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Full Papers

Mechanistic study of decomposition of cyclohexyl hydroperoxide catalysed by manganese(III) tetraarylporphyrins [a]

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Abstract. The reaction between manganese(III) tetraarylporphyrins and cyclohexyl hydroperoxide has been investigated. Since pyridine increases the decomposition rate of cyclohexyl hydroperoxide, all experiments were performed in the presence of pyridine. Experiments with 2,6-di-tert-butylpyridine showed that pyridine increases the reaction rate by ligation to the manganese porphyrin as well as by acting as a base. Cyclohexyl hydroperoxide is decomposed into cyclohexanol and cyclohexanone. Since neither 3,3,5,5-tetramethylcyclohexanol nor cyclohexanol-d_{12} are oxidized under these reaction conditions, cyclohexanone is formed directly from the peroxide and not by oxidation of the alcohol. During the reaction, a manganese(V)oxo porphyrin complex is formed. This complex may react with (i) the peroxide under formation of cyclohexanol and molecular oxygen, (ii) the solvent cyclohexane, or (iii) manganese(III) porphyrin. The latter reaction leads to destruction of the catalyst. This destruction is prevented by introduction of bulky groups on the ortho positions of the phenyl. The scission of the hydroperoxide is suggested to be heterolytic. It is also base-catalysed. The rate-determining step in the decomposition of cyclohexyl hydroperoxide is scission of the oxygen–oxygen bond of the manganese peroxyl porphyrin complex. A mechanism in line with the kinetic data is proposed.

Introduction

In the last decade, extensive research has been carried out on manganese porphyrins as catalysts in oxidation reactions. In these reactions, several single oxygen donors were applied, such as hydrogen peroxide [1], iodosylbenzene [2], sodium hypochlorite [2e,f,3] and alkyl hydroperoxides [4]. Much attention has been focussed on the reaction between tertiary alkyl hydroperoxides and manganese porphyrins. To our knowledge, comparable studies with secondary alkyl hydroperoxides have not been reported. In the present research, we wanted to investigate the reaction between a secondary hydroperoxide, viz. cyclohexyl hydroperoxide, (CHHP) [5] and manganese porphyrins. The decomposition of this peroxide is also of commercial interest because CHHP is an intermediate in the air oxidation of cyclohexane to cyclohexanol (CHOL) and cyclohexanone (CHON) [5], the latter being a starting material for the production of ϵ-caprolactam.

Experimental section

Materials

Cyclohexane was distilled from molecular sieves (4 Å) under N_2. CH_2Cl_2 was dried for 1 week over $CaCl_2$, distilled from $CaCl_2$ and stored under N_2. Toluene was dried over KOH for 1 week, and distilled from sodium sand under N_2. The CHHP was donated by DSM Research. It had been isolated by HPLC from a mixture containing CHOL, CHON, cyclohexane and CHHP. This mixture is an intermediate in the industrial process. After removing the HPLC solvent, pure peroxide was obtained which was dissolved in cyclohexane for safety reasons. The CHHP concentration of these solutions was determined by iodometric titration. Pure peroxide for the hydroxylation experiments was obtained by removing the cyclohexane *in vacuo*. ^{1}H NMR ($CDCl_3$): δ 1.2, m, 5H; 1.5, m, 1H; 1.7, m, 2H; 1.9, m, 2H; 3.9, m, 1H; 8.6, m, 1H. ^{13}C NMR ($CDCl_3$): δ 23.6, s, 2C; 25.7, s, 1C; 30.0, s, 2C; 83.2, s, 1C. HRMS calcd. for $C_6H_{12}O_2$: 116.161; found: 116.083. MS m/z (rel. intensity): 116, M^+, 14; 83, $M-OOH^+$, 81; 55, $M-C_2H_4OOH^+$, 100; 41, $m-C_3H_6OOH^+$, 78. Every day, fresh $Fe(SCN)_2$ solution was prepared by mixing equal volumes of an $FeCl_2$ solution and NH_4SCN solution (30 g NH_4SCN in 100 cm^3 water). The $FeCl_2$ solution was obtained by adding acidified $BaCl_2$ solution (0.8 g $BaCl_2$, 50 cm^3 water and 2.0 cm^3 concd. HCl) to $FeSO_4 \cdot 7H_2O$ solution (1.0 g $FeSO_4 \cdot 7H_2O$ in 50 cm^3 water) resulting in a white precipitate. After filtration, the thus prepared $FeCl_2$ solution could be used for 10 days [6]. The porphyrin ligands were prepared according to published procedures: H_2TPP [7] (TPP = 5,10,15,20-tetraphenylporphyrin dianion), H_2TDCPP [8] [TDCPP = 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin dianion], TPCPP [8] [TPCPP = 5,10,15,20-tetrakis(2,3,4,5,6-pentachlorophenyl) porphyrin dianion] and TMP [8] [TMP = 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrin dianion]. Manganese was inserted by treating with $Mn(OAc)_2 \cdot 4H_2O$ in boiling DMF [9].

