mutually hydrogen-bonded hydroxy groups, not those with isolated siloxy groups[7c,29] or geminally[7g] or vicinally[23] hydrogen-bonded disiloxy groups. If these sites represent a significant proportion of surface sites with hydrogen-bonded siloxy groups, extensive surface modification should occur via multiply hydrogen-bonded sites. Our work has specifically addressed silylation with TMSCl, but similar selectivities should be observed with other electrophilic reagents (e.g., dichloro- or trichlorsilanes, alkoxysilanes, phosphorus or sulfur halides, metal halides). Surface sites possessing three (or more) adjacent siloxy groups may therefore play an important role in the chemistry of silica and silica-supported catalysts.

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Supplementary Material Available: X-ray crystal data for **2b** including experimental procedures and tables of crystal data, atomic coordinates, thermal parameters, bond lengths, and bond angles (12 pages); listing of calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

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Iron-Induced Activation of Hydrogen Peroxide for the Direct Ketonization of Methylenic Carbon [c-C_6H_{12} → c-$C_6H_{10}(O)$] and the Dioxygenation of Acetylenes and Arylolefins

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Abstract: In pyridine/acetic acid solvent bis(picolinato)iron(II) [$Fe(PA)_2$], (2,6-dicarboxylatopyridine)iron(II) [Fe(DPA)], and their μ-oxo dimers [$(PA)_2FeOFe(PA)_2$ and (DPA)FeOFe(DPA)] catalyze hydrogen peroxide for the selective ketonization of methylenic carbons ($>CH_2 \rightarrow >C{=}O$) and the dioxygenation of acetylenes to α-diketones and arylolefins to aldehydes. Cyclohexane is transformed with 72% efficiency (c-C_6H_{12} oxidized per two HOOH) to give 95% cyclohexanone and 5% cyclohexanol, ethyl benzene with 51% efficiency to give acetophenone as the only detectable product, and *n*-hexane with 52% efficiency to give 53% 3-hexanone, 46% 2-hexanone, and <2% 1-hexanol. Suspensions of $KO_2(s)$ or $(Me_4N)O_2(s)$ in a pyridine/acetic acid solvent system are catalyzed by several iron complexes [$(py)_4FeCl_2$, $(py)_4Fe(OAc)_2$, $FeCl_3{\cdot}6H_2O$, $(MeCN)_4Fe(ClO_4)_2$, $(Ph_3PO)_4Fe(ClO_4)_2$, $Fe(PA)_2$, and $(PA)_2FeOFe(PA)_2$] to give HOOH and transform methylenic carbons to ketones, and to dioxygenate acetylenes and arylolefins. Electrolytic reduction of dioxygen (O_2) in the same solvent/catalyst systems results in analogous substrate transformations. The $Fe(PA)_2$ complex is uniquely efficient and exhibits catalytic turnover for $KO_2(s)$ suspensions as well as for electro-reduced O_2. All systems appear to produce a common reactive intermediate **3** $[(PA)_2\overset{\frown O \frown}{FeOOFe}(PA)_2]$ via in situ formation of HOOH and $(PA)_2FeOFe(PA)_2$ (**1**).

During the past 6 years several reports[1-5] have described the selective transformation of methylenic groups ($>CH_2$) to ketones via four heterogeneous iron–dioxygen systems: (a) iron powder/sodium sulfide/O_2, (b) $Fe_3O(OAc)_6{\cdot}3.5py$/zinc dust/O_2, (c) $(py)_4FeCl_2/KO_2(s)$, and (d) $(py)_4FeCl_2/(O_2 + e^- \rightarrow O_2^{\bullet -})$ in 4:1 pyridine/acetic acid. These systems are postulated to contain σ-bonded iron–carbon intermediates[6] with superoxide ion ($O_2^{\bullet -}$) as the active form of reduced oxygen, which oxidizes the iron catalyst within the catalytic cycle. Pyridine is believed to be essential to the system as a trap for hydroxyl radical and thereby prevent Fenton chemistry. Acetic acid serves as a proton source to transform superoxide ion to hydroperoxyl radical ($HOO^\bullet$).

This background prompted us to undertake a detailed study to characterize and to optimize the iron/reduced dioxygen/(py/HOAc) systems.[1-5] In particular the investigations have sought to elucidate (a) the optimum complex for the iron catalyst, (b) the most efficient form of superoxide [(homogeneous $(Me_4N)O_2$, $(Me_4N)O_2(s)$, $KO_2(s)$, $KO_2(s)$/pyridine slurry, or electro-reduced dioxygen], and (c) the optimum solvent composition for the selective transformation of methylenic carbons to ketones.

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During the course of the investigations to characterize the reactive intermediate we added hydrogen peroxide to a pyridine/acetic acid solution of an iron–picolinate complex [$Fe(PA)_2$] and cyclohexane (eq 1). To our surprise this system brought about

$$\text{c-}C_6H_{12} + 2HOOH \xrightarrow[\text{py/HOAc}]{Fe(PA)_2} \text{c-}C_6H_{10}(O) + 3H_2O \quad (1)$$

the near-stoichiometric transformation of cyclohexane to cyclohexanone [72% efficient to give c-$C_6H_{10}(O)$ (95%) and c-$C_6H_{11}OH$ (5%)]. Because experiments with other iron complexes, or other solvent matrices, yield a spectrum of products that are characteristic of Fenton chemistry ($^{\bullet}OH$),[4] this iron picolinate/(pyridine/acetic acid)/HOOH combination is a unique system for the direct transformation of methylenic carbons to ketones. As such, it represents a new type of metal-induced activation of hydrogen peroxide via an exceptional reactive intermediate and has prompted a systematic investigation to characterize the system and the chemistry of the $Fe(PA)_2$/HOOH intermediate.

In a previous communication[7] we reported that [$Fe(MeCN)_4$]$(ClO_4)_2$ in anhydrous acetonitrile activates excess HOOH for the dioxygenation of diphenylisobenzofuran, rubrene, acetylenes, *cis*-stilbene, and methylstyrene. However, the system is essentially unreactive with saturated hydrocarbons, and the presence of basic ligands (H_2O or pyridine) causes the system to promote Fenton chemistry [Fe(II) + HOOH → $Fe^{III}OH$ + ·OH].[8] Here we discuss the activation of HOOH by iron–picolinate complexes in a pyridine/acetic acid solvent for the efficient and selective transformation of methylenic carbons to ketones and the dioxygenation of acetylenes and arylolefins.

Experimental Section

Equipment. The reaction products were separated and identified with a Hewlett-Packard 5880A Series gas chromatograph equipped with a HP-1 capillary column (cross-linked methyl silicone gum phase, 12 m × 0.2 mm i.d.) and by gas chromatography–mass spectrometry (Hewlett-Packard 5790A Series gas chromatograph with mass-selective detector). Reference samples were used to confirm product identification. The quantities of products were calculated from standard curves for authentic samples. Direct injections of the product solution (1–2 μL) were made.

Cyclic voltammetry was accomplished with a Bioanalytical Systems Model CV-27 voltammograph and a Houston Instruments Model 200 XY recorder. Controlled-potential electrolysis was performed with a three-electrode potentiostat (Princeton Applied Research Model 173 potentiostat–galvanostat, Model 175 universal programmer, and Model 179 digital coulometer). A Vacuum Atmospheres inert-atmosphere glovebox was used for storage, preparation, and addition of the superoxide species.

