Perfluoroalkylporphyrin complexes as active catalysts for the reaction of isobutane with oxygen and the decomposition of tert-butyl hydroperoxide

Tilak P. Wijesekera, James E. Lyons and Paul E. Ellis Jr.

Research and Development Department, Sun Company, Marcus Hook, PA 19061, USA

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A new family of metalloporphyrin complexes having perfluoroalkyl groups in the meso-positions of the ring are active catalysts for the oxidation of isobutane to tert-butyl alcohol, TBA, and for the decomposition of tert-butyl hydroperoxide to TBA. This discovery extends the limited number of meso-substituents that can be used to enhance catalytic activity and fits the postulate that groups that withdraw electrons from the porphyrin periphery give rise to active catalysts for alkane oxidation. The perfluoroalkyl groups also confer oxidative stability, hydrophobicity and lower cost to the catalyst.

Keywords: oxidation; metalloporphyrins; hydroperoxide decomposition

1. Introduction

It has recently been shown that electron withdrawing substituents such as perfluorophenyl and nitro groups in the meso-positions of iron porphyrin complexes have an enormously beneficial effect on the catalytic activity of these complexes for both the direct reaction of aliphatic hydrocarbons with molecular oxygen as well as the rapid and selective decomposition of alkyl hydroperoxides to the corresponding alcohols [1–5]. This enhanced catalytic activity can be correlated directly with increased Fe(III)/Fe(II) reduction potentials of the electron deficient complexes in question [6].

A novel series of electron-deficient porphyrin complexes has recently been prepared in our laboratories [7] by a new and general synthetic route involving 5-perfluoroalkyldipyrromethanes as the key intermediates. This route allows us to prepare, for the first time, complexes having perfluoroalkyl groups at opposite (5,15-) meso-positions while the substituents at the other two meso- (10,20-) positions can be varied as desired, fig. 1. This method furnishes a convenient high yield synthesis of 5,10,15,20-tetrakisperfluoroalkyl porphyrin complexes [7]. We are now in a position to examine the effect of a meso-perfluoroalkyl substituent on the catalytic activity of a metalloporphyrin catalyst and to compare this effect with that of either the meso-nitro or meso-pentafluorophenyl groups which we have examined earlier.

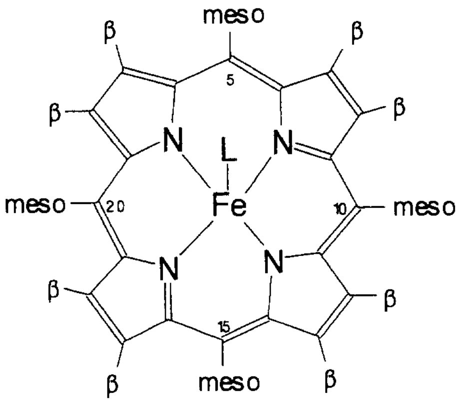

Fig. 1. The substituted porphyrinato ring system: meso-substituents = C_6H_5, C_6F_5, CF_3, C_3F_7, β-groups = H, Br; axial ligand = OH, μ-oxo (PFeOFeP).

Not only does this new route make available a series of potentially inexpensive perhaloporphyrin catalysts but also provides a family of truly "teflon" porphyrins having pendant perfluoroalkyl chains which might be both more robust and more highly hydrophobic [7] than any currently available[#1]. Moreover, perfluoroalkyl substituents, though highly electron withdrawing, are chemically distinct from the two types that we have investigated in the past. Past substituents included haloaryl groups such as meso-C_6F_5 and the highly electron-withdrawing meso-nitro group both of which might participate in electron withdrawal through π-interactions with the delocalized π-system of the porphyrin ring. The perfluoroalkyl substituent, on the other hand, can only withdraw electrons from the porphyrin π-system via a sigma-inductive interaction. Whether this type of interaction will provide a superior catalyst has been up until now an interesting question. *In this communication we demonstrate for the first time that perfluoroalkyl groups in the meso-position of iron porphyrin complexes result in highly active catalysts for the oxidation of alkanes and the decomposition of alkyl hydroperoxides.*

[#1] Other synthetic approaches to these compounds are given in ref. [8].