Instrumentation

^{1}H-NMR spectra were recorded on Bruker WP 200 or Bruker WP 300 instruments, with the solvent $CDCl_3$ as internal standard. UV/Vis spectra were recorded on a Perkin–Elmer 552 or 555 spectrophotometer. Gas chromatography was performed on a Varian

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3700 instrument, equipped with a flame-ionization detector, using a Chrompack 25% carbowax 20M on chromosorb WAW 60–80 mesh (2m×2 mm) column. Peak areas were measured using a Shimadzu C-3RA electronic integrator.

Decomposition reaction

Decomposition reactions were carried out in a Schlenk tube, containing a N_2 atmosphere, temperature-controlled at 25.0±0.2°C. The tube was filled with 10.0 cm^3 of a 0.158 mol·dm^{-3} CHHP solution in cyclohexane. 500 mm^3 of porphyrin solution in CH_2Cl_2 was added. The reaction was stirred magnetically (stirring rod 0.5×0.7 cm at 1000 rpm). Two samples were taken, the first one, 10.0 mm^3, was required for the determination of the CHOL and CHON concentrations and the second, 1.0 mm^3, was necessary for the determination of the CHHP concentration. All reactions were at least carried out twice. Rates that are presented are initial rates.

Spectroscopic determination of the CHHP concentration

This procedure is a modification of the procedure of *Kolthoff* [6]. A Schlenk tube was filled with 10.0 cm^3 of toluene/MeOH (7:3 v/v), followed by 1.0 mm^3 of sample. The tube was shaken. 100 mm^3 of the $Fe(SCN)_2$ solution was added, the tube was shaken again and placed for exactly 5 min in a water bath at 50.0±0.5°C and subsequently for 10 min in a water bath at room temperature. The absorption at 510 nm was measured and compared with a blank containing no CHHP. The exact concentration was determined from a calibration curve. The determination was performed under a N_2 atmosphere; all solvents were made oxygen-free.

Gas-chromatographic determination of the CHOL and CHON concentration

1,1'-Bicyclohexyl (5.0 mm^3 of internal standard) was added to 10.0 cm^3 of a triphenylphosphine solution in ethanol (12 g.dm^{-3}). No 1,1'-bicyclohexyl was formed during the reaction. 10.0 mm^3 sample were added to 500 mm^3 of the thus prepared solution. The solution was shaken for a few seconds. Approximately 1 mm^3 of this solution was immediately analysed by GLC (temperature programme 115°C, 0 min 5°C/min., 160°C, 0 min). The measured CHOL concentration had to be corrected for the CHHP concentration in the sample. Reaction products were identified by comparison with authentic samples and GC/MS. The determination was carried out under a N_2 atmosphere; all solvents were made oxygen-free.