The UV–vis spectrophotometric measurements were performed on a Hewlett-Packard Model 8450 diode-array spectrophotometer. Infrared spectra were recorded with an IBM IR/44 (IR/40S spectrometer with IR/30S upgrade unit) FTIR instrument. Solid-state samples were made by use of a KBr pellet press. Solid magnetic susceptibility measurements were performed with a Johnson Matthey Model MSB1 Magnetic Susceptibility Balance.

Singlet dioxygen production was detected by measurement of its characteristic 1268-nm chemiluminescence. The chemiluminescence spectrometer that was used for these measurements has been described.[9] Singlet oxygen quenching constants for the iron complexes were derived from $^1O_2$-phosphorescence measurements as previously described.[10]

Chemicals and Reagents. The reagents for the investigations and syntheses were the highest purity commercially available and were used without further purification. Burdick and Jackson "distilled in glass" grade acetonitrile (MeCN, 0.004% H_2O), dimethylformamide (DMF, 0.011% H_2O), pyridine (py, 0.014% H_2O), and glacial acetic acid (HOAc, ACS grade, Fisher) were used as solvents. The magnetic susceptibility measurements made use of d_7-DMF that contained 1% tetramethylsilane (TMS, Aldrich). High-purity argon gas was used to deaerate the solutions. All compounds were dried in vacuo over $CaSO_4$ for 24 h prior to use.

Synthesis of Concentrated Hydrogen Peroxide. Water was carefully removed from 10 mL of 50% HOOH at 0 °C via high-vacuum evaporation to give 1.5–3 mL of almost pure hydrogen peroxide.[7] This was quickly dissolved in dry acetonitrile (25 mL). The resulting solutions were assayed by iodometric titrations and found to be 1.6 M (94% HOOH) and 3.6 M (82% HOOH).

$(Me_4N)PA$ and $(Me_4N)_2DPA$. Tetramethylammonium picolinate [$(Me_4N)PA$] and tetramethylammonium dipicolinate [$Me_4N)_2DPA$] were prepared by the neutralization of picolinic acid (PAH) and 2,6-pyridinedicarboxylic acid ($DPAH_2$) with tetramethylammonium hydroxide pentahydrate in aqueous solution. $(Me_4N)PA$ was recrystallized from acetonitrile and $(Me_4N)_2DPA$ from 95% MeCN/5% MeOH. The hydroscopic products were stored under vacuum and were used to prepare 50 mM stock solutions in the appropriate solvent mixture.

[$Fe(MeCN)_4$]$(ClO_4)_2$. The [$Fe(MeCN)_4$]$(ClO_4)_2$ complex was prepared by multiple recrystallizations of [$Fe(H_2O)_6$]$(ClO_4)_2$ from MeCN.

Iron Picolinate and Iron Dipicolinate Solutions. Solutions of $Fe(PA)_2$, $Fe(PA)_3$, and Fe(DPA) were prepared in situ by mixing [$Fe(MeCN)_4$]$(ClO_4)_2$ or $Fe(ClO_4)_3$ (anhydrous) with various ratios of ligand anion. $Fe(PA)_2$ has a single absorption band [DMF, λ_{max} 462 nm (ϵ 1200 cm^{-1} M^{-1}) and 2Py/HOAc, λ_{max} 402 nm (ϵ 2480 cm^{-1} M^{-1})], which shifts to a longer wavelength with excess ligand [$(Fe(PA)_3^-$ in DMF, λ_{max} 496 nm (ϵ 1670 cm^{-1} M^{-1})]. Likewise, Fe(DPA) has a single absorption band [DMF, λ_{max} 484 nm (ϵ 620 cm^{-1} M^{-1}) and 2Py/HOAc, λ_{max} 395 cm (ϵ 1950 cm^{-1} M^{-1}) with two shoulders [480 nm (ϵ 1280 cm^{-1} M^{-1}) and 500 nm (ϵ 840 cm^{-1} M^{-1})]. The band shifts with the addition of excess ligand [$(Fe(DPA)_2^{2-}$ in DMF, λ_{max} 552 nm (ϵ 540 cm^{-1} M^{-1})].

Syntheses of "$Fe(PA)_2$", [$(PA)_2Fe(OH)]_2$ (1a), [$(PA)_2FeOFe(PA)_2$] (1b), "Fe(DPA)", and [$(DPA)Fe(OH)]_2$. The nominal complexes "$Fe(PA)_2$" and "Fe(DPA)" were prepared by mixing [$Fe(MeCN)_4$]$(ClO_4)_2$ and the stoichiometric amount of the tetramethylammonium salt of the ligand (in acetonitrile under argon), which yielded a brick-red precipitate. The isolated powder gradually turned light brown upon exposure to air. This brown powder ["$Fe(PA)_2$"], when dissolved in DMF, exhibited a broad absorption band [λ_{max} 348 nm (ϵ 1400 cm^{-1} M^{-1}), and the solid had infrared bands at 695, 708, 761, 950, 1025, and 1049 cm^{-1} with a strong, broad band at 1092 cm^{-1}. The ligand, $(Me_4N)PA$, exhibited bands at 689, 774, and 834 cm^{-1} with a broad band at 981 cm^{-1} and small bands at 1034 and 1077 cm^{-1}. The precipitate obtained for "Fe(DPA)" was an orange-brown powder that became light brown upon exposure to air. Dissolution of "$Fe(PA)_2$" and "Fe(DPA)" in DMF and electrochemical characterization confirmed that the materials were each about $^2/_3$ in their reduced states [$Fe(PA)_2$ and Fe(DPA)].

Exposure of MeCN solutions of $Fe(PA)_2$ to air resulted in the precipitation of a pale green powder, [$(PA)_2Fe(OH)]_2$ (**1a**), which in py/HOAc solution exhibited an absorption edge below 400 nm [λ 350 nm (ϵ 2260 cm^{-1} M^{-1})]. The solid had infrared bands at 694, 708, 760, 857, 1020, and 1047 cm^{-1}, and a magnetic moment of 7.0 μ_B per dimer molecule (or 4.9 μ_B per Fe). In DMF **1a** had a magnetic moment (Evan's method)[11] of 3.6 ± 0.3 μ_B per dimer (2.5 μ_B per Fe), an irreversible reduction at –0.65 V vs SCE, and a strong UV absorption band [λ 350 nm (ϵ 3100 cm^{-1} M^{-1})]. The elemental analysis of the pale green powder, [$(PA)_2Fe(OH)]_2$ (**1a**), was performed by Galbraith Laboratories, Inc. Anal. Calcd for $C_{24}H_{18}N_4O_{10}Fe_2$: C, 45.46; H, 2.86; N, 8.84; O, 25.23; Fe, 17.61. Found: C, 45.17; H, 3.08; N, 8.80; O, 25.31; Fe, 16.93.

The 1:1 combination of $Fe(PA)_3$ and $(Me_4N)OH\cdot5H_2O$ in DMF gave a golden-brown solution of a product species, $(PA)_2FeOFe(PA)_2$ (**1b**), with a magnetic moment of 3.1 ± 0.2 μ_B per dimer (2.2 μ_B per Fe), an irreversible reduction potential at –0.85 V vs SCE, and a strong UV absorption band [λ 350 nm (ϵ 3300 cm^{-1} M^{-1}).

