Catalysis Letters 8 (1991) 45–52

SELECTIVE LOW TEMPERATURE HYDROXYLATION OF ISOBUTANE BY MOLECULAR OXYGEN CATALYZED BY AN IRON PERHALOPORPHYRIN COMPLEX

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Received 12 September 1990; accepted 2 November 1990

Low temperature hydroxylation, isobutane, iron perhaloporphyrin complex catalyst, molecular oxygen with isobutane, tert-butyl alcohol, alkane oxydation

Iron *tetrakis*(pentafluorophenyl)β-octabromoporphyrinato complexes have been synthesized for the first time and shown to have unprecedented catalytic activity for the reaction of molecular oxygen with isobutane to give *tert*-butyl alcohol. This is the first report of the use of a perhaloporphyrin complex for mild, selective air-oxidation of an alkane and extends the trend of increased activity with halogen substitution established previously. Replacing the eight β-(pyrrolic) hydrogens in Fe(TPPF$_{20}$) complexes with bromines gives catalysts having twice the room temperature air-oxidation activity of the Fe(TPPF$_{20}$) complexes. Room temperature reaction of isobutane with oxygen catalyzed by Fe(TPPF$_{20}\beta$-Br$_8$)Cl produces 190 moles product per mole catalyst per hour with over 90% selectivity to the alcohol. The catalyst activity is unchanged after 74 hours.

1. Introduction

Direct catalytic conversion of alkanes to alcohols using molecular oxygen as the oxidant is of great interest as a means of converting these available and inexpensive hydrocarbons to valuable products [1]. Porphyrinatoiron complexes are known to catalyze the biomimetic hydroxylation of alkanes using as oxidants oxygen atom transfer reagents such as iodosylbenzene [2–5], hypohalites [6,7], and hydroperoxides [8,9]. Oxygen has been used as the oxidant together with electrons supplied by co-reductant systems. An iron porphyrin complex has been shown to catalyze the oxidation of cyclohexane to cyclohexanone using oxygen as oxidant, zinc amalgam as co-reductant, methyl viologen for electron transfer and acetic anhydride as an acylating agent [10]. Recently, alkane hydroxylation with O_2 has produced alcohols electrochemically [11]. The need for expensive co-reductants or oxygen atom transfer reagents imposes an economic disadvantage on commercial or large scale synthetic application of this chemistry.

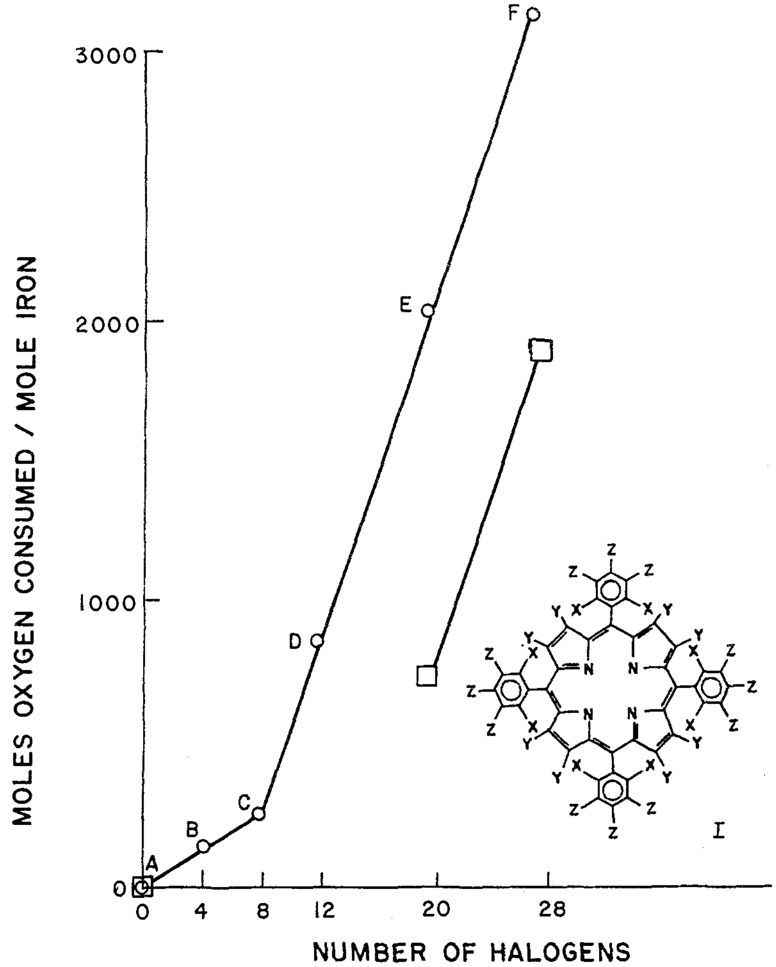
In recent communications [12–15] we have described a series of iron porphyrin complexes that efficiently catalyze the oxidation of light alkanes with oxygen or air under mild conditions without the need for added co-reductants or oxygen atom transfer reagents. During the course of this work we found that halogenation of the porphyrin ring of porphyrinatoiron(III) complexes greatly increased their catalytic activity for the selective mild reaction of alkanes with molecular oxygen [13–15]. Furthermore, the greater the halogen content in the porphyrin ring, the greater was the catalytic activity of the complex. The largest number of halogens in the tetraphenylporphyrinato complexes previously described by us was twenty. The trends which we established suggested that perhalotetraphenylporphyrinato iron complexes having 28 carbon-halogen bonds should be even more active catalysts for reaction of light alkanes with molecular oxygen.

