

Short communication

# The influence of substrate composition on the kinetics of olefin epoxidation by hydrogen peroxide catalyzed by iron(III) [tetrakis(pentafluorophenyl)] porphyrin

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## Abstract

We have recently proposed a mechanism for the epoxidation of cyclooctene by hydrogen peroxide catalyzed by iron(III) [tetrakis(pentafluorophenyl)] porphyrin chloride. The expressions for the rate of hydrogen peroxide consumption and the yield of epoxide derived from this mechanism are in excellent agreement with experimental observations for a wide range of reaction conditions. An interesting feature of the expressions for the apparent rate coefficient and the yield of epoxide relative to peroxide consumed is that they are independent of the properties of the olefin. The present work was undertaken with the aim of determining whether this is a general result applicable to the epoxidation of other olefins. To this end, the rates of epoxidation of cyclooctene, styrene, *cis*-stilbene, cyclohexene, and norbornene were measured under identical conditions. For cyclooctene, styrene, and *cis*-stilbene, the observed kinetics and yield of epoxide were independent of the substrate, and no evidence was found by either UV–visible or <sup>1</sup>H NMR spectroscopy for olefin coordination to the iron cation of the porphyrin. By contrast, the rates of cyclohexene and norbornene epoxidation and the corresponding epoxide yields were significantly lower than those of the other three olefins. The lower catalyst activity and lower epoxide yield correlated with both UV–visible and <sup>1</sup>H NMR evidence for olefin coordination to the iron cation of the porphyrin. Olefin coordination increases the electron density on the iron cation and promotes homolytic cleavage relative to heterolytic cleavage of the oxygen–oxygen bond of coordinated hydrogen peroxide. This has the effect of reducing both the apparent rate coefficient for hydrogen peroxide consumption and the epoxide yield.

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## 1. Introduction

Iron(III) [tetrakis(pentafluorophenyl)] porphyrin (F<sub>20</sub>TPP)Fe is an effective catalyst for the oxidation of hydrocarbons using H<sub>2</sub>O<sub>2</sub> as the oxidant [1–15]. However, a universal mechanism has not been presented that is applicable for a range of substrates. Building on ideas originally proposed by Cunningham et al. [1], we have proposed a mechanism for the oxidation of cyclooctene by H<sub>2</sub>O<sub>2</sub> that fully explains the effects of solvent composition, substrate concentration, reactant concentration, and catalyst concentration on the reaction kinetics [2–4]. The proposed mechanism is shown in Fig. 1. Reaction 1 represents

the dissociation of (F<sub>20</sub>TPP)FeCl via interaction with methanol to produce [(F<sub>20</sub>TPP)Fe(MeOH)]<sup>+</sup> and Cl<sup>−</sup>. This reaction does not proceed in aprotic solvents (e.g., acetonitrile, methylene chloride) but does take place in protic solvents (e.g., methanol), which can solvate effectively the Cl<sup>−</sup> anion and coordinate to the [(F<sub>20</sub>TPP)Fe]<sup>+</sup> cation. The [(F<sub>20</sub>TPP)Fe(MeOH)]<sup>+</sup> cation then complexes with hydrogen peroxide, Reaction 2. Note that the alcohol ligand is not shown throughout the mechanism for the sake of clarity. The oxygen–oxygen bond of coordinated hydrogen peroxide can undergo either heterolytic cleavage (Reaction 3) or homolytic cleavage (Reaction 4). The pi-radical cation species produced by Reaction 3 can then either oxidize the hydrocarbon substrate or react with another molecule of hydrogen peroxide initiating the process of peroxide decomposition (Reaction 6). The iron(IV) species produced via homolytic cleavage of coordinated hydrogen peroxide contributes exclu-

