High-Pressure NMR Studies of (Porphinato)iron-Catalyzed Isobutane Oxidation Utilizing Dioxygen as the Stoichiometric Oxidant

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We report the first high-pressure NMR[1] study of *any* metal-catalyzed oxidation reaction, enabling us to identify the predominant species present in solution during a (porphinato)iron [PFe]-catalyzed oxidation of isobutane in which the hydrocarbon oxidizing equivalents are derived from dioxygen.[2−7] This is particularly important given (i) the potential commercial importance of these catalytic reactions and (ii) the fact that in contrast to the wealth of information regarding both mechanism and reactivity for catalytic oxidations of hydrocarbons involving PFe[III] complexes and O atom donors, such as iodosylbenzene,[8] comparatively little is known regarding analogous catalytic oxidations that utilize O$_2$. Our work demonstrates that the nature of the porphyrinic species under catalytic conditions differs from what has previously been surmised.[2,4]

We have performed catalytic isobutane oxidation reactions at 80 °C in sapphire high-pressure NMR tubes.[1b,9] *In situ* ^{19}F NMR experiments are particularly useful to establish the nature of PFe species, since the magnitude of the ^{19}F chemical shifts for fluorine-containing porphyrins depends intimately on metal-centered electronic properties.[10] Parallel experiments in glass-lined autoclaves[9] enable us to monitor the formation of the oxidation products by GC and the fate of the catalysts by electronic absorption spectroscopy. These catalytic isobutane

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(1) (a) Horváth, I. T.; Millar, J. M. *Chem. Rev.* **1991,** *91,* 1339−1351. (b) Horváth, I. T.; Ponce, E. C. *Rev. Sci. Instrum.* **1991,** *62,* 1104−1105.

(2) (a) Ellis, P. E., Jr.; Lyons, J. E. *Coord. Chem. Rev.* **1990,** *105,* 181−193 and references therein. (b) Lyons, J. E.; Ellis, P. E., Jr. *Catal. Lett.* **1991,** *8,* 45−52. (c) Lyons, J. E.; Ellis, P. E., Jr. *Appl. Catalysis A. General* **1992,** *84,* L1−L6. (d) Lyons, J. E.; Ellis, P. E., Jr.; Myers, H. K., Jr.; Wagner, R. W. *J. Catalysis* **1993,** *141,* 311−315. (e) Lyons, J. E.; Ellis, P. E., Jr.; Myers, H. K., Jr. *J. Catalysis* **1995,** *155,* 59−73. (f) Wijesekera, T. P.; Lyons, J. E.; Ellis, P. E., Jr. *Catal. Lett.* **1996,** *36,* 69−73.

(3) (a) Ellis, P. E.; Lyons, J. E. U.S. Patent 4 898 989, 1990. (b) Ellis, P. E.; Lyons, J. E. U.S. Patent 5 118 886, 1992. (c) Ellis, P. E.; Lyons, J. E.; Myers, H. K. Eur. Patent 471 561, 1992. (d) Ellis, P. E.; Lyons, J. E. U.S. Patent 5 120 882, 1992. (e) Ellis, P. E.; Lyons, J. E. U.S. Patent 5 120 886, 1992.

(4) (a) Grinstaff, M. W.; Hill, M. G.; Labinger, J. A.; Gray, H. B. *Science* **1994,** *264,* 1311−1313. (b) Labinger, J. A. *Catal. Lett.* **1994,** *26,* 95−99.

(5) (a) Balch, A. L.; Olmstead, M. M.; Safari, N.; St. Claire, T. N. *Inorg. Chem.* **1994,** *33,* 2815−2822. (b) Chin, D.-H.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1980,** *102,* 4344−4350.

(6) Rodgers, K. R.; Arafa, I. M.; Goff, H. M. *J. Chem. Soc., Chem. Commun.* **1990,** 1323−1324.

(7) Momenteau, M.; Reed, C. A. *Chem. Rev.* **1994,** *94,* 659−698.