2. Experimental

2.1. *Solvents and reagents*

All solvents used were HPLC grade from Aldrich and were used as purchased. All non-porphyrin reagents were purchased from Aldrich unless noted and were certified ACS reagent grade or better. $[(C_6H_5)_4PFe]Cl$, I, and $[(C_6H_5)_4PFe]_2O$, II, were purchased from Strem Chemicals. $[(C_6F_5)_4PFe]OH$, III [9] and $[(C_6F_5)_4\beta\text{-}Br_4PFe]OH$ [10] were made by the referenced methods. $[(C_6F_5)_4\beta\text{-}Br_8PFe]OH$, IV, was prepared by chromatographic elution of the corresponding chloride complex on activated alumina. The syntheses of the meso-perhaloalkylporphyrins used to prepare the catalysts for this study, $(C_6F_5)_2(CF_3)_2PH_2$, $(CF_3)_4PH_2$, $(C_6F_5)_2(C_3F_7)_2PH_2$, and $(C_3F_7)_4PH_2$ are reported elsewhere [7]. The syntheses of $[5,15\text{-}(C_6F_5)_2\text{-}10,20\text{-}(CF_3)_2PFe]_2O$, V, $[(CF_3)_4PFe]OH$, VI, $[5,15\text{-}(C_6F_5)_2\text{-}10,20\text{-}(C_3F_7)_2PFe]_2O$, VII and $[(C_3F_7)_4PFe]OH$, VIII were accomplished by iron insertion into the porphyrin macrocycle as described below.

Iron insertion was carried out in hot glacial acetic acid (110°C) under argon using $FeCl_2 \cdot 4H_2O$. The reaction mixture was cooled to room temperature after 25 min, allowed to stir overnight exposed to air and treated with an equal volume of 3 M HCl. In each case, the crude product was isolated by filtration, chromatographed on neutral alumina using $CHCl_3$ as the eluting solvent and retreated with 6 M HCl to obtain the hemin [iron(III) chloride] in >90% yield.

2.1.1. *Analytical data for the hemins [iron (III) chloride] (see table 1)*

The catalytic species were prepared by passing a $CHCl_3$ solution through deactivated alumina (neutral; 15% water added) using $CHCl_3$ for elution. ^1H NMR (δ_{CDCl3}) indicate that they are μ-oxo dimers: $[(C_6F_5)_2(CF_3)_2PFe]_2O$ (β_H at 14.22, 14.49 ppm), $[(C_6F_5)_2(C_3F_7)_2PFe]_2O$ (β_H at 14.06, 14.45 ppm) and $[(C_3F_7)_4PFe]_2O$ (β_H at 14.45 ppm). In the case of $(CF_3)_4PFe$, extensive molecular aggregation resulted in the loss of significant quantities of material on the column, and the dimer $[(CF_3)_4PFe]_2O$ isolated was highly insoluble in most organic solvents.

2.1.2. *β-bromination of 5,15-bis(pentafluorophenyl)-10,20-bis(trifluoromethyl)porphyrin*

The brominated complexes: $[5,15\text{-}(C_6F_5)_2\text{-}10,20\text{-}(CF_3)_2\beta\text{-}Br_xPFe]_yX$, $x = 1\text{–}7$, $y = 1$ or 2; X = OH and/or μ-O, V–Vd, were prepared by direct bromination of V. β-bromination was carried out on the iron(III) chloride $[(C_6F_5)_2(CF_3)_2PFe]Cl$ using four different procedures described below. In each case, the reaction mixture was treated with 2 M NaOH and chromatographed on neutral alumina (15% water added) using $CHCl_3$ as the eluting solvent prior to isolation of the product. This was to ensure that the catalyst is either in the hydroxo- or μ-oxo dimer form depending on the extent of β-bromination (determined by FABMS).

(1) $[(C_6F_5)_2(CF_3)_2PFe]Cl$, was refluxed with bromine for 30 h. The isolated material exhibited a μ-oxo dimer type UV-visible spectrum with a Soret at $\lambda_{max} = 396$ nm (10 nm red-shift from that of $[(C_6F_5)_2(CF_3)_2PFe]_2O$) and a shoulder at 430 nm. The predominant species: $[(C_6F_5)_2(CF_3)_2\beta\text{-}Br_3PFe]OH$ and dimers of mono- and di-brominated material, (Va).