In this communication we report for the first time the syntheses of the iron(III) perhaloporphyrin complexes of *tetrakis*(pentafluorophenyl)β-octabromoporphyrin, and their use in the low temperature reaction of isobutane with oxygen to give *tert*-butyl alcohol. Replacement of all twenty-eight of the carbon-hydrogen bonds of the macrocycle by halogens resulted in *the most highly active complex for low temperature isobutane air-oxidation yet reported.*

2. Experimental

Fe(TPPF$_{20}$-β-Br$_8$)Cl-A 6 M solution of bromine in dry, deaerated CCl$_4$ (100 ml) was added to a solution of *tetrakis*(pentafluorophenyl)porphyrinatoiron(III)chloride, Fe(TPPF$_{20}$)Cl, 0.500 g, in 300 ml of dry, deaerated CCl$_4$, and the mixture stirred 18 hours at reflux. At this point an additional 50 ml of 6 M bromine in CCl$_4$ were added and the solution refluxed several hours longer. The Soret absorption of the solution had moved from 418 nm to 429 nm indicating that bromination of the pyrrole ring had occurred. The solution was cooled, filtered and washed three times with water then evaporated to dryness. The crude product was obtained by column chromatography on neutral alumina using chloroform as the eluant. The first green band was collected, treated with dilute HCl and evaporated to dryness. After drying in vacuo at 110 ° C, 590 mg of the desired Fe(TPPF$_{20}$-β-Br$_8$)Cl was obtained. The proton nmr spectrum showed the absence of all pyrrolic β-C-H bonds; UV/VIS, toluene 429 nm, 480 nm, sh, 598 nm, and infrared spectrum are consistent with a highly halogenated iron porphyrin compound [5]. Anal. Calcd. for $C_{44}N_4Br_8ClF_{20}Fe$: C, 31.2; N, 3.3; Br, 37.7; Fe, 3.3; Found: C, 32.2; N, 3.9; Br, 36.8; Fe, 3.1.

The synthesis of *tetrakis*(pentafluorophenyl)-β-octabromoporphyrinatoiron (III)azide was accomplished by metathesis of the corresponding chloride with hydrazoic acid. Fe(TPPF$_{20}$-β-Br$_8$)Cl, 150 mg, was dissolved in a mixture of 300 ml methanol and 1200 ml acetone. To this solution was added 10.0 grams of sodium azide then 10 drops of glacial acetic acid. The solution was stirred for 72 hours,



	LIGAND,I	X	Y	Z
A	(TPP)	8H	8H	12H
B	(TPPβ-Br$_4$)	8H	4H,4Br	12H
C	(TPPCl$_8$)	8Cl	8H	12H
D	(TPPCl$_8$β-Br$_4$)	8Cl	4H,4Br	12H
E	(TPPF$_{20}$)	8F	8H	12F
F	(TPPF$_{20}$β-Br$_8$)	8F	8Br	12F

Fig. 1. Effect of ring halogenation on isobutane oxidation activity of chloroiron(III) porphyrin complexes, Fe(L)Cl. Reactions run for 6 hours as indicated in table 1: ○, 80 ° C, □, 60 ° C.

then rotary evaporated to dryness. The dry material was washed with water and dried in vacuo. Yield 95 mg. IR analysis shows a strong $\nu_{\text{N-N}}$ for the azide at 2049 cm^{-1} consistent with known iron porphyrin azide complexes [13].

