (53800), 359 (16700), 496 (2070) nm ($CH_2Cl_2/1\%$ DMF). IR: $\nu_{amideNH}$ = 3450 cm^{-1}, $\nu_{amideCO}$ = 1607 cm^{-1}. (c) $[Fe^{3+}(H_2HBAB)]_2O\cdot EtOH\cdot Et_2O$ (III). Anal. Calcd for $C_{46}H_{44}N_4O_{11}Fe_2$: C, 58.8; H, 4.69; N, 5.97; O, 18.75; Fe, 11.90. Found: C, 58.74; H, 4.78; N, 5.93; Fe, 12,38. UV/vis: λ_{max} (ϵ_M) = 306 (sh, 17400), 452 (2700) nm ($CH_2Cl_2/1\%$ DMF). IR: $\nu_{amideCO}$ = 1606, $\nu_{as,Fe\text{-}16O\text{-}Fe}$ = 837 cm^{-1}.

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(24) Upon completion of reactions (10 h), all reaction solutions were treated with 1.5 mL of a freshly prepared solution of CH_2N_2 in Et_2O. Analysis by gas chromatography was performed after venting the reaction mixture inside an inert atmosphere box for 1 h.[25]

(25) All gas chromatographic analyses were performed on a Varian 3700 gas chromatograph using a methyl silicon capillary column (50 m × 0.25 mm i.d.). Gradient temperature programs were required to allow base-line resolution of methyl phenylacetate, toluene, benzaldehyde, benzyl alcohol, bibenzyl, benzyl phenylacetate, methylal, and methyl formate or cyclohexene, cyclohexene epoxide, cyclohexenol, cyclohexenone, and cyclohexanone. Expected reaction products were stable to GC conditions.

Scheme I

(Table I). In the absence of PhIO, I and II in the presence of substrates were stable for ≥ 15 h. In the case of cyclohexene, GC product analysis for I showed significant increase in product formation (≈ 30 turnovers) over control reactions. The reaction products include cyclohexene epoxide, cyclohexenol, cyclohexenone, and cyclohexanone (1:2:4:1) and represent $\geq 95\%$ of the oxygenated products.[25] Iodobenzene was recovered in quantitative yield. No detectable amounts of chlorinated products were identified by GC-MS analysis. Analogous experiments with II and III indicated that both species are inert as atom-transfer catalysts.

Upon completion of the catalytic reactions, [I] remaining in solution (UV/vis) is significantly decreased owing to the formation of insoluble μ-oxo-bridged Fe^{3+} species. The reaction of 0.5 equiv of $PhI^{16}O$ with 1.0 equiv of I under strictly anaerobic conditions in $CH_2Cl_2/1\%$ DMF led to the production of two products, the major species ($\approx 90\%$) being a μ-oxo Fe^{3+} dimer which was spectroscopically identical (UV/vis, IR) with III. Use of $PhI^{18}O$ led to the incorporation of ^{18}O in the oxo bridge of the dimer ($\nu_{as,Fe\text{-}^{18}O\text{-}Fe}$ = 797 cm^{-1}). The minor product, $[Fe^{3+}(H_2HBAB)OMe]_2$ (V) ($\approx 10\%$), was crystallographically characterized and found to contain bridging H_2HBAB ligands with cis μ-OMe, cis phenoxide, and trans amide oxygen coordination spheres about each Fe center.[26]

The addition of either PhIO, C_6F_5IO, or excess peracid to an anaerobic solution of I in the absence of substrate at ambient temperature generates a transient species (IV) characterized by an intense orange-red color. This intermediate rapidly bleaches upon precipitation of III or the addition of substrate generating product. Spectroscopic characterization of this species, which has a solution half-life of $\approx 1^1/_2$ h at -78 °C, is currently in progress. We are currently unable to isolate IV at low temperatures.

The reactivity of I toward oxygen atom donors and the obligatory production of intermediate IV prior to atom transfer can be rationalized in terms of the following catalytic cycle (Scheme I). The mechanism of peracid and PhIO decomposition and the observation that IV in the absence of substrate leads to III and V are consistent with the assignment of IV either as an adduct

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of I with the oxygen atom donor molecule (Scheme I, IVa) or as an [$Fe^{2+}O \leftrightarrow Fe^{4+}=O$] intermediate (Scheme I, IVb). Finally, the observation that neither II nor III is capable of catalytic oxygen atom transfer chemistry precludes their direct active involvement in the proposed scheme.