Results and discussion

Influence of pyridine

Many authors have mentioned the positive influence of axial ligands, such as imidazole and pyridine on reactions catalysed by manganese(III) porphyrins [1c-e,3p,10]. Therefore, we tested pyridine as axial ligand and investigated whether there is a correspondence between the role of pyridine in our system and the role of imidazole in the systems of *Mansuy* et al. [11] and *Legemaat* [1e]. The results are presented in Table I.

As can be seen in Table I, the decomposition rate of CHHP is enhanced, and the selectivity for CHON is increased by addition of pyridine. Because of this twofold positive influence of pyridine on the reaction, all subsequent experiments were carried out in the presence of pyridine. In Figure 1, the influence of the pyridine concentration on the decomposition rate of CHHP is presented. An increase in pyridine concentration led to an increase in reaction rate. The CHON/CHOL ratio, which had increased compared to the reaction without pyridine (Table I), did not increase further.

Table I Influence of pyridine on amount of decomposed peroxide and on selectivity [a].

	Without pyridine	With pyridine
CHHP decomposed/% [b]	50	97
CHOL formed/% [b]	24	41
CHON formed/% [c]	23	65
Selectivity (CHON/CHOL)	1.0	1.6

[a] Conditions: [CHHP] = 150 mmol·dm^{-3}, [Mn(TPP)Cl] = 0.1 mmol·dm^{-3}, [pyridine] = 10 mmol·dm^{-3} at 25°C in c-C_6H_{12}/CH_2Cl_2 (20:1) for 48 h. The results are expressed as percentage of the initial CHHP concentration. [b] Standard deviation 10%. [c] Standard deviation 2%.

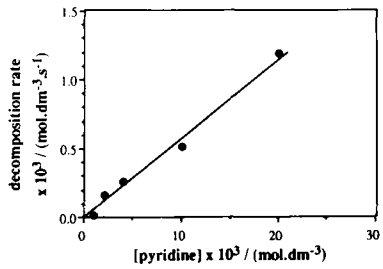

Figure 1. Influence of pyridine concentration on decomposition rate. Conditions: [CHHP] = 150 mmol·dm^{-3}, [Mn(TDCPP)Cl] = 0.02 mmol·dm^{-3} at 25°C in c-C_6H_{12}/CH_2Cl_2 (20:1).

In order to examine more closely the role of pyridine in our case, experiments with a sterically hindered pyridine, 2,6-di-tert-butylpyridine [12], were carried out. Because of steric hindrance, this pyridine derivative should not be able to coordinate to the metal. Addition of 2,6-di-tert-butylpyridine instead of pyridine changed neither the rate of decomposition nor the CHON/CHOL ratio with respect to the reaction without pyridine. Therefore, coordination of pyridine is essential for an increase in reaction rate. Fortunately, pyridine is not oxidized under our reaction conditions. Although under certain reaction conditions, pyridine is oxidized in the presence of oxygen donors and manganese porphyrins [1e,3s], it is not under the conditions used here.

In hydrogen peroxide/imidazole systems, imidazole acts as a ligand and as a base. To examine whether pyridine shows this behaviour, in addition to the common amount of pyridine, various amounts of 2,6-di-tert-butylpyridine were added. These additions led to an increase in reaction rate. The rate appeared to be approximately half order in 2,6-di-tert-butylpyridine. The results are presented in Figure 2. Thus, the role of pyridine in our system is the same as the role of imidazole in the hydrogen peroxide system, i.e., as axial ligand for the donation of electrons and as base. The only difference is that pyridine is stable in our system, whereas, in the hydrogen peroxide/imidazole system, destruction of imidazole has been observed [1e].