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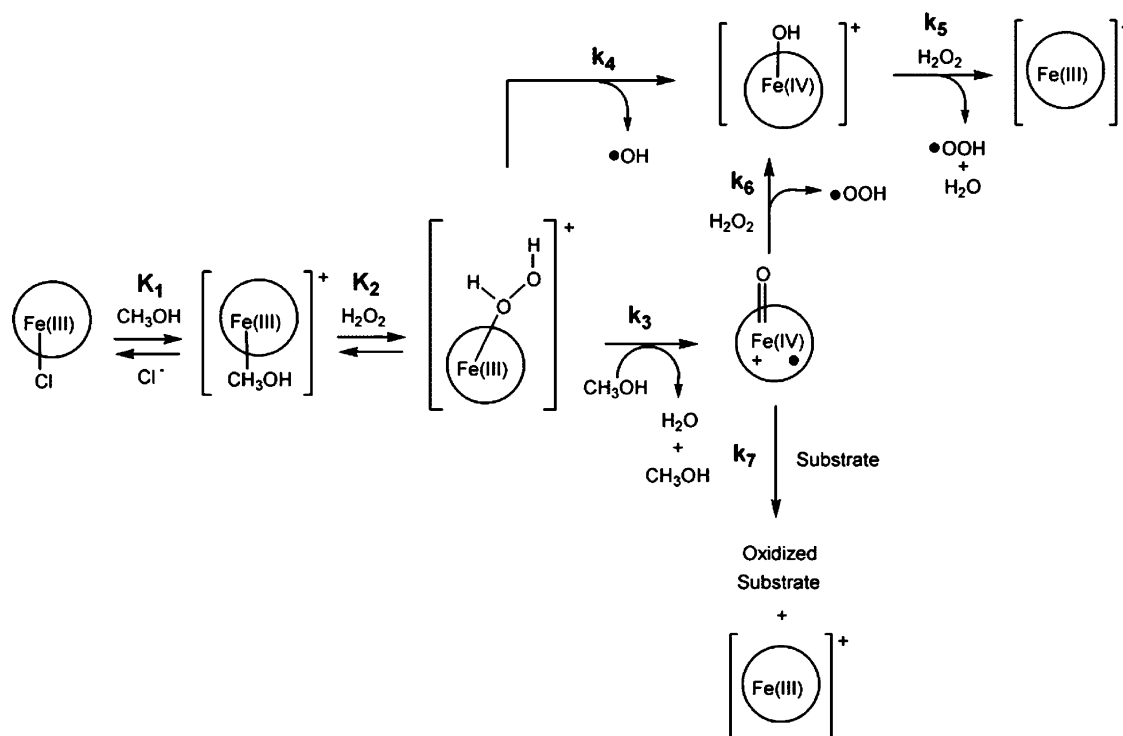


Fig. 1. Proposed mechanism for the epoxidation of olefins by iron(III) [tetrakis(pentafluorophenyl)] porphyrin chloride.

sively to peroxide decomposition. The competition between Reactions 3 and 4 and between Reactions 6 and 7 determines the yield of oxidized product relative to the amount of initial oxidant.

Application of the pseudo-steady-state hypothesis to the iron(IV) pi-radical cation species in the presence of high substrate concentrations results in an observed rate constant (Eq. (1)) that is independent of the substrate concentration and the rate constant for epoxidation (i.e.,  $k_7$ ).  $Y_\infty$  (Eq. (2)) is the final yield of oxidized substrate and relates the concentration of epoxide formed to the concentration of hydrogen peroxide consumed.  $[\text{H}_2\text{O}_2]_0$  is the initial concentration of hydrogen peroxide, and  $[\text{C}_8\text{-O}]_\infty$  is the concentration of cyclooctene epoxide after the consumption of all hydrogen peroxide. Eq. (3) represents the equilibrium concentration of  $[(\text{F}_{20}\text{TPP})\text{Fe}(\text{MeOH})]^+$ ;  $[\text{Fe-Cl}]_0$  is the concentration of all porphyrin species in solution and  $[\text{Fe-CH}_3\text{OH}^+]$  is the concentration of alcohol-coordinated porphyrin species,  $[(\text{F}_{20}\text{TPP})\text{Fe}(\text{MeOH})]^+$  [3]. The rate and equilibrium constants appearing in Eqs. (1) and (2) are for the corresponding reactions shown in Fig. 1.

