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Halogen Substituent Effects on the Catalytic Activity of Iron Porphyrin Complexes for the Decomposition of *tert*-Butyl Hydroperoxide

It has long been known that iron complexes are effective promoters of the decomposition of alkyl hydroperoxides in the liquid phase (*1*). There has been considerable recent interest in the efficient catalytic conversion of *tert*-butyl hydroperoxide to *tert*-butyl alcohol (*2–12*), Eq. (1), but with currently available catalyst systems, elevated temperatures are often required and reaction selectivity is typically around 80%. Tetraphenylporphyrinatoiron(III)chloride was recently shown to be one of the more active catalysts for decomposition of *tert*-butylhydroperoxide (*4*), but in order to obtain relatively rapid rates it was necessary to either conduct reactions at somewhat elevated temperatures (60°C) or to add imidazole which resulted in a hydroperoxide decomposition catalyst that was active at room temperature:

$$\mathrm{ROOH} \rightarrow \mathrm{ROH} + \tfrac{1}{2}\mathrm{O_2}. \qquad (1)$$

In this communication we report that by halogenating the porphyrin ring of iron tetraphenylporphyrinato complexes we were able to greatly enhance catalytic activity, reduce reaction temperatures, and observe reaction selectivities of 90%. Perhaloporphyrinatoiron(III) complexes gave the fastest rate of hydroperoxide decomposition by any metal complex observed to date. In fact, with room temperature reaction rates of well over 100 catalyst cycles per second, these are among the fastest reactions catalyzed by a synthetic transition metal complex in solution (*14*). Rates are within an order of magnitude of the activity of the catalase enzyme which decomposes hydrogen peroxide to water and oxygen (*15*). In addition, this study may have relevance to the mechanism of some recently disclosed rapid air-oxidations of isobutane catalyzed by iron haloporphyrin catalysts (*16, 17*).

Metal complexes used as catalysts: tetrakispentafluorophenylβ-octachloroporphyrinatoiron(III)chloride, $\mathrm{Fe(TPPF_{20}\beta\text{-}Cl_8)Cl}$, tetrakispentafluorophenylβ-octabromoporphyrinatoiron(III)chloride, $\mathrm{Fe(TPPF_{20}\beta\text{-}Br_8)Cl}$, and tetrakispentafluorophenylporphyrinatoiron(III)chloride, $\mathrm{Fe(TPPF_{20})Cl}$, were prepared by methods described previously (*16, 17*). Benzene, (99.99%, Aldrich), *tert*-butyl alcohol, (99.6%, Aldrich), and *p*-xylene, (99 + %, Aldrich) were used as purchased. *tert*-Butyl hydroperoxide (90%, 5% water, 5% *tert*-butyl alcohol) was used as purchased from Aldrich.

A solution of the catalyst in *p*-xylene (internal standard) was quickly added to a rapidly stirring solution of *tert*-butyl hydroperoxide in benzene at room temperature. Oxygen evolution was measured manometrically and liquid products were analyzed periodically by standardized gas chromatography. [*CAUTION*—Reactions should be run in dilute solutions of catalyst and/or hydroperoxide to avoid exotherms and dangerously fast gas evolution.]

Figure 1 compares the activity of a number of iron complexes for the decomposition of *tert*-butyl hydroperoxide, TBH, in benzene. It is clear that porphyrinatoiron(III) complexes are quite active for catalyzing this transformation and that the extent of porphyrin ring halogenation has a dramatic effect on the catalytic activity of the porphyrinatoiron(III) complex used. Very low concentrations of the perhaloporphyrin complexes $\mathrm{Fe(TPPF_{20}\beta\text{-}Y_8)Cl}$, Y = Cl, Br, were extremely effective in catalyzing room tem-

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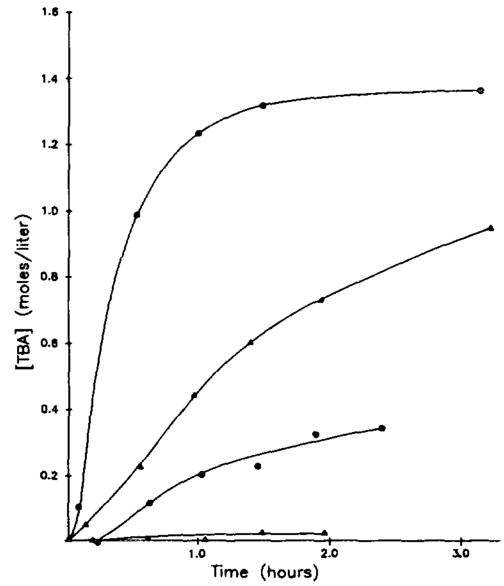


FIG. 1. Formation of *tert*-butyl alcohol, TBA, from *tert*-butyl hydroperoxide (10 ml) in benzene (48 ml)–p-xylene (2.4 ml) using 2×10^{-4} mmoles of catalyst: ○, Fe(TPPF$_{20}$β-Cl$_8$)Cl; △, Fe (TPPF$_{20}$)Cl; ●, Fe(TPP)Cl; and ▲, Fe(acac)$_3$.

perature TBH decomposition. Table 1 compares the product profile and extent of conversion of TBH in benzene after 2 or 3 h. Selectivity to *tert*-butyl alcohol, TBA, was found to be 90% in all instances in which perhaloporphyrinato complexes were used as catalysts and was relatively insensitive to the conversion level. Selectivity was lower when partially halogenated or unhalogenated porphyrins were used.