(8) For example, see: (a) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983,** *105,* 5786−5791. (b) Nappa, M. J.; Tolman, C. A. *Inorg. Chem.* **1985,** *24,* 4711−4719. (c) Traylor, T. G.; Tsuchiya, S. *Inorg. Chem.* **1987,** *26,* 1338−1339. (d) Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988,** *110,* 158−162. (e) Collman, J. P.; Zhang, X.; Lee, V. J.; Uffelman, E. S.; Brauman, J. I. *Science* **1993,** 261, 1404−1411. (f) Sorokin, A.; Robert, A.; Meunier, B. *J. Am. Chem. Soc.* **1993,** *115,* 7293−7299. (g) Mansuy, D. *Coord. Chem. Rev.* **1993,** *125,* 129−142.

(9) Reaction conditions for the autoclave (Table 1) and high-pressure NMR tube experiments were identical with respect to [catalyst], [isobutane], reaction time, and temperature. While a continuous O$_2$ feed maintained a constant pressure in the autoclave experiments, pressure decreased simultaneously with oxygen consumption in our NMR experiments.

(10) (a) Birnbaum, E. R.; Hodge, J. A.; Grinstaff, M. W.; Schaefer, W. P.; Henling, L.; Labinger, J. A.; Bercaw, J. E.; Gray, H. B. *Inorg. Chem.* **1995,** *34,* 3625−3632. (b) Toi, H.; Homma, M.; Suzuki, A.; Ogoshi, H. *J. Chem. Soc., Chem. Commun.* **1985,** 1791−1792.

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oxidations utilized two archetypal electron deficient PFe oxidation catalysts; one is based on the well-studied 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin [(C$_6$F$_5$)$_4$PH$_2$] ligand system, while the other features the recently developed, significantly more electron poor, 5,10,15,20-tetrakis(heptafluoropropyl)-porphyrin [(C$_3$F$_7$)$_4$PH$_2$] macrocycle.[11−12]

Because the Fe[II] oxidation state is postulated to play a primary role in the generation of a dioxygen-derived active alkane-hydroxylating species,[2,4] the autoclave reactors and the sapphire NMR tubes were initially charged with PFe[II]·(ligand)$_2$ complexes. 3-Fluoropyridine (3-F-py) was used as the axial ligand for this study, since it has moderate Lewis basicity[13] and provides a convenient marker band for ^{19}F NMR.

Variable temperature ^{19}F NMR spectra show reversible dissociation of axial 3-F-py over a moderate temperature domain for both complexes in benzene-d_6 in the absence of isobutane and oxygen. Consistent with the electronic properties of the macrocycle,[11] the (C$_3$F$_7$)$_4$PFe[II]·(3-F-py)$_2$ complex (Figure 1A) exists primarily as six-coordinate iron(II) at 26 °C in benzene-d_6, ($\delta = -127.1$ ppm for free 3-F-py; $\delta = -126.1$ ppm for 3-F-py in (C$_3$F$_7$)$_4$PFe[II]·(3-F-py)$_2$ at 26 °C); in contrast, (C$_6$F$_5$)$_4$-PFe[II]·(3-F-py)$_2$ (Figure 1E) exhibits an equally sharp 3-F-py resonance at −40 °C, but shows a significantly broadened ligand peak at 26 °C, congruent with reversible 3-F-py dissociation at ambient temperature. At 80 °C, both complexes display broad ^{19}F NMR chemical shifts for 3-F-py.[14]