(2) Bromination as in (1) but with added N-bromosuccinimide. Product exhibited a Soret at $\lambda_{max} = 406$ nm with peaks at 446(sh) and 640(wk). The predominant species: $[(C_6F_5)_2(CF_3)_2\beta\text{-}Br_4PFe]OH$, (Vb).

(3) $[(C_6F_5)_2(CF_3)_2PFe]Cl$ in CCl_4/pyridine (20 : 1) was refluxed with bromine and N-bromosuccinimide for 24 h. The supernatant solution was decanted from insoluble material and washed with HCl to remove excess pyridine prior to the standard work-up. The isolated material exhibited a broad Soret at $\lambda_{max} = 407$ nm with a peak at 655(wk). The predominant species: monomeric penta- and hexa-brominated material, (Vc).

(4) Bromination as in (3) with no added N-bromosuccinimide. The reaction mixture exhibited a 30 nm red-shift of the Soret band within 1 h with no further change even in 7 h. The isolated material exhibited a very broad Soret at $\lambda_{max} = 418$ nm and a peak at 685(wk). The predominant species: monomeric hexa-; hepta- and octa-brominated material, (Vd).

2.2. *Isobutane oxidations*

Isobutane was oxidized in the liquid phase according to the procedures given in tables 2 and 3. Glass vessels

Table 1
Analytical data for the hemins [iron(III) chloride]

Complex	UV (λ_{max} (nm))	300 MHz ^{1}H NMR (δ_{CDCl3}) (β_H)	MS (m/z)
$(C_6F_5)_2(CF_3)_2PFeCl$	348/406 (Soret), 504, 622(wk)	85.62, 89.51	EIMS: 832 (M–Cl)
$(CF_3)_4PFeCl$	348/404 (Soret), 506, 634(wk)	93.38	EIMS: 636 (M–Cl)
$(C_6F_5)_2(C_3F_7)_2PFeCl$	348/406 (Soret), 510, 622(wk)	83.39, 86.05, 87.45, 88.86	FABMS: 1032 (M–Cl)
$(C_3F_7)_4PFeCl$	348/406 (Soret), 506, 630(wk)	84.86, 96.20, 99.98	LDMS: 1037 (M–Cl + H)

Table 2
Effect of meso-perfluoroalkyl substituents on the catalytic activity of electron deficient iron porphyrin complexes

Catalyst	Meso-groups	β-groups	Axial ligand, L[c]	Isobutane oxidations[a]			TBHP decompositions[b]	
				Time[d] (h)	TO[e]	TBA sel[f] (%)	Time[d] (h)	TO[g]
I	$4C_6H_5$	8H	OH	12	0	–	1	13,040
II	$4C_6H_5$	8H	μ-O	12	0	–		
III	$4C_6F_5$	8H	OH	6	1090	90	1	66,200
V	$2C_6F_5, 2CF_3$	8H	μ-O	6	530	90	1	62,500
VII	$2C_6F_5, 2C_3F_7$	8H	μ-O	6[h]	90	na	1	72,160
				12	710	90		
VIII	$4C_3F_7$	8H	μ-O	6[h]	110	na	1	82,780
				12	1110	81		

[a] Approximately 7 g isobutane was bubbled into a chilled solution of ~ 0.013 mmol of catalyst in 25 ml benzene in a Fisher–Porter aerosol tube. The tube was fitted to a gas manifold, flushed with O_2 and then filled with pure O_2. The tube was plunged into a constant temperature bath at 60 ± 2°C and filled with O_2 to 100 psig. The solution was stirred magnetically at 60°C for 6 h between 90 and 100 psig total gas pressure. As O_2 was consumed, it was replenished from a reservoir. After 6 h reaction mixture was cooled, returned to atmospheric pressure and the liquid analyzed by standard glpc.