[$(Ph_3PO)_4FeOOFe(OPPh_3)]_4(ClO_4)_4$ (4). The synthesis and characterization of this complex have been described.[12]

Tetramethylammonium superoxide [$(Me_4N)O_2$] was prepared by combination of KO_2 (Aldrich) and $(Me_4N)OH\cdot5H_2O$ (Fluka).[13,14] The $(py)_4FeCl_2$ complex was prepared by multiple recrystallizations of $FeCl_2\cdot4H_2O$ (Mallinckrodt) in dry pyridine. Combination of $(py)_4FeCl_2$ and AgOAc (Strem) in dry pyridine gave a white AgCl precipitate, which was removed prior to the evaporation of the filtrate to give $(py)_4Fe(OAc)_2$. The [$Fe(OPPh_3)_4$]$(ClO_4)_2$ complex was synthesized from [$Fe(MeCN)_4$]$(ClO_4)_2$ and triphenylphosphine oxide (Aldrich).[15]

Methods. The investigations of HOOH activation by the iron complexes used solutions that contained 0.5–1.0 M substrate and 1–20 mM

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Table I. Products and Conversion Efficiencies for the Iron-Catalyzed Ketonization of Cyclohexane by HOOH in Various Solvents[a]

A. Cyclohexane (1 M), HOOH (96 mM), Pyridine/HOAc (2:1 Molar Ratio)

			products[e]	
iron catalysts, 3.3 mM[b]	reactn efficiency,[c] % (±3)	catalyst[d] turnovers	cyclohexanone, % (±4)	cyclohexanol, % (±4)
$Fe(PA)_2$	72	11	93	7
$Fe(PA)_2$ (56 mM HOOH)	72	6	95	5
$Fe(PA)_2$ (56 mM HOOH, 101 mM H_2O)	58	5	94	6
0.9 mM $Fe(PA)_2$ (56 mM HOOH)[f]	71	23	94	6
0.9 mM $Fe(PA)_2$ (56 mM HOOH, 101 mM H_2O)	17	5	94	6
$(PA)_2FeOFe(PA)_2$ (**1**) (1.7 mM)	72	11	93	7
$Fe(PA)_3$	64	10	85	15
$Fe(PA)(ClO_4)$	65	9	94	6
Fe(DPA)	73	12	>97	<3
(DPA)FeOFe(DPA) (**5**) (1.7 mM)	76	13	>97	<3
$Fe(8\text{-}Q)_3$	47	7	90	10

B. Cyclohexane (1 M), $Fe(PA)_2$ (3.5 mM), HOOH (56 mM)

		products[e]	
solvent	reactn efficiency,[c] % (±3)	cyclohexanone, % (±4)	cyclohexanol, % (±4)
pyridine (py)	6	93	7
py/HOAc (4.5:1 molar ratio)	65	93	7
py/HOAc (1.9:1 molar ratio)	72	93	7
py/HOAc (1.0:1 molar ratio)	66	93	7
py/HOAc (0.6:1 molar ratio)	58	93	7
MeCN	9	40	60
MeCN/HOAc (3.6:1 molar ratio)	11	73	27

[a] Substrate and catalyst combined in 3.5 mL of pyridine/HOAc solvent (2:1 molar ratio), followed by the slow addition (1–2 min) of 13 μL of 17.3 M HOOH (49%) in H_2O or 60–100 μL of 1.6–3.8 M HOOH (92%) in MeCN to give 56–96 mM HOOH. Reaction time and temperature: 4 h at 22 ± 2 °C. DPA, 2,6-dicarboxylatopyridine. [b] No reaction occurs when $[Fe(MeCN)_4](ClO_4)_2$, $(py)_4Fe(OAc)_2$, and $Fe(acac)_2$ are used as catalysts; and $(py)_4FeCl_2$, $(bpy)_3Fe(ClO_4)_2$, and $FeCl_3$ give reaction efficiencies of less than 15%, with cyclohexanol the major product (>90%). [c] 100% represents one substrate oxygenation per two HOOH molecules added; the remainder of the HOOH was unreacted or consumed via slow O_2 evolution and Fenton chemistry to produce $[py(OH)]_n$. [d] Moles of substrate oxygenated per mole of catalyst. [e] The product solutions were analyzed by capillary gas chromatography and GC–MS (either direct injection of the product solution, or by quenching with water and extracting with diethyl ether). [f] Reaction time, 15 h.

iron complex in 3.5 mL of a pyridine/acetic acid mixture. Hydrogen peroxide (56 or 100 mM) was injected as an anhydrous solution in MeCN or as undiluted 50% HOOH in water. After 4 h with constant stirring at room temperature (22 ± 2 °C), samples of the reaction solution were injected into a capillary-column gas chromatograph for analysis. In some cases the reaction was quenched with water, and the product solution was extracted with diethyl ether. Product species were characterized by GC–MS. Reference samples were used to confirm product identifications and to produce standard curves for quantitative assays of the product species.

The activation of superoxide salts for reaction with the various substrates (0.5–1.0 M) used 3.5–56 mM of an iron complex in 3.5 mL of a pyridine/acetic acid mixture. Superoxide was slowly added to the solutions [$(Me_4N)O_2$ in pyridine, $(Me_4N)O_2(s)$, $KO_2(s)$, or a slurry of $KO_2(s)$ in pyridine] under an argon atmosphere.

The electrochemical studies were carried out in a microcell assembly (10-mL capacity) that included a glassy-carbon-plate working electrode, a platinum-flag auxiliary electrode, and a Ag/AgCl reference electrode ajusted to 0.00 V vs SCE[16] (placed inside a luggin capillary).[17] The platinum-flag auxiliary electrode was contained in a glass tube sealed with a medium or coarse porosity glass frit and filled with a concentrated solution of supporting electrolyte.

Results

The addition of HOOH to pyridine/acetic acid solutions that contain $Fe(PA)_2$ and cyclohexane ($c\text{-}C_6H_{12}$) results in the catalyzed transformation of $c\text{-}C_6H_{12}$ to cyclohexanone [$c\text{-}C_6H_{10}(O)$]. Table IA summarizes the conversion efficiencies ($c\text{-}C_6H_{12}$ oxidized per two HOOH) and product yields for the catalyzed oxygenation of cyclohexane by HOOH. Several iron–picolinate (PA), iron–(2,6-dicarboxylatopyridine) (DPA), and iron–(8-quinolinolate) (8-Q) complexes are compared in terms of catalytic efficiency and product selectivity in a pyridine/acetic acid solution matrix. The effects of the solvent matrix on the yields for the $c\text{-}C_6H_{12}/HOOH/Fe(PA)_2$ reaction system are summarized in Table IB.

The presence of substantial amounts of water (100 mM) reduces the reaction efficiency (especially for low $Fe(PA)_2$ concentrations) but does not reduce the selectivity for ketone formation. The use of acetonitrile in place of the pyridine/HOAc solvent system greatly reduces the reaction efficiency and eliminates any selectivity. With pure pyridine as the solvent, there is no reactivity. In the absence of substrate the $Fe(PA)_2/HOOH/(py_2/HOAc)$ system slowly decomposes to give O_2, H_2O, and $[py(OH)]_n$ (half-life >6 h).