$$k_{\text{obs}} = \frac{k_3 K_2 [\text{Fe-CH}_3\text{OH}^+][\text{CH}_3\text{OH}]}{Y_\infty} \quad (1)$$

$$Y_\infty = \frac{[\text{C}_8\text{-O}]_\infty}{[\text{H}_2\text{O}_2]_0} \times 100\% \cong \frac{k_3 [\text{CH}_3\text{OH}]}{k_3 [\text{CH}_3\text{OH}] + 2k_4} \times 100\% \quad (2)$$

$$[\text{Fe-CH}_3\text{OH}^+] = \frac{-K_1 [\text{CH}_3\text{OH}] + \sqrt{(K_1 [\text{CH}_3\text{OH}])^2 + 4K_1 [\text{CH}_3\text{OH}][\text{Fe-Cl}]_0}}{2} \quad (3)$$

Eqs. (1)–(3) provide a very accurate description of the kinetics of cyclooctene epoxidation by  $\text{H}_2\text{O}_2$  for  $(\text{F}_{20}\text{TPP})\text{FeCl}$  dissolved in mixtures of acetonitrile and methanol [2–4]. What

is notable about these equations is that they are independent of the nature of the olefin undergoing epoxidation. It is, therefore, interesting to ask whether this is a general phenomena, i.e., are the values of  $k_{\text{obs}}$  and  $Y_\infty$  always independent of the olefin composition. Equally important is to understand under what circumstances the values of these parameters become dependent on olefin composition. In the present study, we have measured the values of  $k_{\text{obs}}$  and  $Y_\infty$  for cyclooctene, styrene, *cis*-stilbene, cyclohexene, and norbornene. This set of olefins was chosen on the basis of previous studies that demonstrated the epoxidation of these substrates by  $(\text{F}_{20}\text{TPP})\text{FeCl}$  [1–13].

## 2. Experimental

### 2.1. Materials

Iron(III) [tetrakis(pentafluorophenyl)] porphyrin chloride, hydrogen peroxide (30%), silver-trifluoromethanesulfonate (99.95+%), *cis*-stilbene (96%), norbornene (99%), cyclohexene (99%), and dodecane (99+%) were obtained from Sigma–Aldrich. HPLC grade methanol (99.9%) and OmniSolv grade acetonitrile (99.99+%) were obtained from EMD Chemicals. Cyclooctene (95%) and styrene (99%) were obtained from Alfa-Aesar. Deuterium oxide (99.9%) was obtained from Cambridge Isotope Laboratories.

Iron(III) [tetrakis(pentafluorophenyl)] porphyrin triflate was synthesized by stirring silver triflate (93 mg) and iron(III) [tetrakis(pentafluorophenyl)] porphyrin chloride (70 mg) in ace-

tonitrile (7.5 mL) for several days. A change from chloride to triflate coordination was evidenced by an upfield shift in the  $\beta$ -pyrrole  $^1\text{H}$  NMR resonance from 83 to 60 ppm.

## 2.2. Measurement of reaction rates

Olefin (0.72 M) and iron(III) [tetrakis(pentafluorophenyl)] porphyrin chloride (75  $\mu\text{M}$ , final concentration) were added to a 3.0 mL solvent mixture of acetonitrile and methanol (3:1) in a 5.0 mL vial with magnetic stirring. None of the olefins contained a stabilizer and all were used as received. Reactions were initiated by the addition of hydrogen peroxide (5  $\mu\text{L}$ ). An HP6890 series gas chromatograph fitted with an Agilent DB Wax (30 m  $\times$  0.32 mm  $\times$  0.5  $\mu\text{m}$ ) capillary column and an FID detector was used to detect the production of oxidation products. Oxidation products were quantified relative to an internal standard (dodecane). Analysis of the olefins by gas chromatography verified the purity. Impurities were identified as oxidized products of the olefin or as inert hydrocarbons. The presence of any oxidized product in the olefin prior to reaction was taken into account during the analysis of the kinetic data. Rate data were taken as a function of time by analyzing multiple reactions. Reactions were performed in triplicate to verify repeatability.