Reaction orders

In order to investigate the mechanism of the decomposition of cyclohexyl hydroperoxide (CHHP), the order of

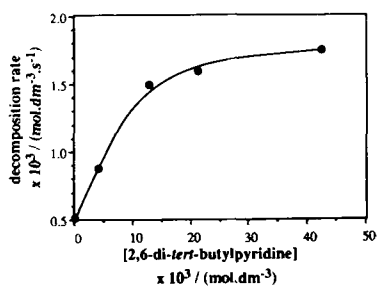

Figure 2. Influence of 2,6-di-tert-butylpyridine concentration on decomposition rate. Conditions: [CHHP] = 150 mmol·dm^{-3}, [Mn(TDCPP)Cl] = 0.02 mmol·dm^{-3}, [pyridine] = 10 mmol·dm^{-3} at 25°C in c-C_6H_{12}/CH_2Cl_2 (20:1).

Table II Initial decomposition rate of CHHP catalysed by various manganese porphyrins [a].

Catalyst	Catalyst concentration /mmol·dm^{-3}	Rate [b]
Mn(TPP)Cl	0.10	0.22 ± 0.02
Mn(TMP)Cl	0.10	0.53 ± 0.08
Mn(TDCPP)Cl	0.02	0.52 ± 0.04
Mn(TDCPP)Cl	0.10	2.62 ± 0.19
Mn(TPCPP)Cl	0.02	0.54 ± 0.04

[a] Conditions: [CHHP] = 150 mmol·dm^{-3}, [pyridine] = 10 mmol·dm^{-3} at 25°C in c-C_6H_{12}/CH_2Cl_2 (20:1). [b] Rate = initial decomposition rate × 10^3/mol.·dm^{-3}·s^{-1}.

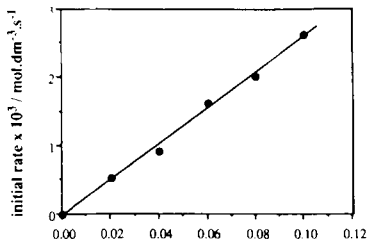

Figure 3. Influence of Mn(TDCPP)Cl concentration on decomposition rate. Conditions: [CHHP] = 150 mmol·dm^{-3}, [pyridine] = 10 mmol·dm^{-3} at 25°C in c-C_6H_{12}/CH_2Cl_2 (20:1).

reaction in the various reactants was determined. From experiments with various non-sterically hindered tetraarylporphyrins we could not determine whether the reaction was first or second order in peroxide. When only the initial period of the reaction was monitored, it was impossible to determine the order in peroxide. For sterically hindered porphyrins, however, the initial decomposition rate (up to 50% conversion) appeared to be first order in peroxide when low porphyrin concentrations (< 0.05 mmol·dm^{-3}, catalyst/peroxide < 3000) were used. The order in catalyst was determined for the sterically hindered Mn(TDCPP)Cl as well as for the non-sterically hindered Mn(TPP)Cl. In Figure 3, the initial first-order decomposition rate of cyclohexyl hydroperoxide is plotted versus the concentration of Mn(TDCPP)Cl. When the first-order decomposition rate for the Mn(TPP)Cl-catalysed reaction was plotted versus the catalyst concentration, a linear correlation was also found. In conclusion, the reaction initially is first order in catalyst and between first and second order in peroxide.

Influence of catalyst

In order to further investigate the reaction mechanism, the activities of two sterically hindered porphyrins, Mn(TDCPP)Cl and Mn(TPCPP)Cl, were determined. In Table II, these activities and, for comparison, also those of Mn(TMP)Cl and Mn(TPP)Cl, are summarized.
No significant difference exists between the reaction rates obtained with Mn(TDCPP)Cl and Mn(TPCPP)Cl as catalyst. Remarkably, a large difference in reaction rate was found between Mn(TDCPP)Cl and Mn(TMP)Cl. This may be due to electronic effects, although considering the formation of an oxomanganese complex is rate-determining, an opposite electronic effect would be expected. Such effects have sometimes been ascribed to a 'cage effect' [3s]. In the apolar solvent, cyclohexane, the eight chlorine atoms on the porphyrin may form a polar cage. The polar CHHP may have a preference for this cage over the solvent, leading to higher reaction rates. A similar but opposite effect was mentioned for methanol; methanol preferred the polar solvent above the apolar cage of MnO(TMP)Cl [3s].