Within 15 min of pressurizing the sapphire NMR tubes containing the PFe[II] species in benzene-d_6 with isobutane and O$_2$, the spectra shown in Figure 1C,G are manifest. The porphyrinic ^{19}F NMR signals of Figure 1C correspond to the electron poor μ-oxo dimer [(C$_3$F$_7$)$_4$PFe[III]]$_2$O, while those of Figure 1G verify that a mixture of [(C$_6$F$_5$)$_4$PFe[III]]$_2$O and [(C$_6$F$_5$)$_4$-PFe[III]·OH] is present for the more sterically encumbered and electron rich (C$_6$F$_5$)$_4$PH$_2$-based catalyst.[12b,15,16] Because the free ligand peaks integrate 2:1 relative to the porphyrin NMR peaks, we conclude that PFe[III] species are produced stoichiometrically from these PFe[II](L)$_2$ precursors; thus, within the detection limits of the experiment, no other porphyrinic species other than PFe[III]·OH and (PFe[III])$_2$O are observable in either system prior to the onset of catalysis. ^{13}C NMR spectroscopy shows at this time that no oxidation of isobutane has taken place in either sample; in fact, significant induction periods (∼hours) are required before any oxidation products are observable.[17] Analogous NMR experiments show a similar distribution of PFe[III] species in the absence of isobutane; furthermore, the nature of these products does not change as the catalyst concentration is increased to 0.1 M.

After the induction period, ^{13}C NMR shows the formation of isobutanol, acetone, and *tert*-butyl peroxide. ^{19}F NMR shows the presence of several new resonances that correspond to

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(11) (a) DiMagno, S. G.; Williams, R. A.; Therien, M. J. *J. Org. Chem.* **1994,** *59,* 6943−6948. (b) Goll, J. G.; Moore, K. T.; Ghosh, A.; Therien, M. J. *J. Am. Chem. Soc.* **1996,** *118,* 8344−8354.

(12) (a) The Fe[II] redox state for (C$_3$F$_7$)$_4$PFe[II]·(ligand)$_2$ complexes is stabilized with respect to that observed for (C$_6$F$_5$)$_4$PFe[II]·(ligand)$_2$ species, consistent with the superior electron-withdrawing properties of the former macrocycle. (b) Moore, K. T.; Therien, M. J. Manuscript in preparation.

(13) (a) Henderson, W. A.; Streuli, C. A. *J. Am. Chem. Soc.* **1960,** *82,* 5791−5794. (b) Gordon, A. J.; Ford, R. A. In *Chemist's Companion*; Wiley: New York, 1972; p 145.

(14) For (C$_3$F$_7$)$_4$PFe[II]·(3-F-py)$_2$, the ^{19}F NMR chemical shift at −126.5 ppm progressively broadens over the 26−80 °C temperature domain. For (C$_6$F$_5$)$_4$PFe[II]·(3-F-py)$_2$, we initially observed broadening of the signal at −126.5 ppm, followed by a progressive shift of this resonance to −122.2 ppm on warming the sample from 26 to 80 °C.

(15) Spectroscopic assignments were made via independently synthesized PFe[III] complexes (see Supporting Information). The nature of the PFe[III] species present along with their chemical shifts have been shown to be independent of isobutane concentration.[16]

(16) Moore, K. T.; Horváth, I. T.; Therien M. J. In preparation.

(17) Induction periods could be as high as several days and do not correlate with the electronic structure of the porphyrin ligand.

Table 1. Effects of (Porphinato)Iron Electronic Structure on Exhaustive Isobutane Oxidation in Benzene[a]

catalyst	PFe species obsd at initiation of catalysis[c]	reaction time (h)[d]	convsn of isobutane to oxidized products (%)	product distribution (%)[b]		
				tert-butyl alcohol	acetone	*tert*-butyl peroxide
$(C_3F_7)_4$PFe·(3-F-py)$_2$	$[(C_3F_7)_4$PFe$^{III}]_2$O (major) $(C_3F_7)_4$PFe·OH (minor)	91[a]	31	84	8.1	7.8
$(C_6F_5)_4$PFe·(3-F-py)$_2$	$[(C_6F_5)_4$PFe$^{III}]_2$O (minor) $(C_6F_5)_4$PFe·OH (major)	20[a]	12	86	3.6	10.3
$(C_6F_5)_4$PFe·OH[e]	not reported	3	17	80	20	not reported[a]