Table II summarizes the conversion efficiencies and product yields for the oxygenation by the $HOOH/Fe(PA)_2$ combination of several organic substrates (hydrocarbons with methylenic carbons, acetylenes, and arylolefins). Catalyst turnovers (moles of product per mole of catalyst) also are tabulated. The relative reaction efficiencies for cyclohexane, *n*-hexane, cyclohexene, and 1,4-cyclohexadiene are roughly proportional to the number of ($>CH_2$) groups per molecule (6, 4, 4, and 2), and the product for each is the ketone from the transformation of a single methylenic carbon. Addition of a second 56 mM increment of HOOH to a reacted cyclohexane system (Table II) results in an additional ketonization (68% reaction efficiency). The conversion of 1,4-cyclohexadiene to phenol (apparently via ketonization of a methylenic carbon) without any epoxide formation confirms the selectivity of the reactive intermediate. Likewise, the ketonization of cyclohexene further supports the selective reactivity toward methylenic carbon. However, 1,3-cyclohexadiene is dehydrogenated to give benzene.

The lower reactivity of cyclohexanol relative to cyclohexane ($\sim ^1/_3$) indicates that $c\text{-}C_6H_{11}OH$ is not an intermediate for the ketonization of $c\text{-}C_6H_{12}$. This is further supported by the results for a combined substrate of 1 M $c\text{-}C_6H_{12}$ and 1 M $c\text{-}C_6H_{11}OH$, which has a ketonization efficiency of 65% (in contrast to 72% for 1 M $c\text{-}C_6H_{12}$ alone, Table II). Likewise the presence of 1 M

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Table II. Products and Conversion Efficiencies for the $Fe(PA)_2$-Catalyzed (3.5 mM) Ketonization of Methylenic Carbon and the Dioxygenation of Acetylenes and Arylolefins by HOOH (56 mM) in Pyridine/HOAc (2:1 Molar Ratio)[a]

substrate (1 M)	reactn efficiency,[b] % (±3)	catalyst[c] turnovers	products[d]
cyclohexane	72	6	cyclohexanone (97%), cyclohexanol (3%)
n-hexane	52	4	3-hexanone (53%), 2-hexanone (46%), 1-hexanol (<2%)
$PhCH_2CH_3$	51	5	$PhC(O)CH_3$ (>96%)
$PhCH_2Ph$ (0.6 M)	35	3	PhC(O)Ph (>96%)
$PhCH_3$	9	<1	PhCH(O) (>96%)
2-methylbutane	32	3	3-methyl-2butanone (>95%), 2-methyl-1-butanol (<2%)
adamantane (0.1 M)	32	3	2-adamantanone (43%), 1-adamantanol (29%), 1-pyridyladamantane (two isomers, 18% and 10%)
cyclododecane (0.5 M)	70	6	cyclododecanone (90%), cyclododecanol (10%)
cyclohexene	59	5	2-cyclohexen-1-one (>95%)
1,3-cyclohexadiene	33	5	PhH (>95%)
1,4-cyclohexadiene	30 [70]	3 [11]	PhOH (17%), [PhH] (83%)
cyclohexanone	0		
cyclohexanol	25	4	cyclohexanone (>95%)
PhC≡CPh (0.6 M)	40	3	PhC(O)C(O)Ph (>97%)
c-PhCH=CHPh	36	4	PhCH(O) (75%), $\mathrm{Ph\overbrace{CHCH}^{O}Ph}$ (25%)
t-PhCH=CHMe	48	4	PhCH(O) (63%), $\mathrm{Ph\overbrace{CHCH}^{O}Me}$ (16%), two others (21%)

[a] Substrate and $Fe(PA)_2$ combined in 3.5 mL of pyridine/HOAc solvent (2:1 molar ratio), followed by the slow addition (1–2 min) of 13 μL of 17.3 M HOOH (49%) in H_2O or 60–100 μL of 1.6–3.8 M HOOH (92%) in MeCN to give 56 mM HOOH. Reaction time and temperature; 4 h at 22 ± 2 °C. [b] 100% represents one substrate oxygenation per two HOOH molecules added; the remainder of the HOOH was unreacted or consumed via slow O_2 evolution and Fenton chemistry to produce $^1/_n[py(OH)]_n$. [c] Moles of substrate oxygenated per mole of catalyst. [d] The product solution was analyzed by capillary gas chromatography and GC–MS (either direct injection of the product solution or by quenching with water and extracting with diethyl ether). [e] 100% represents one substrate dehydrogenation per HOOH.

i-PrOH with 1 M c-C_6H_{12} causes a reduction in the conversion efficiency for c-C_6H_{12} to 56%, but no acetone. Analysis of the product solution during the course of the ketonization of 1 M c-C_6H_{12} gives a constant 19:1 c-C_6H_{10}(O)/c-C_6H_{11}OH ratio (0.1 to 1.0 fractional reaction).

The reactive intermediate dioxygenates acetylenes to give the α-dione as the sole product. With the $Fe(PA)_2$/HOOH/(py_2/HOAc) system arylolefins are dioxygenated and epoxidized. Table IIIA provides a comparison of HOOH, *m*-ClPhC(O)OOH, and *t*-BuOOH as oxygenation agents for *cis*-PhCH=CHPh and PhC≡CPh. Hydrogen peroxide is uniquely effective with $Fe(PA)_2$ for the dioxygenation of these substrates.

Characterization of Catalysts. The results of Table IA indicate that in the presence of excess HOOH, $Fe(PA)_2$ and $(PA)_2FeOFe(PA)_2$ (**1**) [and Fe(DPA) and (DPA)FeOFe(DPA) (**5**)] are equally effective. However, when the concentrations of catalyst and HOOH are the same, the efficiency of $Fe(PA)_2$ for the oxygenation of *cis*-PhCH=CHPh is significantly less than with $(PA)_2FeOFe(PA)_2$ (Table IIIB). Addition of reduced amounts of HOOH (19 mM) to 19 mM $Fe(PA)_2$ or 19 mM $(PA)_2FeOFe(PA)_2$ and 1 M c-C_6H_{12} in pyridine/HOAc results in major amounts of products [c-C_6H_{11}-py and (c-C_6H_{12})$_2$] from the production of c-$C_6H_{11}^\bullet$ radicals via Fenton chemistry (Table IIIC). When $Fe(PA)_2$ is added to c-C_6H_{12}/HOOH the reaction efficiency is enhanced as is the yield of c-C_6H_{10}(O). The apparent second-order rate constant for the 1:1 combination of $Fe(PA)_2$/HOOH in py/HOAc is (2 ± 1) × 10^3 M^{-1} s^{-1}, but decreases to (2 ± 1) × 10^2 M^{-1} s^{-1} when the $Fe(PA)_2$/HOOH ratio is 1:200.

In the absence of substrate the combination of excess HOOH with two $Fe(PA)_2$ molecules (λ 402 nm) in the pyridine/HOAc solvent yields $(PA)_2FeOFe(PA)_2$ (**1**) (irreversible reduction at −0.1 V vs SCE and UV-visible absorption at <400 nm) and $(PA)_2$Fe(OAc) (reversible cyclic voltammogram at +0.2 V vs SCE) in 2:1 pyridine/HOAc.[18] As Table IA indicates, the use of $(PA)_2FeOFe(PA)_2$ (**1**) gives results that are equivalent to those for $Fe(PA)_2$, and prompts the conclusion that the latter is transformed in situ to **1**.