Oxidations were carried out in a barricaded laboratory equipped for conducting hazardous reactions since some reactions were conducted within the explosion limits. Reactions reported in fig. 1 and table 1 were carried out in 50 cc

Table 1
Isobutane oxidations using $(TFFP_{20}\text{-}\beta\text{-}Br_8)Fe(III)$ as catalysts [a]

	mmoles	*T* (°C)	*t* (hr)	T.O. [b]	TBA Sel. (%) [c]
$Fe(TPPF_{20})N_3$	0.016	60	6	1050	88
		40	6	470	89
		27	6	54	95
		27	24	440	94
$Fe(TPPF_{20}\text{-}\beta\text{-}Br_4)OH$	0.013	60	6	1220	86
		40	6	360	90
		26	6	70	91
		26	24	300	90
$Fe(TPPF_{20}\text{-}\beta\text{-}Br_8)Br$	0.013	60	6	1490	87
		40	6	470	89
		25	24	470	na
$Fe(TPPF_{20}\text{-}\beta\text{-}Br_8)Cl$	0.013	60	6	1860	91
		40	6	690	90
		27	6	130	90
		27	24	870	90
		27	72	1890	90
		27	124	2580	91
$Fe(TPPF_{20}\text{-}\beta\text{-}Br_8)N_3$	0.013	60	6	1550	87
		40	6	670	89
		25	6	620	na
		25	27	2180	na
		25	47	2960	na
		25	53	3180	90

[a] A solution of the catalyst in 25 ml benzene containing 6 grams of isobutane was stirred at the designated temperature under 100 psig of O_2 for the designated time.

[b] Moles O_2 consumed/mole catalyst used.

[c] (Moles t-butyl alcohol produced/total moles liquid product) ×100.

Fisher-Porter glass aerosol tubes with magnetic stirring. Reactions reported in table 2 were conducted in a glass lined autoclave with Teflon coated internals (impeller, dip-tube, etc.). Gas and liquid products were analyzed by a combination of standardized gc, ms, and gcms analysis.

3. Results

Recently we reported that the systematic replacement of the C–H bonds of tetraphenylporphyrinatoiron(III) complexes gave increasingly active catalysts for the selective hydroxylation of isobutane to *tert*-butyl alcohol. The most extensively halogenated members of the series which were investigated were

Table 2
Iron haloporphyrin-catalyzed isobutane oxidations [a]

Catalyst	T (° C)	Charge to reactor		O_2	Reaction products (mmoles)				Conversion i-C_4H_{10} (%)	Select. TBA (%) [b]	TON [c]
		t (hrs)	i-C_4H_{10}		TBA	Acetone	CO_2	CO			
Fe(TPPF$_{20}$-β-Br$_8$)Cl	80	3	1870	53	277	43	23	8.0	17	87	10,660
	80	3	1862	100	429	86	26	4.9	28	83	17,150
	80	3	1862	148	414	81	28	6.0	27	84	16,500
	80	3	1869	205	290	45	37	10.5	18	87	11,180
	60	3	1865	47	230	23	20	tr	14	91	8,420
	60	3	1874	139	184	18	17	tr	11	91	6,730
	25	71.5	1862	53	372	35	27	tr	22	92	13,560
Fe(TPPF$_{20}$)OH	24	143	1871	53	332	17	18	0	18	95	12,150

[a] Isobutane was oxidized by an oxygen-containing gas mixture (75 atm, diluent = N_2) in the liquid phase (180 ml) for 3 hours. Oxygen added as consumed.

[b] (moles TBA/moles liquid product) ×100.