Formation of CHON

CHON may be formed via two pathways: directly from CHHP or by oxidation of CHOL. To distinguish between these two pathways, 3,3,5,5-tetramethylcyclohexanol (molar ratio CHHP/alcohol 1.74) was added to the reaction mixture. No 3,3,5,5-tetramethylcyclohexanone was found at the end of the reaction, suggesting that the pathway to CHON via CHOL does not play a significant role. However, although unlikely, this result could be due to a steric effect. Therefore, the experiment was repeated with cyclohexanol-d_{12} (molar ratio CHHP/alcohol 1.00). After complete reaction, a negligible amount (2%) of the added cyclohexanol-d_{12} had been oxidized to cyclohexanone-d_{10}. Although, in the latter experiment, an isotope effect may play a role, both experiments strongly suggest that, under our conditions, CHOL is not appreciably oxidized to CHON.
A distinction between the direct formation of CHON and its formation by oxidation of the alcohol can also be made from a plot of the formation of CHON versus time. When the slope of this plot, when extrapolated to zero time, verges towards zero, formation of CHON is occurring via an intermediate. When the slope is clearly larger than zero, at least part of the CHON is formed directly from the peroxide. The latter effect is actually observed, providing another indication for the formation of CHON directly from the peroxide.
Formation of CHON directly in the coordination sphere of the porphyrin has earlier been proposed by *Haber* et al. [13] who found that, with [tetrakis(4-methylphenyl) porphyrinato]chromium(III) chloride and hydrogen peroxide, cyclohexane could be oxidized to CHOL and CHON, but that it was impossible to oxidize CHOL to CHON under the conditions applied.

Homolytic or heterolytic mechanism?

By testing the properties of the catalytic system, it should be possible to determine whether a homolytic or heterolytic mechanism plays a role. Irrespective of the mechanism of the scission, a high valent oxomanganese com-

Table III Stereoselectivity obtained in epoxidation of cis-stilbene with various systems based on metalloporphyrins.

Catalyst	Oxygen donor	Additive	cis-Stilbene oxide/%	trans-Stilbene oxide/%	Ref.
Fe(TPP)Cl	PhIO	-	mainly	traces	14
Fe(TPP)Cl	TBHP	-	traces	main product	14
Fe(TPP)Cl	TBHP	Im	50	50	14
Mn(TPP)Cl	NaOCl	4-MePy	92	8	3s
Mn(TDCPP)OH	H_2O_2	Im	90	10	1c
Mn(TDCPP)Cl [a]	CHHP	Py	80	20	

[a] Conditions: [CHHP] = 150 mmol·dm^{-3}, [Mn(TDCPP)Cl] = 0.02 mmol·dm^{-3}, [pyridine] = 10 mmol·dm^{-3} at 25°C in c-C_6H_{12}/CH_2Cl_2 (20:1).

plex will be involved. In addition, in both mechanisms, a compound is present which is capable of epoxidation. In the homolytic mechanism, this species is the peroxyl radical, whereas in the heterolytic mechanism it is the $[Mn^{V}(P)O]^{+}$ complex [14]. A method to distinguish between a homolytic and heterolytic mechanism applies cis-stilbene as substrate [14]. The pathway of hydroperoxide cleavage by manganese porphyrin should be reflected in the oxidation products generated from cis-stilbene. When the epoxidation is performed by peroxyl radicals, it will lead to the formation of the most stable epoxide, trans-stilbene oxide [15]. However, for sterically hindered porphyrins in the presence of an axial ligand, it is found that $[Mn^{V}(P)O]^{+}$ is the epoxidizing species and that cis-stilbene epoxide is formed almost exclusively [16]. Therefore, cis-stilbene was added to the reaction mixture. After chromatography over a Florisil column to remove the porphyrin, the ratio of cis- to trans-stilbene oxide was determined by ^{1}H NMR as 80:20. In Table III, a comparison between our results and those obtained by others is given. Although some trans-stilbene oxide was formed, we can conclude that, in our system, epoxidation is mainly performed by $[Mn^{V}(P)O]^{+}$. This is an indication that scission of CHHP is heterolytic. Sometimes, it is possible to distinguish between a non-radical and a radical mechanism by addition of a radical scavenger to the reaction mixture. Galvinoxyl was chosen as radical scavenger [17]. Addition of galvinoxyl (molar ratio CHHP/galvinoxyl 3.95) to the reaction mixture influenced neither the reaction rate nor the product distribution. Although from this experiment a definite conclusion can not be drawn, it does not contradict with a heterolytic mechanism.