These reactions are thought to proceed by metal complex catalyzed decomposition of the hydroperoxide to radicals followed by reactions of radical intermediates to produce the alcohol and molecular oxygen (*1*, *9–12*, *20*). Hindered phenols are well-known, efficient radical traps and have also been shown to react with iron porphyrin complexes (*20*). It was therefore of interest to examine the effect of radical traps on the decomposition of hydroperoxides catalyzed by iron porphyrin complexes. Although addition of radical inhibitor affected the length of the induction period, once underway, reaction rates were not greatly changed even in the presence of inhibitor concentrations far in excess of the metal complex used. Incremental addition of the radical inhibitor, 2,4-di-*tert*-butyl-*p*-cresol, prolonged an induction period which grew longer by a time that was proportional to the concentration of inhibitor used; see Fig. 2. At inhibitor concentrations 10,000 fold greater than that of the iron porphyrin complex, the induction period was still less than fifteen minutes long.

There has been much discussion in the recent literature (*9*, *13*, *18*) surrounding the issue of heterolytic vs homolytic O–O bond

TABLE 1

Conversion of *tert*-Butyl Hydroperoxide to *tert*-Butyl Alcohol

Catalyst[a]	TIME Hr	t-BuO$_2$H conv. (%)	Product, molar sel. (%)		
			t-BuOH	(tBuO)$_2$	(CH$_3$)$_2$CO
Fe(ACAC)$_3$	2.3	<5	67	tr	32
Fe(TPP)Cl	1.9	27	82	7	11
Fe(TPPF$_{20}$)Cl	3.3	72	87	10	3
Fe(TPPF$_{20}$β-Br$_8$)Cl	1.9	95	90	8	2
Fe(TPPF$_{20}$β-Cl$_8$)Cl	3.3	100	90	8	2

[a] The catalyst, 2×10^{-4} mmoles, in 2.4 ml p-xylene was rapidly added to a stirred solution of 10 ml t-BuO$_2$H (90%) in 48 ml benzene. O$_2$ evolved was measured manometrically and liquid samples taken periodically and analyzed by standardized GC.

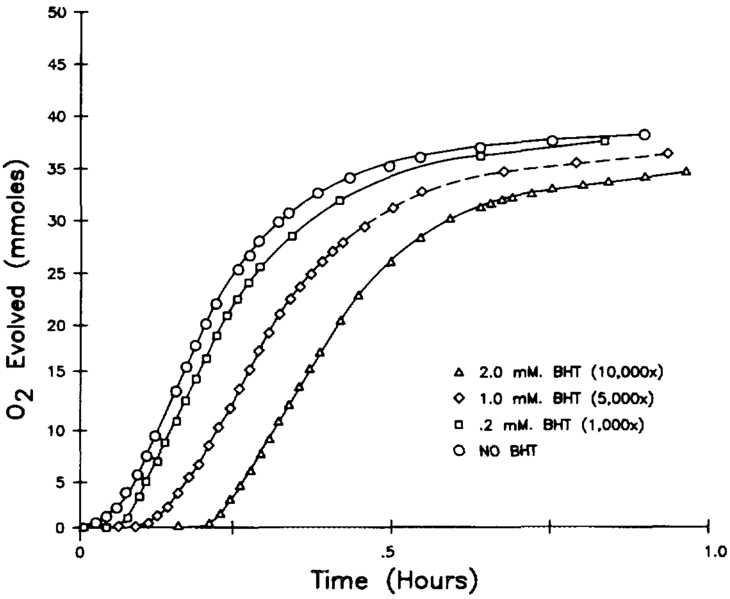
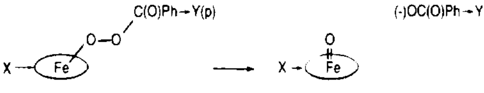


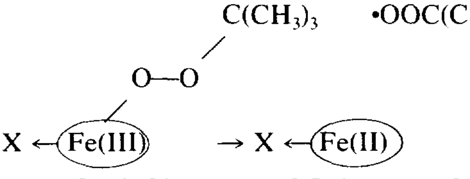
FIG. 2. Effect of BHT on the decomposition of *tert*-butyl hydroperoxide (10 ml) catalyzed by Fe(TPPF$_{20}\beta$-Cl$_8$)Cl, 2 × 10^{-4}, mmoles, in benzene (48 ml)-*p*-xylene (2.4 ml).