In the case of cyclohexene epoxidation, it was necessary to work in an oxygen-free environment, since dissolved  $\text{O}_2$  was observed to cause additional oxidation via a radical mechanism. Thus, all procedures were conducted in a nitrogen-filled glove bag. Oxygen was removed from solvents and substrates by bubbling with nitrogen. Reaction mixtures of solvent, internal standard, catalyst and substrate were prepared in air-tight, sealed 5.0 mL reaction vials with septa caps. Hydrogen peroxide was added to the reaction mixture via a Hamilton Gastight<sup>®</sup> microsyringe through the septa cap. Samples for GC analysis were removed via a Hamilton Gastight<sup>®</sup> microsyringe to prevent exposure to oxygen.

## 2.3. UV–visible experiments

Analysis of porphyrin solutions by UV–visible spectroscopy was carried out using a Varian Cary 400 Bio UV–visible spectrometer. Samples were prepared in a manner similar to that used for the rate studies; however, porphyrin and substrate concentrations were reduced by a factor of five to prevent complete absorbance. Due to experimental limitations, all samples were analyzed in the presence of air.

## 2.4. $^1\text{H}$ NMR experiments

Paramagnetic  $^1\text{H}$  NMR spectra were obtained using a 400 MHz VMX spectrometer. Samples for  $^1\text{H}$  NMR were prepared in precision NMR tubes by addition of 0.5 mmol of substrate to 400  $\mu\text{L}$  of 5.5 mM iron(III) [tetrakis(pentafluorophenyl)] porphyrin triflate dissolved in acetonitrile. A capillary containing  $\text{D}_2\text{O}$  was also added to each NMR tube for NMR signal locking. The NMR sample containing cyclohexene was prepared under nitrogen.

$^1\text{H}$  NMR experiments were also conducted to study the effect of the catalyst on the peak position of the resonances for the substrate protons. Samples for these experiments were prepared by combining iron(III) [tetrakis(pentafluorophenyl)] porphyrin triflate (5.6 mM) and substrate (1.9 mM) in acetonitrile (400  $\mu\text{L}$  total sample volume). Signal locking was obtained by using a capillary filled with  $\text{D}_2\text{O}$ .

## 3. Results and discussion

### 3.1. Reaction kinetics

If the mechanism shown in Fig. 1 is universally valid and the pseudo-steady-state hypothesis is applicable as applied to the pi-radical cation species, then both the yield and observed rate constant should be independent of the nature of the substrate at high substrate concentrations (see Eqs. (1)–(3)). As shown in Table 1, the values of  $k_{\text{obs}}$  and  $Y_{\infty}$  are identical for cyclooctene, *cis*-stilbene, and styrene, whereas the values of  $k_{\text{obs}}$  and  $Y_{\infty}$  are noticeably smaller for norbornene and cyclohexene. Differences between the first three substrates and the latter two could also be observed visually. Upon dissolution of  $(\text{F}_{20}\text{TPP})\text{FeCl}$  in a methanol/acetonitrile solvent mixture, an emerald green solution was produced. When cyclooctene, *cis*-stilbene, or styrene was added to the reaction mixture no further color change occurred. However, the addition of cyclohexene or norbornene resulted in a brown solution, suggesting that these substrates interact with the iron(III) porphyrin cation. NMR and UV–visible spectroscopy was used to determine which of the olefins coordinate to the  $[(\text{F}_{20}\text{TPP})\text{Fe}(\text{MeOH})]^+$  cation.