Table III. Comparison of Hydroperoxides (ROOH) and Iron Catalysts for the Oxygenation of *cis*-Stilbene (*cis*-PhCH=CHPh), PhC≡CPh, and c-C_6H_{12} in Pyridine/Acetic Acid (2:1 Molar Ratio)[a]

A. ROOH, 56 mM; $Fe(PA)_2$, 3.5 mM

1. *cis*-PhCH=CHPh, 1M

ROOH	reactn efficiency, % (±3)	products PhCH(O), % (±4)	 $\mathrm{Ph\overbrace{CH\text{-}CH}^{O}Ph}$, % (±4)
HOOH	36	75	25
m-ClPhC(O)OOH	11	45	55
t-BuOOH	6	6	94

2. PhC≡CPh, 1M

ROOH	reactn efficiency, % (±3)	products
HOOH	40	PhC(O)C(O)Ph (>97%)
m-ClPhC(O)OOH	10	PhC(O)C(O)Ph (>97%)
t-BuOOH	0	

B. *cis*-PhCH=CHPh, 0.7 M; HOOH, 15 mM

catalyst, 15 mM	reactn efficiency, % (±3)	products PhCH(O), %	 $\mathrm{Ph\overbrace{CH\text{-}CH}^{O}Ph}$, %
$Fe(PA)_2$	13	59	41
$(PA)_2FeOFe(PA)_2$	18	52	48

C. c-C_6H_{12}, 1M; HOOH, 19 mM

catalyst, 19 mM	reactn efficiency, % (±3)	products c-C_6H_{10}(O), %	 (c-C_6H_{11})$_2$, %	 py-C_6H_{11}, %
$(PA)_2Fe$	53	20	14	66
$(PA)_2Fe$ (9 mM) (9 mM HOOH)	85	34	3	63
$(PA)_2Fe$ (catalysis added to [S]/HOOH)	67	36	10	54
$(PA)_2FeOFe(PA)_2$	39	30	13	57

[a] See footnotes of Tables I and II.

In the constrast to the py/HOAc solvent, addition of HOOH to a solution of species **1** in Me_2SO rapidly evolves dioxygen (**1** is insoluble in MeCN). The [2,6-dicarboxylatopyridine]iron(II) complex, Fe(DPA), appears to be a slightly superior catalyst to $Fe(PA)_2$ and parallels the latter's transformation by HOOH to give the most active and selective catalyst, (DPA)FeOFe(DPA) (**5**).

In dimethylformamide the combination of two $Fe(PA)_2$ molecules with one HOOH results in the stoichiometric formation

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[18] This chemistry has been monitored by UV–visible spectrophotometry and cyclic voltammetry. The redox characterization of $Fe(PA)_2$, $[(PA)_2Fe(OH)]_2$ (**1a**), $(PA)_2FeOFe(PA)_2$ (**1b**), Fe(DPA) and $[(DPA)Fe(OH)]_2$, and their reaction products with HOOH and O_2 is the focus of a detailed study; Cofré, P.; Richert, S. A.; Sawyer, D. T. *Inorg. Chem.* **1989**, submitted for publication.

Table IV. Yields of Singlet Dioxygen ($^1O_2$) from the Combination of $[(PA)_2Fe(OH)]_2$ (**1a**) with Hydrogen Peroxide in Dimethylformamide

$[(PA)_2Fe(OH)]_2$ (**1a**), μM	HOOH, mM	$^1O_2$, μM (uncorrected)[a]	$^1O_2$, μM (corrected)[b]
20	50	20	24
50	50	28	45
100	50	32	69
250	50	37	153
500	50	46	273
1000	50	53	544
2000	50	53 ± 2[c]	1013 ± 34[c]
2000	100	103	1950
2000	25	24	457

[a] The reaction of hydrogen peroxide with hypochlorous acid in deuterium oxide solvent was used as a $^1O_2$ standard ($^1O_2$ lifetimes, 62 μs for deuterium oxide and 17 μs for dimethylformamide). Spectral analysis of near-infrared emission; filter, nm (signal): 1170 (0.01), 1268 (1.00), 1375 (0.59), 1470 (0.11). [b] Corrected for quenching by **1a** ($k_{q,a} = 6.0 \times 10^7$ M^{-1} s^{-1}) and the anhydrous product complex, $[(PA)_2FeOFe(PA)_2]$ (**1b**) ($k_{q,b} = 2.0 \times 10^9$ M^{-1} s^{-1}), where the total quenching at any reaction time is given by $k_{q,a}$ [**1a**] + $k_{q,b}$ [**1b**]. These rate constants were evaluated in DMF via photochemical generation of $^1O_2$ with rose bengal [bis(triethylammonium salt)]. Because the apparent quenching constant for **1a** decreased for concentrations above 250 μM, this correction method may overestimate the $^1O_2$ yield for these high concentrations by as much as 20%. [c] Mean value ± standard error for three measurements. Other values are for single measurements.

of $[(PA)_2Fe(OH)]_2$ (**1a**); the apparent second-order rate constant is 2.5×10^3 M^{-1} s^{-1}. The same process occurs in pyridine/acetic acid, at approximately the same rate ($k = \sim 1 \times 10^3$ M^{-1} s^{-1}). Likewise, Fe(DPA) is transformed by HOOH to $[(DPA)Fe(OH)]_2$; the rate of reaction is about 1 order of magnitude faster than for $Fe(PA)_2$.[18]

When excess HOOH is added to $[(PA)_2Fe(OH)]_2$ (**1a**) or $[(DPA)_2Fe(OH)]_2$ in DMF it is decomposed rapidly to dioxygen and water. In contrast, the same experiment in pyridine/acetic acid does not result in the rapid decomposition of HOOH.[18]

Production of Singlet Dioxygen ($^1O_2$). Table IV summarizes the yields of singlet dioxygen from the addition of $[(PA)_2Fe(OH)]_2$ (**1a**) to HOOH in dimethylformamide. Both this complex and its μ-oxo form, $(PA)_2FeOFe(PA)_2$ (**1b**), quench $^1O_2$ with apparent second-order rate constants of 6.0×10^7 and 2.0×10^9 M^{-1} s^{-1}, respectively. Because essentially stoichiometric yields of singlet dioxygen result (one $^1O_2$ per **1a** at high HOOH concentrations) the transition-state complex must involve a dioxygen adduct from the combination of two HOOH molecules with **1a**. In contrast, control experiments with $Fe(MeCN)_4(ClO_4)_2$ result in the stoichiometric decomposition of HOOH to $^3O_2$ and H_2O, but there is no detectable production of $^1O_2$.

Dioxygenation by $[(Ph_3PO)_4FeOOFe(OPPh_3)_4](ClO_4)_4$ (4). In pyridine/HOAc (molar ratio, 2:1) a binuclear iron–μ-dioxygen complex (**4**) reacts with excess PhC≡CPh to give PhC(O)C(O)Ph exclusively (3% efficient in 15 min; 0.6 M PhC≡CPh and 56 mM **4**) and with excess cyclohexane to give cyclohexanone exclusively (3% efficient in 15 min; 1 M c-C_6H_{12} and 56 mM **4**). In MeCN neither substrate reacts with **4**; however, the addition of sufficient $HClO_4$ to make the solution 3.7 M causes PhC≡CPh to be transformed almost completely (one PhC≡CPh per **4**) within 10 min [yield 78% of PhC(O)C(O)Ph and 14% PhC(O)OH].