The data presented above is consistent with two possible mechanisms for oxygen atom transfer: (i) coordination of iodine of PhIO to the Fe^{2+} center resulting in oxygen activation[27] (IVa) or (ii) an oxygen rebound process whereby the oxygen atom from PhIO is transferred to substrate via the formation of an Fe–oxenoid species[7d] (IVb). Although the details of the reaction are under investigation, we prefer mechanism ii on the basis of the qualitative similarity of chromophore IV produced by either PhIO, C_6F_5IO, or excess peracid (*m*CPBA, PPAA), the observed reactivity of I with peracids, the quantitative conversion in the absence of substrate of I to III (via IV), the similarity of the observed product distribution with that generated by FeTPP-Cl and PhIO[7d], and the production of methyl phenyl sulfoxide and sulfone from methyl phenyl sulfide and sulfoxide, respectively. Since sulfide to sulfoxide and sulfoxide to sulfone transformations are catalyzed by metal–oxo species, the oxidation of cyclohexene must also involve such a species.[28] Furthermore, the observation that II is unable to act as an oxygen atom transfer catalyst in the presence of PhIO is inconsistent with a simple PhIO adduct of I or II acting as the active species. Work directed toward elucidating the mechanism of oxygen atom transfer reactions by I, determination of the nature of the active catalyst, the kinetic/structural characterization of species IV, and understanding the relevance of these observations to non-heme Fe containing monooxygenases is in progress.

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Spectroscopic Observation of Individual sp3-Nitrogen Stereoisomers. Supersonic Jet Studies of 2-Aminobenzyl Alcohol[‡]

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Assessment of the stereodynamics at the template associated with a pyramidal trivalent nitrogen is complicated by the presence of two low-energy processes, nitrogen inversion and internal rotation about various single bonds.[1-6] Supersonic molecular jet

‡ Dedicated to Professor Tetsuo Nozoe, to commemorate his Beiju (88th birthday) and to honor his commitments to science.

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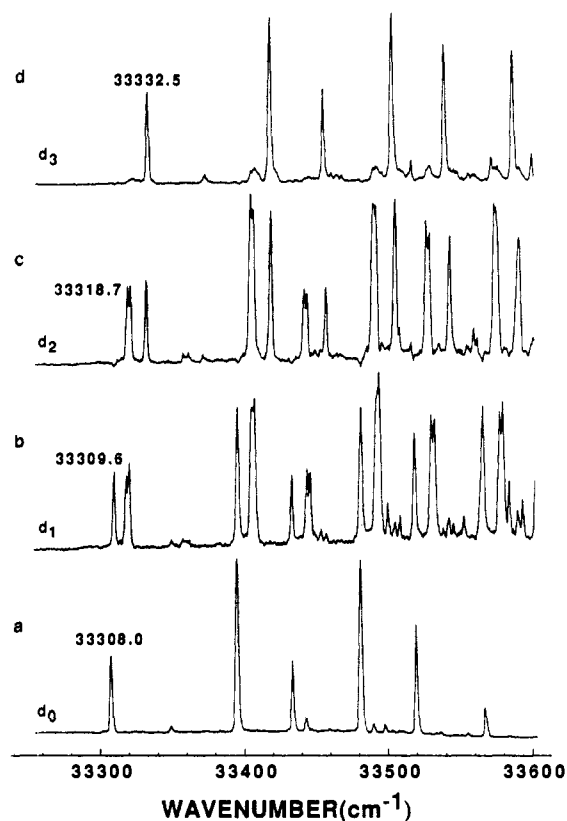

Figure 1. Mass-resolved excitation spectra of (a) 2-aminobenzyl alcohol (2), (b) 2-aminobenzyl alcohol-d_1 (4a-4c), (c) 2-aminobenzyl alcohol-d_2 (5a-5c), and 2-aminobenzyl alcohol-d_3 (3) about the 0_0^0 transition region.

laser spectroscopy has a number of particular advantages for conformational analysis for systems having low-energy interconversion processes:[7-9] the expansion results in molecules at near 0 K; the molecules are isolated; one 0_0^0 (origin) transition is observed for each individual stable conformation; and the resolution of the experiment is excellent (<1 cm^{-1}). Minimum energy conformations of a variety of alkyl-substituted and heterosub-

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