### 3.2. Olefin coordination evidenced by UV–visible and NMR spectroscopies

Fig. 2(a) shows that the addition of cyclooctene, *cis*-stilbene, or styrene to a 3:1 acetonitrile/methanol solution of  $[(\text{F}_{20}\text{TPP})\text{Fe}]\text{Cl}$  has no significant effect on the shape of the UV–visible spectrum of the porphyrin, indicating no change in the electronic nature of the porphyrin catalyst. However, as shown in Fig. 2(b), there is a red-field shift in the Soret peak when norbornene is present, indicating a change in the electronic properties of the porphyrin. We suggest that this is due to

Table 1  
Summary of results for the oxidation of various alkenes (0.7 M) by  $\text{H}_2\text{O}_2$  (14 mM) using iron(III) [tetrakis(pentafluorophenyl)] porphyrin chloride as catalyst (75  $\mu\text{M}$ )

Substrate	$k_{\text{obs}}$ ( $\text{min}^{-1}$ )	Yield (%)
Cyclooctene	$0.25 \pm 0.02$	$88 \pm 2$
<i>cis</i> -Stilbene <sup>a</sup>	$0.26 \pm 0.04$	$88 \pm 4$
Styrene	$0.26 \pm 0.03$	$88 \pm 2$
Norbornene <sup>b</sup>	$0.07 \pm 0.01$	$45 \pm 2$
Cyclohexene <sup>c</sup>	$0.18 \pm 0.04$	$74 \pm 3$

<sup>a</sup> Products include epoxide and benzaldehyde (9:1).

<sup>b</sup> Trace amounts of 1,2,3,6-tetrahydrobenzaldehyde formed.

<sup>c</sup> Reaction conducted under nitrogen with deoxygenated solvents and substrate.

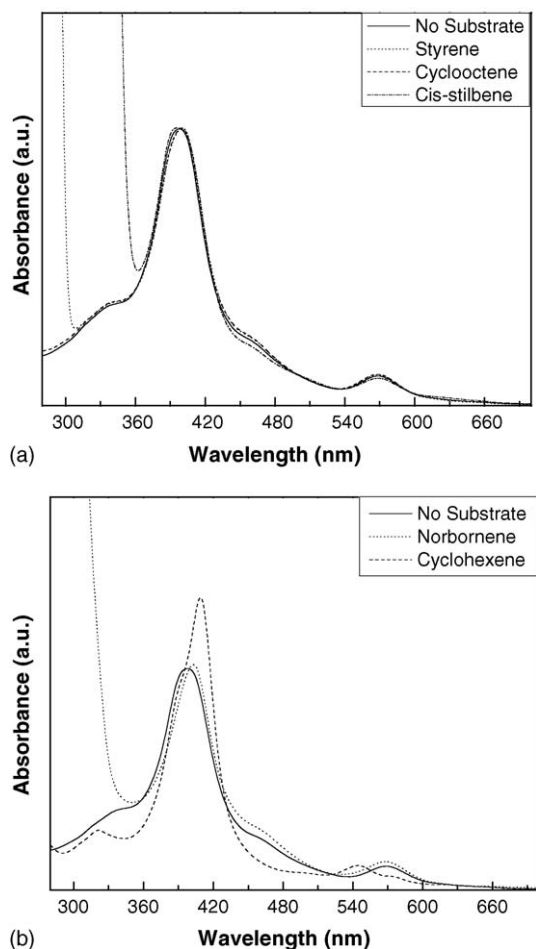


Fig. 2. Effects of the presence of substrate on the UV–visible spectra of iron(III) [tetrakis(pentafluorophenyl)] porphyrin chloride dissolved in a 3:1 mixture of acetonitrile and methanol. (a) Substrates which do not coordinate to the porphyrin. (b) Substrates which coordinate to the porphyrin and affect the observed kinetics.

the coordination of norbornene to the iron cation. The absorption spectrum is very different when cyclohexene is present. The peaks at 410 and 540 nm are indicative of an iron(IV) species [6]. It was not possible to conduct UV–visible experiments in the absence of oxygen, and the radical oxidation mechanism that proceeds in the presence of cyclohexene and oxygen results in the formation of iron(IV) porphyrin species. We also note that the differences in the UV–visible spectra observed at low wave numbers are due to absorbance by the alkene substrates.