Dioxygenation by $Fe^{II}(DPA)(DPAH)^-$ plus O_2. When the reduced-iron $Fe^{II}(DPA)(DPAH)^-$ complex (32 mM) is introduced into a py/HOAc (2:1) solution that is saturated with O_2 (4 mM) and contains 1 M c-C_6H_{12}, there is a rapid reaction (half-life, ~10 min) to give 4.5 mM c-$C_6H_{10}(O)$ and oxidized iron complex (DPA)FeOFe(DPA)(s) as the only products.

Superoxide Oxidant. The reaction efficiencies and selectivities for the conversion of cyclohexane to cyclohexanone by a KO_2(s)/py slurry in the presence of several iron complexes are summarized in Table V. The $(py)_4FeCl_2$ and $Fe(PA)_2$ complexes are clearly superior to the others, and the latter's efficiency is independent of concentration down to 3.5 mM. At this concentration 3.5 catalytic turnovers are achieved for the conversion of cyclohexane to cyclohexanone.

Table V. Conversion Efficiencies for the Oxygenation of Cyclohexane by KO_2(s)/Pyridine Slurry in the Presence of Various Iron Complexes in Pyridine/Acetic Acid[a]

		selectivity	
iron complex, 56 mM	reactn efficiency,[b] % (±3)	cyclohexanone, %	cyclohexanol, %
$(py)_4FeCl_2$	41	95	5
$(py)_4FeCl_2$ (3.5 mM)	9	96	4
$Fe(PA)_2$	46	97	3
$Fe(PA)_2$ (3.5 mM)	43	97	3
$(py)_4Fe(OAc)_2$	22	96	4
$(MeCN)_4Fe(ClO_4)_2$	30	95	5
$FeCl_3 \cdot 6H_2O$	19	94	6
$[Fe(OPPh_3)_4](ClO_4)_2$	18	95	5

[a] KO_2(s) (0.15 mL, 1.49 mmol per mL of pyridine) was added slowly to the substrate solution that contained the iron complex, 1.16 M cyclohexane, and 3.5 mL of 4.2:1 molar ratio pyridine/acetic acid. Reaction time and temperature: 20 min at 20–23 °C. [b] Moles of substrate oxygenated per four moles of KO_2(s). When other sources of superoxide were used with $(py)_4FeCl_2$, the reaction efficiencies were KO_2(s) 22%, $(Me_4N)O_2$(s) 18%, and solution of $(Me_4N)O_2$ in pyridine 0%.

Table VI. Reaction Efficiencies for the Oxygenation of Cyclohexane by Electro-Reduced Dioxygen in the Presence of $(py)_4FeCl_2$ or $Fe(PA)_2$ Catalysts in Pyridine/Acetic Acid[a]

catalyst concn, mM	reactn efficiency, % (±5)[b]	
	$(py)_4FeCl_2$	$Fe(PA)_2$
60	83 (suspension)	–
45	59	–
30	60	52 (suspension)
15	58	76
7.5	64	77
3.8	56	80
1.9	49	79
0.9	45	86
0.5	<30	40
0	0	0

[a] Controlled-potential electrolysis (−0.6 V vs SCE, 25 C) at a glassy-carbon-plate working electrode. Solvent compoisition: Py/HOAc/H_2O (10:1:1 by volume), 1 M C_1H_{12}, 0.1 M tetraethylammonium perchlorate, 1 atm O_2. [b] Efficiency based on ketone per 4 e^- of electrolysis; product >97% cyclohexanone and <3% cyclohexanol.

The solvent matrix (pyridine/acetic acid ratio) has a profound effect upon the reaction efficiency and selectivity for the ketonization of cyclohexane by the iron-activated KO_2(s)/py slurry. In pure pyridine there is essentially no reaction, but the reaction efficiency dramatically increases as acetic acid is introduced. Product selectivity for 56 mM $(py)_4FeCl_2$ in 4.2:1 py/HOAc is 95% cyclohexanone, but in 1.8:1 py/HOAc drops to 76%. In contrast, the efficiency (50%) and product selectivity (97%) with $Fe(PA)_2$ is unchanged for py/HOAc ratios from 4.2:1 to 0.5:1.

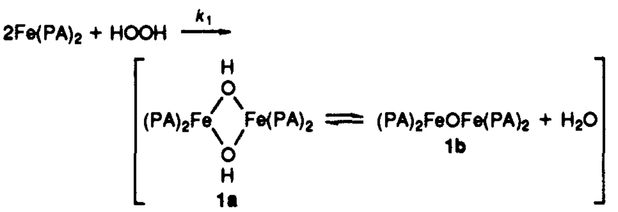
The optimal reaction conditions [3.5 mM $Fe(PA)_2$ with KO_2(s)/py slurry in py/HOAc (1.8:1 molar ratio)] give conversion efficiencies of 45% for c-C_6H_{12}, 27% for *n*-C_6H_{12}, 27% for EtPh, 11% for PhC≡CPh, and 16% for c-PhCH=CHPh [all 0.6–1.0 M and with product profiles that are identical with those for the $Fe(PA)_2$/HOOH system (Table II)].

Electro-Reduced Dioxygen. The reaction efficiencies for the $(py)_4FeCl_2$- or $Fe(PA)_2$-catalyzed conversion of cyclohexane to cyclohexanone by electrochemically reduced dioxygen are summarized in Table VI. Cyclohexanone is the sole product, and a 60 mM suspension of $(py)_4FeCl_2$ gives the highest efficiency. Similar efficiencies are obtained for $(py)_4FeCl_2$ concentrations that range from 3.8 to 45 mM. The optimal catalyst concentration for $Fe(PA)_2$ is 1–15 mM. Two to five catalytic turnovers (based on moles of oxygenated product per mole of iron complex added) result with 3.8 mM $Fe(PA)_2$ (or less). The yields of cyclohexanone with $Fe(PA)_2$ are substantially higher than with

$(py)_4FeCl_2$. Again, the ketonization of cyclohexane by electroreduced dioxygen in the presence of 3.5 mM $Fe(PA)_2$ is optimal for a py/HOAc molar ratio from 5:1 to 2:1 [100% efficient (4 e^- per ketone product) and >97% $c\text{-}C_6H_{10}(O)$].

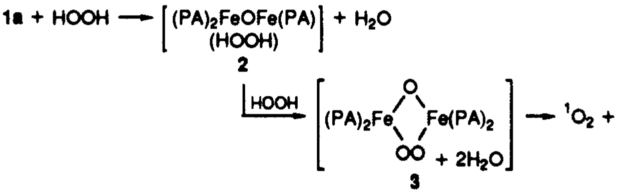
Discussion and Conclusions

The results of Table I establish that the pyridine/HOAc (molar ratio, 2:1) solvent system is optimal for the efficient and selective ketonization of methylenic carbons by the $Fe(PA)_2$/HOOH system. On the basis of the relative reaction efficiencies for $Fe(PA)_2$ and $(PA)_2FeOFe(PA)_2$ (Tables IA and III), the initial step when $Fe(PA)_2$ is used as the catalyst is its transformation to $(PA)_2FeOFe(PA)_2$ (**1**). The spectrophotometric, electrochemical,[18] and magnetic results for the combination of $Fe(PA)_2$ and HOOH in DMF confirm a 2:1 reaction stoichiometry to give a binuclear product ($k_1 = 2 \times 10^3$ M^{-1} s^{-1}) (eq 2). Electrochemical measurements[18] establish that (a) autoxidation of $Fe(PA)_2$ in MeCN yields a product that is a mixture of **1a** and **1b** and (b) the product from the 1:1 combination of $Fe(PA)_3$ and ^-OH in DMF is mainly **1b** (eq 3).