[c] models (TBA + acetone) produced/mole catalyst used.

tetrakis(pentafluorophenyl)porphyrinatoiron(III) complexes which proved to be the most active catalysts of the series. Using these catalysts it was possible to achieve unprecedented rates and high selectivities. Table 1 shows that by replacing all of the pyrrolic β-hydrogens of Fe(TPPF$_{20}$)Cl with bromines, one can now produce a catalyst with even greater activity. The room temperature activity of this complex is twice that of the previously most active tetraphenylporphyrin catalyst.

The activity of other halogenated complexes is compared with that of the perhalo complex at 80° and 60°C in figure 1. The remarkably steady increase in activity with extend of halogenation is shown to occur starting with the parent complex which contains no halogens up to the perhalo complex in which all 28 of the hydrogens in the porphyrin ring have now been replaced with halogens. The linearity from 8 to 28 halogens is surprising and perhaps fortuitous since the nature and position of the halogen substituents is varied from complex to complex. Halogens at both the β-pyrrolic and the *meso*-phenyl positions are effective in increasing catalytic activity.

Since the highly halogenated iron tetraphenylporphyrin complexes are somewhat soluble in alkanes, it was of interest to investigate the oxidation activity of the perhaloporphyrin complex in neat isobutane. Table 2 shows that oxidations are rapid at 60° and 80°C and selectivity is good. Unprecedented room temperature productivity of 190 moles of product per gram atom of iron per hour continued for over 70 hours. The catalyst showed so signs of deactivating over this time period. Conversion reached 22% in less than half the time with the perhalo complex, Fe(TPPF$_{20}\beta$-Br$_8$)Cl, than when Fe(TPPF$_{20}$)OH was used as the catalyst.

4. Conclusions

The iron perhaloporphyrin complexes: Fe(TPPF$_{20}\beta$-Br$_8$)X (X = Br, Cl, N$_3$), catalyze the efficient, mild and selective hydroxylation of isobutane using molecular oxygen at temperature as low as room temperature. We have demonstrated that the perhaloporphyrinatoiron(III) catalyst is by far the most active catalyst yet employed in this reaction. It appears that electron withdrawal from the porphyrin ring system enhances catalyst activity. Bromination of the pyrrole positions of Fe(TPPF$_{20}$)X complexes not only provides a catalyst with much higher activity, but also results in a substantial increase in the reduction potential of the Fe$^{+3/+2}$ couple [Fe^{+3} + e$^{-} \rightleftharpoons$ Fe^{+2}] over that of the unbrominated complex [16].

We have discussed possible mechanistic implications of enhanced reduction potential on the continued production of Fe(II) during oxidation, eqs. (1)–(3), in a previous communication [15]. It may be necessary to continually reduce the iron to Fe(II) to activate and cleave the O$_2$ bond. It should be further pointed out that systematic electron withdrawal from the metal center would be expected to shift the position of equilibrium of eq. (1) to the left. This may allow a standing Fe(II) concentration to be present for O–O bond cleavage. eq. (2). Furthermore, we may be seeing the effects of oxygen concentration on eq. (1), table 2, since the rates of catalytic oxidation go through a maximum as a function of oxygen partial pressure. If too much of the iron is in the $Fe(III)O_2$ state then too little Fe(II) may be left for binding and splitting the bound O_2, eq. (2).

$$\mathrm{Fe(II)} + \mathrm{O_2} \rightleftharpoons \mathrm{Fe(III)O_2} \tag{1}$$

$$\mathrm{Fe(III)O_2} + \mathrm{Fe(II)} \rightarrow \mathrm{Fe(III)O_2Fe(III)} \rightarrow \mathrm{2Fe(IV)O} \tag{2}$$

$$\mathrm{Fe(IV)O} + \mathrm{RH} \rightarrow [\mathrm{Fe(III)OH} + \mathrm{R}\cdot] \rightarrow \text{Products.} \tag{3}$$

In any case, the complete bromination of the pyrrole positions of the active catalyst, $Fe(TPPF_{20})X$, has further increased the catalytic activity and suggests that even greater electron withdrawal from the porphyrin ring will produce an even more active catalyst. The rapid room temperature hydroxylation of isobutane and the mild oxidations of other light alkanes may indeed be possible. Work continues to produce even more active catalysts for the mild oxidation of light alkanes.

Acknowledgements

The authors thank the Morgantown Energy Technology Center of the Department of Energy, the Gas Research Institute and the Sun Company for financial support of this work.

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