cleavage in hydroperoxides during metalloporphyrin catalyzed hydroperoxide decomposition. It has been shown that *tert*-butyl hydroperoxide undergoes homolytic O–O bond cleavage in the presence of porphyrinato iron complexes (*18–20*). Peracidic compounds undergo heterolytic cleavage under the same conditions (*18*). A recent report (*13*) indicates that electron "push" from electron donating substituent groups on the macrocycle coupled with electron "pull" from the peroxide bound to an iron in the macrocycle result in enhanced rate of heterolytic O–O bond cleavage, Eq. (2). Electron pull from the bound peroxide is generated by electron withdrawing groups, Y(p), in the *p*-position on the aromatic peracids used in the study. These observations are reasonable since by pushing electron density from the macrocylic ligand toward the iron center one might stabilize a high-oxidation state ferryl and by removing electron density from the aromatic peracid portion of the complex one would stablize developing negative charge:



(2)

The studies reported in *this* communication demonstrate the effects of electron "pull" from the porphyrin macrocyle and electron "push" from the alkyl hydroperoxide that is decomposed. Surprisingly, the result is that of greatly enhanced decomposition rates. These observations could be rationalized by a mechanism shift to homolytic O–O bond cleavage, Eq. (3), which is enhanced by electron withdrawal from the macrocyclic ligand and thus from the metal center which it surrounds. Electron withdrawal would be expected to raise the Fe(III)/Fe(II) reduction potential (*16, 17*) and favor the homolytic O–O bond dissociation step, resulting in the production of iron(II) from the iron(III) peroxy complex with release of alkylperoxy radicals. The resulting *tert*-butylperoxy radical could react further to produce oxygen and the *tert*-butoxy radical, Eq. (4), which ultimately gives TBA (*9, 12, 18*):



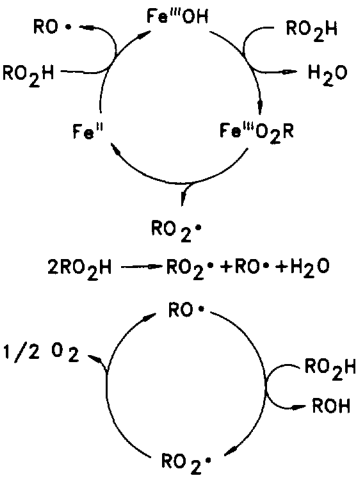
$$X \leftarrow \mathrm{Fe(III)}{-}\mathrm{O{-}O{-}C(CH_3)_3} \rightarrow X \leftarrow \mathrm{Fe(II)} + {\cdot}\mathrm{OOC(CH_3)_3} \qquad (3)$$

$$2\ {\cdot}\mathrm{OOC(CH_3)_3} \rightarrow 2\ {\cdot}\mathrm{OC(CH_3)_3} + \mathrm{O_2} \qquad (4)$$

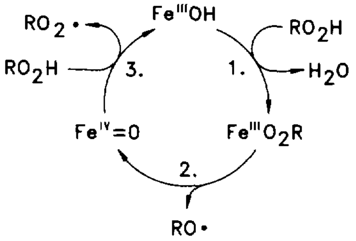
A catalytic reaction which is consistent with the observations presented above can be envisioned as proceeding via the pathway shown in Scheme 1. Early studies of metal complex catalyzed hydroperoxide decomposition were rationalized based on M(III)/M(II) catalysis via the well-known Haber–Weiss cycle shown in Scheme 1.

More recent studies, however, have indicated that metal oxo species may be involved (*18–20*) in metalloporphyrin-catalyzed alkylhydroperoxide decomposition. Balch and his co-workers have found (*19*) that Fe(TPP)OH reacts stoichiometrically with *tert*-butylhydroperoxide to form the alkylperoxy iron(III) complex suggested in Scheme 1. In the presence of a suitable base (*19*) this complex homolyzes to form not Fe(II), but the ferryl complex, Eq. (5). Scheme 2 shows the possible generation of alkoxy and alkylperoxy radicals by a mechanism in which no iron(II) species take part, but rather the catalysis occurs via a one-electron homolytic Fe(III)/Fe(IV)=O couple. At this time it is not possible to assess the relative contributions from pathways shown in Schemes 1 and 2.

$$\mathrm{(TPP)FeOO(\mathit{t}\text{-}Bu)} + \mathrm{B} \rightarrow \mathrm{(B)(TPP)Fe(IV){=}O} + \mathit{t}\text{-}\mathrm{BuO}{\cdot}. \qquad (5)$$



SCHEME 1. Haber–Weiss decomposition of hydroperoxides using metalloporphyrins as catalysts (porphyrin ring omitted).



SCHEME 2. Possible metal oxo pathways for decomposition of hydroperoxides using metalloporphyrin catalysts (porphyrin ring omitted).

The similarity between the effects of reduction potential on catalytic activity for both the decomposition of *tert*-butyl hydroperoxide to *tert*-butyl alcohol and the air-oxidation of isobutane (*16, 17*) to *tert*-butyl alcohol raises the possibility that these reactions have pathways in common. We continue to pursue the synthetic potential of this reaction, extend the trends in catalytic activity with increasing reduction potential, and consider possible implications of this work for air oxidations using perhaloporphyrin catalysts.

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