Heterolytic scission

Assuming a heterolytic mechanism, the question arises: What are the details of this O–O bond scission? Various acid-, base- and non-catalysed mechanisms have been proposed [18]. We have determined the influence of acids and bases on the reaction. Addition of acetic acid (molar ratio CHHP/acetic-acid 0.90) to the reaction mixture caused an unexpected decrease in reaction rate. Acetic acid may protonate pyridine, leading to a decrease in Mn(P)Py concentration [19] or it may lead to a decrease in ROO^{-} concentration; vide infra. The effect of added base was then determined. We chose 2,6-di-tert-butylpyridine, which does not coordinate. As shown in Figure 2, addition of this sterically hindered pyridine increases the reaction rate. The first step in the mechanism is, therefore, proposed to be an equilibrium between ROOH and ROO^{-}.

Hydroxylation

From experiments with cyclopentane and cycloheptane instead of cyclohexane as solvent, it appeared that approximately 10% of CHHP is used for oxidation of the solvent to ketone and alcohol. For cyclopentane, 9% was found and, for cycloheptane, 13%. The ketone/alcohol ratio for hydroxylation of the solvent appeared to be 3. Hydroxylation will be performed by the $[Mn(P)O]^{+}$ complex.

Mechanistic proposal

From the experiments described earlier, it appears that addition of pyridine has a profound effect on the mechanism by which peroxide reacts with porphyrins. The role of pyridine is two-fold. It acts as a ligand to the metal and, thus, facilitates the formation of the $[Mn^{V}(P)O]^{+}$ complex. Secondly, it functions as a base. In this section, a mechanism will be presented for the decomposition of

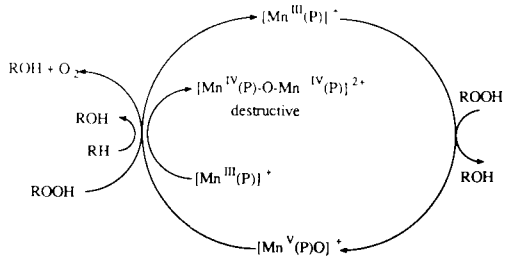

Figure 4. Decomposition of CHHP catalysed by manganese(III) porphyrins.

CHHP catalysed by a manganese porphyrin complex in the presence of pyridine.

The rate-determining step in this reaction is the formation of an oxidized manganese porphyrin complex. Two oxidized porphyrin complexes are possible: $[Mn^{V}(P)O]^{+}$ and $[Mn^{IV}(P)OH]^{+}$. When the scission of the peroxide is heterolytic, the former complex is formed; when the scission is homolytic, the latter one. On the basis of our experiments, we propose that the scission is heterolytic. We must, therefore, consider the species $[Mn^{V}(P)O]^{+}$. This species will undergo several reactions. First, it may react with a peroxide molecule with formation of CHOL and molecular oxygen. The formation of a large amount of molecular oxygen has been shown by mass spectrometry. Secondly, $[Mn^{V}(P)O]^{+}$ may hydroxylate a solvent molecule, cyclohexane, to form CHOL. In the case of a non-sterically hindered porphyrin $[Mn^{V}(P)O]^{+}$ may react with $[Mn(P)]^{+}$ under formation of a μ-oxo dimer, leading to destruction of the catalyst [3s]. These reactions are presented in Figure 4. Pyridine, which is present as a ligand to the metal, is not explicitly mentioned in this figure.