To further investigate whether or not the substrate olefins affect the electronic nature of the porphyrin catalysts,  $^1\text{H}$  NMR spectra were taken of an acetonitrile solution of triflate-coordinated iron(III) [tetrakis(pentafluorophenyl)] porphyrin in the presence of each substrate. Triflate-coordinated species were used because the triflate-ligand is much more weakly bound than the chloride ligand. NMR experiments were conducted in the absence of methanol to preclude coordination of methanol to the porphyrin cation. The triflate-coordinated porphyrin exhibits a  $^1\text{H}$  NMR resonance attributable to the  $\beta$ -pyrrole protons at 60 ppm in the absence of substrate. This resonance remains unaffected by the presence of cyclooctene, *cis*-stilbene, and styrene.

In the presence of cyclohexene, two peaks are observed at 60 and 73 ppm in a 5:1 ratio, and in the presence of norbornene, only a single peak is observed at 73 ppm. It is well known that the position of the  $^1\text{H}$  NMR resonance for the  $\beta$ -pyrrole protons on the porphyrin ring is a good indicator of the field strength of the axial ligand coordinated to the iron porphyrin cation [16,17]. The appearance of the peak at 73 ppm suggests that there is an electronic interaction between the iron(III) cation of the porphyrin and the olefin. The downfield character of the shift in the  $\beta$ -pyrrole resonance indicates that cyclohexene and norbornene result in an increased electron density on the iron cation. The presence of only a single peak in the presence of norbornene also indicates that norbornene interacts with the iron cation to a greater extent than does cyclohexene. Therefore, both UV–visible spectroscopy and  $^1\text{H}$  NMR suggest that norbornene and cyclohexene coordinate to the axial position of the iron porphyrin resulting in increased electron density on the iron cation.

Coordination of the substrate to the iron cation should also result in shifts for the  $^1\text{H}$  NMR resonances of the substrates. Therefore,  $^1\text{H}$  NMR experiments were conducted in attempts to provide further evidence for olefin coordination. The samples prepared for these experiments contained iron(III) [tetrakis(pentafluorophenyl)] porphyrin triflate (5.6 mM) in excess of olefin (1.9 mM) in acetonitrile. Spectra were analyzed both in the presence and absence of porphyrin, and analyses were performed on samples containing cyclooctene and samples containing norbornene. Analysis of the resulting spectra showed that the presence of the iron porphyrin influenced shielding such that all solvent and substrate proton resonances were shifted approximately 0.6 ppm. No direct evidence for olefin binding was observed in the presence of either cyclooctene or norbornene, suggesting that under the conditions of the experiment the degree of coordination is very small.

### 3.3. Factors affecting coordination of substrate

Olefin coordination is envisioned to occur according to the Dewar–Chatt–Duncanson model. Strained alkenes, such as norbornene, are known to bind unusually strongly to metals due to a relief of strain caused by the rehybridization that occurs upon binding [18]. Of the five substrates studied, only norbornene and cyclohexene were found to influence the electronic nature of the iron porphyrin. This may be due to steric effects; norbornene and cyclohexene are the smallest and least sterically hindered of the substrates. The larger cyclical structure of cyclooctene may prevent it from interacting with the iron cation, while the phenyl groups of *cis*-stilbene and styrene may prevent these substrates from interaction. In addition, the relief of steric strain due to rehybridization may also be a factor influencing coordination.