[a] The PFe^{II} catalyst (0.005 mmol) and isobutane (350 mmol) were dissolved in benzene (20 mL) and heated to 80 °C under nitrogen, giving a total pressure of ~110 psi within the autoclave. The reaction is initiated by introducing sufficient O_2 into the autoclave to give a total pressure of 125 psi, corresponding to ~3 mmol of O_2 present under initial conditions. The total pressure was maintained constant throughout the reaction by utilizing a continuous O_2 feed into the autoclave. [b] All reactions show small quantities of CO and CO_2 as well as trace amounts of H_2 and CH_4. See refs 2 and 16. [c] Determined from NMR experiments. [d] Reaction times for the $(C_3F_7)_4$PFe·(3-F-py)$_2$ and $(C_6F_5)_4$PFe·(3-F-py)$_2$ catalysts correspond to the time at which dioxygen ceased to be consumed. [e] See ref 2a.
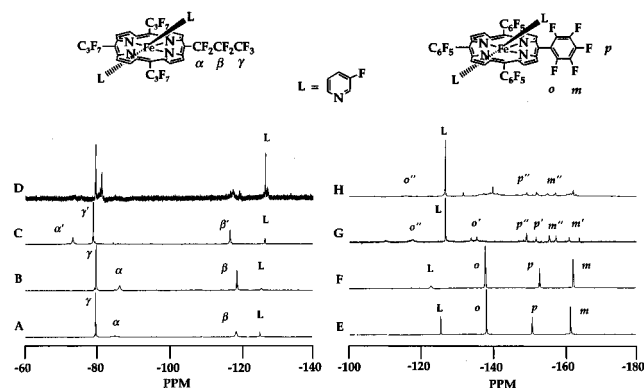
Figure 1. *In situ* ^{19}F NMR spectra of PFe-catalyzed isobutane oxidation reactions. (A) $(C_3F_7)_4$PFe·(3-F-py)$_2$ at 26 °C under Ar. (B) $(C_3F_7)_4$PFe·(3-F-py)$_2$ at 80 °C under Ar. (C) $(C_3F_7)_4$PFe species at 80 °C observed 30 min after addition of isobutane/O_2. (D) $(C_3F_7)_4$PFe species that are observed while isobutane oxidation products are being produced. (E) $(C_6F_5)_4$PFe·(3-F-py)$_2$ at −40 °C under Ar. (F) $(C_6F_5)_4$PFe·(3-F-py)$_2$ at 80 °C under Ar. (G) $(C_6F_5)_4$PFe species at 80 °C observed 30 min after addition of isobutane/O_2. (H) $(C_6F_5)_4$PFe species that are observed while isobutane oxidation products are being produced. The α, β, and γ refer to ^{19}F NMR resonances associated with the perfluoroheptyl group while o, m, and p denote perfluorophenyl ^{19}F NMR resonances for the PFe^{II}·(3-F-py)$_2$ complexes. Prime notation corresponds to ^{19}F NMR resonances for the (PFe^{III})$_2$O species; double prime notation labels resonances for the PFe^{III}·OH complex. The L represents the ^{19}F NMR resonance for the 3-F-py axial ligand ($\delta = -127.1$ ppm for the free ligand). All chemical shifts reported are relative to CFCl$_3$ ($\delta = 0.0$ ppm).

degraded porphyrin ligand (Figure 1D,H).[16] In both cases the intensity of the 3-F-py ^{19}F NMR signal far surpasses the benzene soluble porphyrin-derived ^{19}F NMR resonances, indicating that, whatever the oxidized porphyrin products, they are only sparingly soluble; direct examination of the sapphire NMR tube contents confirms significant bleaching of the solution as well as the presence of considerable precipitate at this juncture. Once PFe^{III} species are no longer detected by ^{19}F NMR, catalysis ceases.