[b] The catalyst, 0.60 mg, was added directly to a stirred solution of tert-butyl hydroperoxide, 13.8 g, in tert-butyl alcohol, 18.1 g, at 80°C. Oxygen evolution was measured manometrically. Liquid products were analyzed by glpc before and after the runs.

[c] Either the axial ligand was OH or the complex was a μ-oxo complex; (Porph)FeOFe(Porph).

[d] Reaction time.

[e] Moles oxygen absorbed/equivalent of iron used.

[f] (Moles tert-butyl alcohol produced/moles liquid product) × 100.

[g] Moles oxygen evolved/equivalent of iron used.

[b] Prolonged induction periods were observed after which facile reaction occurred.

were used and many of the reactions were carried out within the explosive region. For this reason reactors were individually shielded within a laboratory hood and the entire hood front was protected by 1.4" thick polycarbonate shielding.

2.3. *tert-butylhydroperoxide decompositions*

tert-butylhydroperoxide was decomposed under the conditions given in table 2. Reactions were carried out in magnetically stirred Morton flasks immersed in a constant temperature bath kept at 80 ± 1°C during reaction. When the reaction mixture reached 80°C the catalyst was added in a small glass boat to the stirring solution. Oxygen immediately began to evolve. The reflux condenser was connected to a manometer and oxygen evolution measured with time. Liquid samples were removed periodically through an "air-tight" port and subjected

Table 3
Effect of β-bromination of III and V on catalytic isobutane oxidation activity[a]

Catalyst	Meso-groups	β-groups[b]	Axial ligand[c]	Reaction time (h)	O_2 TO[d]	TBA sel.[e] (%)
III	$4C_6F_5$	8H	OH	6	1090	88
IIIA	$4C_6F_5$	4Br, 4H	OH	6	1220	86
IV	$4C_6F_5$	8Br	OH	6	1620	86
V	$2C_6F_5, 2CF_3$	8H	μ-O	6	530	90
Va	$2C_6F_5, 2CF_3$	2Br, 6H	μ-O	6	600	88
Vb	$2C_6F_5, 2CF_3$	4Br, 4H	μ-O, OH	6	960	89
Vc	$2C_6F_5, 2CF_3$	5Br, 3H	μ-O, OH	6	1045	88
Vd	$2C_6F_5, 2CF_3$	7Br, 1H	OH	6	1330	88

[a] Approximately 7 g isobutane was bubbled into a chilled solution of ~ 0.013 mmol of catalyst in 25 ml benzene in a Fisher–Porter aerosol tube. The tube was fitted to a gas manifold, flushed with O_2 and then filled with pure O_2. The tube was plunged into a constant temperature bath at 60 ± 2°C and filled with O_2 to 100 psig. The solution was stirred magnetically at 60°C for 6 h between 90 and 100 psig total gas pressure. As O_2 was consumed, it was replenished from a reservoir. After 6 h the reaction mixture was cooled, returned to atmospheric pressure and the liquid analyzed by standardized glpc.

[b] Bromination of compound V under different conditions led to product mixtures V having different amounts of substitution of bromine into the β-position. The numbers of β-groups given in this table refer to the most abundant compound in the mixture.

[c] With low Br substitution the product was recovered as the μ-oxo dimer; with high Br substitution as the hydroxo complex; with intermediate Br substitution the product was a mixture of hydroxo and μ-oxo complexes.

[d] Moles oxygen absorbed/equivalent of iron used.

[e] (Moles tert-butyl alcohol produced/moles liquid product) × 100.

to standardized glpc analysis. The reactor hood opening was protected with polycarbonate shielding as in the isobutane oxidations above.

3. Results and discussion

Table 2 indicates that iron porphyrin complexes having perfluoroalkyl groups in the meso-position are active catalysts for the selective oxidation of isobutane to tert-butyl alcohol

$$(CH_3)_3CH + \tfrac{1}{2}O_2 \rightarrow (CH_3)_3COH \qquad (1)$$

New complexes tested were iron haloporphyrin complexes having either hydroxo or μ-oxo axial ligands in all cases. It can be seen that replacing two of the perhalophenyl groups of meso-5,10,15,20-tetrakis-(pentafluorophenyl)porphyrinatoiron(III) hydroxide, III, with perhalomethyl substituents results in a catalyst, V, with fair activity.