As described above, coordination of norbornene was not evidenced by a shift in the  $^1\text{H}$  NMR resonances of the norbornene protons under conditions where the olefin-to-porphyrin ratio was  $\sim 0.5$ . Olefins typically act as pi-acceptors rather than electron donors when binding to metal centers [18]. If olefin coordination to the iron(III) cation is in fact occurring, such an interaction is likely to be characterized by a small equilibrium constant. Therefore, it is not surprising that these experiments did not reveal

norbornene coordination to the iron porphyrin cation. The  $^1\text{H}$  NMR experiments were designed such that the iron porphyrin concentration would be in excess of the substrate concentration to prevent having a large excess of non-coordinated substrate. All other experiments investigating the effects of norbornene on the electronics of the porphyrin were carried out at much higher norbornene concentrations (two to three orders of magnitude). Spectroscopic evidence of norbornene coordination to the iron porphyrin at high norbornene concentrations but not at low norbornene concentrations indicates that the equilibrium constant for the coordination of norbornene to the iron cation is in fact small which is consistent with the preference of olefins to act as pi-receptors rather than electron-donors.

### 3.4. Consequences of cyclohexene and norbornene coordination

Our research group [4] and others [10,11] have shown that the nature of the axial ligand has a significant effect on the kinetics of iron(III) [tetrakis(pentafluorophenyl)] porphyrin catalyzed olefin epoxidation by hydrogen peroxide. Nam et al. have shown that porphyrins with strong ligands (e.g.,  $\text{OH}^-$ ,  $\text{OAc}^-$ ,  $\text{Cl}^-$ ) do not catalyze the epoxidation of olefins by hydrogen peroxide, while porphyrins with weakly bound ligands (e.g.,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ ) readily catalyze the epoxidation of olefins [12]. In recent work, we have shown that iron(III) [tetrakis(pentafluorophenyl)] porphyrin chloride becomes active for catalysis in alcohol containing solvents in which the catalyst dissociates in to cations and anions and a molecule of alcohol coordinates at the axial position of the porphyrin [2–4]. Nam et al. have also reported that increased electron donation from the axial ligand favors homolytic cleavage over heterolytic cleavage of the O–O bond of hydrogen peroxide [13] resulting in a decrease in the percentage of hydrogen peroxide utilized for epoxidation. Methanol coordination to the porphyrin is evidenced by a  $\beta$ -pyrrole resonance near 67 ppm [3], while coordination by norbornene or cyclohexene results in a resonance at 73 ppm, indicating that norbornene and cyclohexene exhibit stronger ligand fields than methanol. Therefore, we suggest that it is the binding of norbornene and cyclohexene as axial ligands that results in increased electron density on the iron center and the consequent decreases in catalytic activity and yield seen in Table 1.

## 4. Conclusions

The kinetics of olefin epoxidation by  $\text{H}_2\text{O}_2$  for olefins which do not coordinate to  $(\text{F}_{20}\text{TPP})\text{Fe}$ , such as cyclooctene,

styrene, and *cis*-stilbene are well described by Eqs. (1)–(3), which are derived from the mechanism shown in Fig. 1. In particular,  $k_{\text{obs}}$  and  $Y_{\infty}$  are independent of olefin composition in this case. On the other hand, olefins, such as cyclohexene and norbornene that interact with  $(\text{F}_{20}\text{TPP})\text{Fe}$  change the electronic nature of the catalyst and cause a decrease in  $k_{\text{obs}}$  and  $Y_{\infty}$ . This effect is attributed to an increase in electron donation by the olefin to the iron cation, which, in turn, leads to an increase in the rate of homolytic cleavage relative to heterolytic cleavage of the O–O bond in hydrogen peroxide coordinated to the porphyrin. The present study marks the first time that a reaction mechanism for the epoxidation of olefins by a porphyrin catalyst has been shown to be valid for multiple substrates.

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