The scheme in Figure 4 does not account for the formation of CHON. CHON is formed via a direct route from CHHP. The peroxide may, in theory, react with either $[Mn^{III}(P)]^{+}$ or $[Mn^{V}(P)O]^{+}$ to form CHON. If CHON had been formed via reaction with $[Mn^{V}(P)O]^{+}$, for every mole of CHON at least one mole of CHOL should have been formed. Since the CHON/CHOL ratio is larger than one, the CHON must be formed by reaction between CHHP and $[Mn^{III}(P)]^{+}$.

Formation of $[Mn^{V}(P)O]^{+}$ is achieved by heterolytic scission of the peroxide bond. Furthermore, we have shown that this reaction is base-catalysed. Therefore, a mechanism, as presented in Figure 5, is suggested. First, there is an equilibrium between ROOH and ROO^{-}; the latter will be present in an ion pair with BH^{+}. The ROO^{-} will coordinate to the manganese porphyrin with formation of [Mn(P)OOR] in a second equilibrium. This complex decomposes in a rate-determining step, either by heterolytic cleavage of the peroxide bond into $[Mn^{V}(P)O]^{+}$ with formation of CHOL, or into $Mn^{III}(P)OH$ and CHON. Similar formation of ketone but via decomposition of an iron porphyrin, [Fe(P)OOR], has been mentioned by *Balch* et al. [20].

For the formation of $[Mn^{V}(P)O]^{+}$ from [Mn(P)OOR], a proton donor is required, because RO^{-} is a poor leaving group. Since the CHON/CHOL ratio is independent of the base concentration, protonated pyridine will not act as donor in this reaction. Probably, the peroxide acts as a proton donor. In that case, the CHON/CHOL ratio will be determined by the $k_4/k_3 \cdot [ROOH]$ ratio. In the beginning of the reaction, when the CHHP concentration is high, a relatively high percentage of CHOL will be formed, whereas in the course of the reaction, when the peroxide concentration decreases, the formation rate of CHON will increase. This prediction is in agreement with our observations.

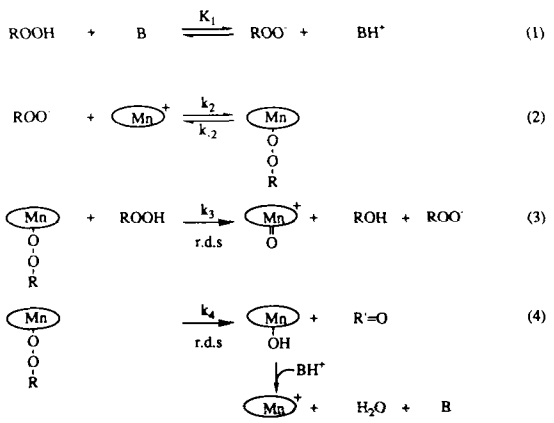

Figure 5. Heterolytic scission of peroxide catalysed by manganese(III) porphyrins.

From applying the steady-state approximation to the concentration of Mn(P)OOR, Eqn. 1 is derived.

$$\frac{d[Mn(P)OOR]}{dt} = 0, \text{ thus: } [Mn(P)OOR] = \frac{k_2 \cdot [ROO^-] \cdot [Mn(P)^+]}{k_{-2} + k_3 \cdot [ROOH] + k_4} \quad (1)$$