It was of considerable interest, therefore, to prepare the analogous complex in which all four of the meso-substituents were CF_3 groups to determine its catalytic activity. In addition there are economic incentives for studying the activity of tetra(meso-trifluoromethyl) substituted iron porphyrin complexes as replacements for the tetra(meso-pentafluorophenyl) substituted complexes. One is that the perhalogenated precursors used for the introduction of meso-CF_3 groups are less expensive than those required for introducing meso-C_6F_5 groups. Another is that the substitution of four CF_3 groups for four C_6F_5 groups lowers the weight of catalyst required per active iron, thus lowering the catalyst cost directly. We, therefore, prepared the 5,10,15,20-tetrakis(trifluoromethyl)iron(III) complex, VI, with the intention of using this complex as an isobutane oxidation catalyst. It was, unfortunately, insoluble in all nonpolar aprotic solvent systems compatible with isobutane.

We then prepared and tested the complexes analogous to V and VI in which n-C_3F_7 groups were substituted for CF_3 (complexes VII and VIII respectively). Both of these new complexes were readily soluble in benzene, and isobutane oxidations could be smoothly run in this solvent, table 2. Unexpectedly, an induction period of four to five hours was observed in these reactions. After this time, however, smooth and rapid oxidation of isobutane occurred giving tert-butyl alcohol as the major product, eq. (1). The complex with four pendant n-C_3F_7 groups, bis[5,10,15,20-tetrakis-(heptafluoropropyl)porphyrinatoiron(III)]μ-oxide, VIII, was not only very active after the initial induction period, but reaction rates were then comparable with those of the tetrakis(pentafluorophenyl)porphyrin complex, III. *This is the first demonstration of catalytic oxidation activity for metalloporphyrin complexes with perhaloalkyl groups on the periphery of the porphyrin ring and further extends the general observation that although metalloporphyrin complexes are generally poor alkane oxidation catalysts, the presence of electron withdrawing groups on the periphery of the porphyrin ring, results in high catalytic activity.*

Electron-deficient metalloporphyrin complexes that are active catalysts for the selective low temperature oxidations of light alkanes are also highly efficient catalysts for the selective decomposition of alkylhydroperoxides to alcohols [4],

$$(CH_3)_3COOH \rightarrow (CH_3)_3COH + \tfrac{1}{2}O_2 \qquad (2)$$

Iron complexes having perhaloalkyl groups in the meso-positions are no exception to this trend. Table 2 indicates that when some or all of the meso-perfluorophenyl groups in an iron porphyrin complex are replaced with perfluoroalkyl groups, similarly high hydroperoxide decomposition activity is observed.

We have shown in earlier reports that halogenation of the pyrrolic positions of an electron-deficient metalloporphyrin complex causes an increase in the catalytic activity of the metal complex. Table 3 shows that the same holds true for a complex having meso-trifluoromethyl groups. As the number of pyrrolic hydrogens replaced by bromo substituents increases, the catalytic activity of the complex steadily increases as well. Thus, by adding a perfluoroalkyl group in the meso-position we create an active catalyst, *and* then by brominating the pyrrolic position one can enhance catalytic activity even further.

4. Conclusions

The unprecedented activity for selective light alkane oxidation observed when electron-deficient metalloporphyrins are used as catalysts encourages one to consider their potential practical application. A major impediment to the use of perhaloporphyrinato metal porphyrins is their high cost. The perfluoroalkyl moiety can be introduced into a dipyrromethane via a relatively inexpensive perfluoroaldehyde in up to 70% yield. The overall cyclization step [7] of the resulting dipyrromethane with an aldehyde is quite efficient and also occurs in good yield. Catalysts which are both highly active and inexpensive are very desirable for the direct air-oxidation of isobutane to tert-butyl alcohol.

This work not only provides a novel method for creating a wide range of new and potentially less expensive porphyrinatometal complexes, but expands further the range of electron withdrawing substituents which can be used to enhance activity. Work continues toward practical catalysts for light alkane oxidation based on first-row transition metals in highly electron deficient porphyrinic macrocycles.

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