$$2Fe(PA)_2 + HOOH \xrightarrow{k_1} \left[\underset{\textbf{1a}}{(PA)_2Fe(\mu\text{-}OH)_2Fe(PA)_2} \rightleftharpoons \underset{\textbf{1b}}{(PA)_2FeOFe(PA)_2} + H_2O \right] \quad (2)$$

$$2Fe(PA)_3 + 2^-OH \rightarrow \underset{\textbf{1b}}{(PA)_2FeOFe(PA)_2} + 2PA^- + H_2O \quad (3)$$

The addition of species **1a** to excess HOOH in DMF results in near stoichiometric production of $^1O_2$ (Table IV) and yields species **1b** during catalytic turnover


$$\textbf{1a} + HOOH \rightarrow \underset{\textbf{2}}{\left[\begin{matrix} (PA)_2FeOFe(PA) \\ (HOOH) \end{matrix} \right]} + H_2O \xrightarrow{HOOH} \underset{\textbf{3}}{\left[(PA)_2Fe(O)(OO)Fe(PA)_2 + 2H_2O \right]} \rightarrow {}^1O_2 + \textbf{1b} \quad (4)$$

With low concentrations of HOOH as well as for reaction conditions with 1:1 $Fe(PA)_2$/HOOH, the Fenton process becomes dominant (Table IIIC, eq 5a–d).[19] For the conditions of the experiments that are summarized in Tables I and II (excess HOOH added to catalyst/substrate), the reaction sequence of eq 2 and 4 prevails to a major degree [with no evidence of Fenton chemistry (eq 5) in the product profiles]. The results of Table II indicate that the relative reactivity of species **3** with hydrocarbon substrates is in the order $>CH_2 > PhC{\equiv}CPh \gg ArCH{=}CHR \gg Ar{-}CH_3 \gg {>}CH$, which is completely at odds with radical processes.[19]

$$Fe(PA)_2 + HOOH \rightarrow (PA)_2Fe(OH) + {}^{\bullet}OH \quad (5a)$$

$$^{\bullet}OH + RH \rightarrow R^{\bullet} \text{ (or } \tfrac{1}{2} R_2) + H_2O \quad (5b)$$

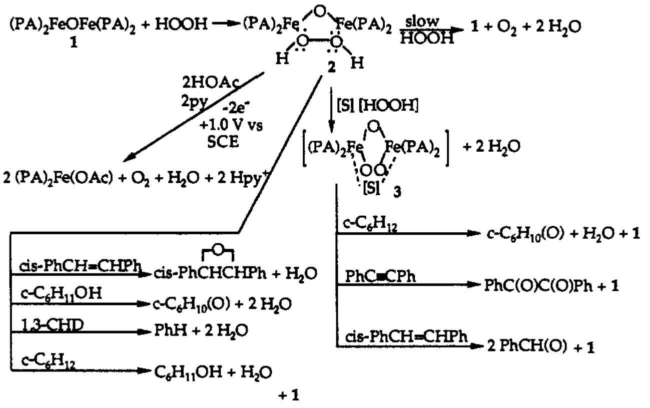
$$^{\bullet}OH + py \rightarrow py^{\bullet} \text{ [or } \tfrac{1}{n} [pyOH)_n] + H_2O \quad (5c)$$

$$R^{\bullet} + py^{\bullet} \rightarrow R{-}py \quad (5d)$$

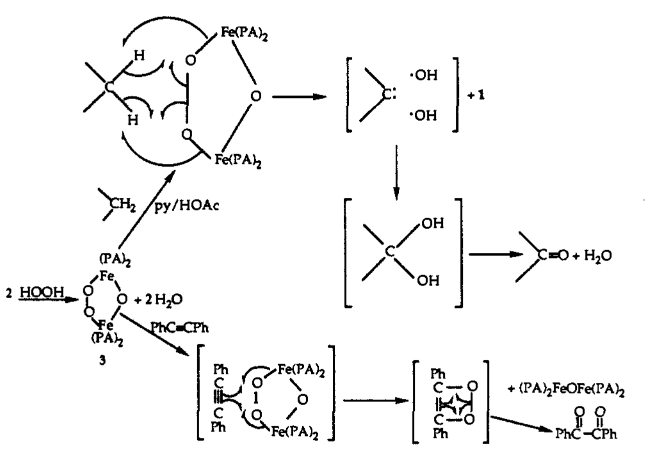
The results of Tables I–III together with the data and discussions for the $[Fe(MeCN)_4](ClO_4)_2$/2HOOH system[7,20] prompt the formulation of reaction steps and pathways for the $(PA)_2FeOFe(PA)_2$/HOOH/(py/HOAc)/substrate system (Scheme Ia). On the basis of the product profiles and reaction efficiencies (Tables I–III) when $(PA)_2FeOFe(PA)_2$ [or its precursor, $Fe(PA)_2$, eq 2] is used as the catalyst, the initial step in the catalytic reaction cycle appears to be the formation of an HOOH adduct $[(PA)_2FeOFe(PA)_2(HOOH)]$ (**2**). In the presence of $>CH_2$ or $RC{\equiv}CR$ groups, species **2** rapidly forms (with another HOOH) the activated complex (species **3**, Scheme Ia). The precatalyst (species **2**) reacts with selective substrates in a manner that is analogous to that of other iron–HOOH adducts.[21] Thus, for conditions that favor formation of species **2** (1:1 $(PA)_2FeOFe(PA)_2$/HOOH, Table IIIB) epoxidation of c-$PhCH{=}CHPh$ is enhanced, but for conditions that favor species **3** dioxygenation is the dominant path (Table II).

Scheme I

(a) Reaction Paths



(b) Proposed Mechanisms



Species **3** transforms methylenic carbons ($>CH_2$) to ketones ($>C{=}O$) and dioxygenates acetylenes and arylolefins, which parallels the reactivity of $[(Ph_3PO)_4FeOOFe(OPPh_3)_4](ClO_4)_4$ (**4**)[12] (eq 6) and the apparent intermediate from the combination of $Fe^{II}(DPA)(DPAH)^-$ and O_2 (eq 7). The catalytic cycles for Fe(DPA) and (DPA)FeOFe(DPA) (**5**), which are the most effective and selective catalysts of the iron complexes investigated (Table IA), appear to be analogous to those for $Fe(PA)_2$ and

$$[(Ph_3PO)_4FeOOFe(OPPh_3)_4](ClO_4)_4 + PhC{\equiv}CPh \xrightarrow[MeCN]{HClO_4} PhC(O)C(O)Ph + 2[(Ph_3PO)_4Fe](ClO_4)_2 \quad (6)$$

$$\underset{\textbf{6}}{2Fe^{II}(DPA)(DPAH)^-} + O_2 \xrightarrow{py/HOAc} [^-(DPAH)(DPA)FeOOFe(DPA)(DPAH)^-] \quad (7)$$

$$\xrightarrow{c\text{-}C_6H_{12}} c\text{-}C_6H_{10}(O) + H_2O + 2\,\textbf{6}$$

$$\xrightarrow{2\,\textbf{6}} 2(DPA)FeOFe(DPA) + 4DPAH^-$$

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(19) Sheu, C.; Sobkowiak, A.; Zhang, L.; Ozbalik, N.; Barton, D. H. R.; Sawyer, D. T. *J. Am. Chem. Soc.* **1989**, *111*, 8030.