We now consider three extreme cases:

i. The second equilibrium is far to the left; then, $[ROO^-] \approx [BH^+]$ and steps 3 and 4 are rate-determining and

$$K_1 = \frac{[ROO^-]^2}{[ROOH] \cdot [B]}, \text{ thus: } [ROO^-] = \{K_1 \cdot [ROOH] \cdot [B]\}^{1/2}$$

$$v = (k_3 \cdot [ROOH] + k_4) \cdot [Mn(P)OOR] = \frac{(k_3 \cdot [ROOH] + k_4) \cdot k_2 \cdot [ROO^-] \cdot [Mn(P)^+]}{k_{-2} + k_3 \cdot [ROOH] + k_4} = \frac{(k_3 \cdot [ROOH] + k_4) \cdot k_2 \cdot K_1^{1/2} \cdot [ROOH]^{1/2} \cdot [B]^{1/2} \cdot [Mn(P)^+]}{k_{-2} + k_3 \cdot [ROOH] + k_4} \quad (2)$$

Since the reactions of Mn(P)OOR are rate-determining, $k_3 \cdot [ROOH] + k_4 \ll k_{-2}$,

$$v = (k_3 \cdot [ROOH] + k_4) \cdot K_2 \cdot K_1^{1/2} \cdot [ROOH]^{1/2} \cdot [B]^{1/2} \cdot [Mn(P)^+] \quad (3)$$

where $K_2 = k_2/k_{-2}$, which is consistent with the measured order in catalyst of one and which could also be consistent with the order in 2,6-di-tert-butyl pyridine of approximately a half (Figure 2).

ii. Again, the second equilibrium is far to the left, but now $k_{-2} \ll k_3 \cdot [ROOH] + k_4$, thus, the formation of Mn(P)OOR is rate-determining,

$$v = k_2 \cdot K_1^{1/2} \cdot [ROOH]^{1/2} \cdot [B]^{1/2} \cdot [Mn(P)^+] \quad (4)$$

This possibility is unlikely since the order in peroxide is at least one.

iii. The second equilibrium is far to the right and steps 3 and 4 are rate-determining, then, $[Mn(P)OOR] \approx [BH^+]$. When K_1 is introduced in Eqn. 1, the following equation is derived:

$$[Mn(P)OOR] = \frac{k_2 \cdot K_1 \cdot [ROOH] \cdot [Mn(P)^+] \cdot [B]}{[BH^+] \cdot (k_{-2} + k_3 \cdot [ROOH] + k_4)} \quad (5)$$

thus,

$$[Mn(P)OOR]^2 = \frac{k_2 \cdot K_1 \cdot [ROOH] \cdot [Mn(P)^+] \cdot [B]}{k_{-2} + k_3 \cdot [ROOH] + k_4}$$

This leads to the following rate equation:

$$v = (k_3 \cdot [ROOH] + k_4) \cdot \left\{ \frac{k_2 \cdot K_1 \cdot [ROOH] \cdot [Mn(P)^+] \cdot [B]}{k_{-2} + k_3 \cdot [ROOH] + k_4} \right\}^{1/2} \quad (6)$$

The reaction rate would be half order in manganese porphyrin, which clearly is not the case (Figure 3). Thus, *i*. applies with the third and fourth step being rate determining, as in Figure 5. The calculated rate v is the rate by which Mn(P)OOR is converted to products. The experimentally determined rate, $-d[ROOH]/dt$, is slightly higher, since part of $[Mn(P)O]^+$ reacts with the peroxide to $[Mn(P)]^+$, CHOL and oxygen. Therefore, the rate equation for the peroxide is equal to the equation for v except that instead of k_3 a somewhat higher constant should be used.

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[5] In this paper, the following abbreviations are used: CHHP = cyclohexyl hydroperoxide; CHOL = cyclohexanol; CHON = cyclohexanone; TDCPP = 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin dianion; TMP = 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrin dianion; TPCPP = 5,10,15,20-tetrakis(2,3,4,5,6-pentachlorophenyl)porphyrin dianion; TPP = 5,10,15,20-tetraphenylporphyrin dianion.

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