Table 1 summarizes data obtained from our catalytic oxidations carried out in the autoclave reactor. The distribution and nature of isobutane oxidation products were confirmed by ^{13}C NMR experiments and GC analysis. In contrast to experiments reported for the $(C_6F_5)_4$PH$_2$ ligand systems,[2,3] these studies show a significant production of *tert*-butyl peroxide in all our catalytic oxidations. While hydrocarbon product distribution varies little with respect to the electronic features of the porphyrin ligand, a larger net conversion of substrate is observed for the $(C_3F_7)_4$-PH$_2$-based catalyst as well as an augmented time domain over which catalytic activity is observed.

In conclusion, we demonstrate the following: (i) High-pressure NMR methods can provide considerable mechanistic insight into catalytic hydrocarbon oxidation reactions. (ii) Even in a $(C_3F_7)_4$PH$_2$ ligand environment, Fe^{II} is not stable under

moderate O_2 pressure; this contrasts the ambient temperature redox stability of such electron deficient PFe^{II} species.[4a] (iii) The equilibrium between (PFe^{III})$_2$O and PFe^{III}·OH complexes depends on ligand steric and electronic parameters, consistent with literature precedent.[18] (iv) Because only high-spin PFe^{III} compounds and no oxidation products are observed soon after pressurizing the sapphire NMR tubes with PFe^{II} catalyst, solvent, oxygen, and isobutane, alkyl radicals that initiate the radical chain may derive from a reaction involving PFe^{III}·OH and isobutane that produces water and a PFe^{II} species; generating HO$^{\bullet}$ in benzene would be expected to yield primary alcohols in addition to isobutanol, the quantity of which would be limited to the absolute mass of catalyst present and thus not detectable under these experimental conditions.[19] (Furthermore, because the production of PFe^{III} compounds occurs in the absence of isobutane at high catalyst concentrations, it argues against peroxide impurities being the sole oxidizing agent for PFe^{II}, although we can not rule out this possibility.) (v) ^{13}C NMR and GC analysis determine that (*t*-BuO)$_2$ is produced in substantial quantity, as predicted by Labinger,[4b] consistent with a radical chain process likely dominating the observed reaction kinetics, and given ii above, this autoxidation reaction pathway for isobutane will likely be rate limited by the transient production of the reduced PFe complex. (vi) Despite the substantial volume of research papers[2] and extensive patent literature to the contrary,[3] the fact that porphyrin decomposition occurs concomitant with the onset of catalytic isobutane oxidation under these conditions sheds considerable doubt on the viability of simple electron deficient porphyrins as commercial isobutane oxidation catalysts which consume stoichiometric oxidants that are derived from dioxygen. Future work in this area must focus on engineering enhanced reactivity in electron deficient (porphinato)iron species as well as tailoring the microenvironment in which these hydrocarbon oxidations are performed.

Supporting Information Available: Data base of NMR spectra corroborating the assignments made in Figure 1 (14 pages). See any current masthead page for ordering and Internet access instructions.

JA961531J

(18) (a) Harel, Y.; Felton, R. H. *J. Chem. Soc., Chem. Commun.* **1984**, 206−208. (b) Cheng, R.-J.; Latos-Grazynski, L.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 2412−2418.

(19) $(CH_3)_3CH \rightarrow (CH_3)_3C^{\bullet} + H^{\bullet}$ ($-\Delta H_{DBE} = 93$ kcal/mol); $CH_4 \rightarrow CH_3^{\bullet} + H^{\bullet}$ ($-\Delta H_{DBE} = 105$ kcal/mol); $H_2O \rightarrow HO^{\bullet} + H^{\bullet}$ ($-\Delta H_{DBE} = 111$ kcal/mol). See: (a) Sawyer, D. T. *J. Phys. Chem.* **1989**, *93*, 7977−7978. (b) Barton, D. H. R.; Sawyer, D. T. In *The Activation of Dioxygen and Homogeneous Catalytic Oxidation*; Barton, D. H. R., Martel, A. E., Sawyer, D. T., Eds.; Plenum Press: New York, 1993; pp 1−7.