(20) Sugimoto, H.; Sawyer, D. T. *J. Am. Chem. Soc.* **1985**, *107*, 5712.

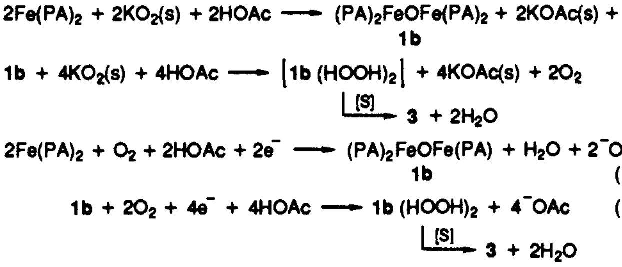
(21) Previous studies have demonstrated that similar iron–oxene species are formed from the 1:1 combination of HOOH and $[Fe(MeCN)_4](ClO_4)_2$,[5,11] $[(Ph_3PO)_4Fe](ClO_4)_2$,[9] and $FeCl_3$; Sugimoto, H.; Sawyer, D. T. *J. Org. Chem.* **1985**, *50*, 1784.

$(PA)_2FeOFe(PA)_2$ (**1**) (eq 2 and 4, and Scheme Ia).

Scheme Ib outlines a proposed concerted, singlet–biradical mechanism for the selective ketonization of methylenic carbons and dioxygenation of acetylenes via a common reactive intermediate, species **3**, which evolves $^1O_2$ in substrate-free DMF (Table IV). The ketonization of a methylene group in cyclohexene and 1,4-cyclohexadiene (Table II) is especially compelling evidence for a concerted selective process that is optimal for the geometry of methylenic carbons. In contrast, the dehydrogenation of 1,3-cyclohexadiene (Table II) probably is the result of selective reactivity with the precatalyst, species **2** (Scheme Ia).

The results for the $Fe(PA)_2$- and $(py)_4FeCl_2$-induced activation of $KO_2(s)$ to transform cyclohexane to cyclohexanone (Tables V) are closely similar to those for heterogeneous iron–dioxygen systems[1–6] and for the $Fe(PA)_2$/HOOH system in py/HOAc (Table I). The optimal efficiencies for the $KO_2(s)$ systems are achieved when the iron catalyst is in high concentration and the superoxide source is in suspension, which is consistent with a heterogeneous process. The irreversible two-electron reduction of dioxygen to hydrogen peroxide in py/HOAc (2:1 molar ratio)[18] confirms that free superoxide ion is not formed, which is incompatible with the protic matrix (the proton-induced disproportionation of superoxide ion to hydrogen peroxide and dioxygen is essentially a diffusion-controlled process).[22]

The reaction efficiencies and product profiles for the various organic substrates in combination with $KO_2(s)$ (Table V) or electro-reduced O_2 (Table VI) in 2:1 py/HOAc are almost identical with those for the $Fe(PA)_2$-induced activation of HOOH (Tables I and II). This and the instability of $O_2^{\bullet -}$ in py/HOAc matrices prompts the conclusion that the reactive intermediates are the same because of the in situ generation of HOOH (eq 8–11). Thus, species **3** transforms methylenic carbons directly



$$2Fe(PA)_2 + 2KO_2(s) + 2HOAc \longrightarrow \underset{\mathbf{1b}}{(PA)_2FeOFe(PA)_2} + 2KOAc(s) + O_2 \quad (8)$$

$$\mathbf{1b} + 4KO_2(s) + 4HOAc \longrightarrow [\mathbf{1b}(HOOH)_2] + 4KOAc(s) + 2O_2 \quad (9)$$
$$[\mathbf{1b}(HOOH)_2] \xrightarrow{[S]} \mathbf{3} + 2H_2O$$

$$2Fe(PA)_2 + O_2 + 2HOAc + 2e^- \longrightarrow \underset{\mathbf{1b}}{(PA)_2FeOFe(PA)} + H_2O + 2\,^-OAc \quad (10)$$

$$\mathbf{1b} + 2O_2 + 4e^- + 4HOAc \longrightarrow \mathbf{1b}(HOOH)_2 + 4\,^-OAc \quad (11)$$
$$\mathbf{1b}(HOOH)_2 \xrightarrow{[S]} \mathbf{3} + 2H_2O$$

to ketones, and acetylenes and arylolefins are dioxygenated to α-dicarbonyls and aldehydes, respectively.

The selective transformation of methylenic groups ($>CH_2$) to ketones via four heterogeneous iron–dioxygen systems[1–5] (a) iron powder/O_2 in 4:1 py/HOAc, (b) $Fe_3O(OAc)_6 \cdot 3.5py$/zinc dust/O_2 in 4:1 py/HOAc, (c) $(py)_4FeCl_2/KO_2(s)$ in 4:1 py/HOAc, and (d) $(py)_4FeCl_2/(O_2 + e^- \rightarrow O_2^{\bullet -})$ in 4:1 py/HOAc parallels the present results. This prompts the conclusion that for each of these systems the reactive intermediate is a binuclear dioxygen complex (**3** or its equivalent) that results from two HOOH molecules per iron catalyst (**1** or its equivalent).

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The Effects of Mg^{2+}, Hydrogen Bonding, and Steric Factors on Rate and Equilibrium Constants for Phosphoryl Transfer between Carboxylate Ions and Pyridines[1]

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Abstract: The reaction of bicarbonate ion with phosphorylated γ-picoline monoanion (PicP), which presumably gives carboxyphosphate, is faster than the reactions of acetate and carbonate by factors of 40 and 6, respectively (25 °C, $I = 1.5$). The rate increase is attributed to hydrogen bonding of the bicarbonate hydroxyl group to a phosphoryl oxygen atom; phosphate monoanion and dianion show similar increases. The reaction of acetate ion with PicP and the reverse reaction of γ-picoline with acetyl phosphate dianion are catalyzed ~20-fold by Mg^{2+}. The reaction of PicP with formate ion is 20-fold faster than with acetate ion and shows no catalysis by Mg^{2+}. This indicates that the rate increases with bicarbonate and with Mg^{2+} arise from overcoming unfavorable electrostatic, solvation, or steric interactions. Catalysis of the reaction of γ-picoline with acetyl phosphate (AcP), in both directions, is described by chelation of Mg^{2+} to the transition state, with $K_a{}^{*} = 97$ M^{-1}, and binding to the ground states with $K_a = 5$ and 4.4 M^{-1} for PicP and AcP, respectively. Equilibrium constants are reported for phosphoryl transfer between pyridines, imidazole, ammonia, and acetate ion; the favorable transfer from pyridine to acetate, by ~100-fold, shows that the P–O bond is stronger than the P–N bond, relative to H–O and H–N bonds.

In this paper we analyze rate constants for nonenzymatic phosphoryl transfer from pyridines to carboxylate ions and related nucleophiles (eq 1) in order to identify factors that stabilize and destablize the transition state.

Carboxylate and nucleotide anions act as nucleophiles in a number of enzyme-catalyzed phosphoryl transfer reactions, many of which require Mg^{2+}. For example, aspartyl residues of the Ca^{2+} and Na^+/K^+ ATPases are phosphorylated in the transport cycles, and acetate and 3-phosphoglycerate ions are phosphorylated by

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