Decomposition of cyclohexyl hydroperoxide catalysed by ruthenium porphyrins. Hydroxylation of the solvent cyclohexane [1]

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Abstract

Ruthenium tetraarylporphyrins have been used as catalysts in the decomposition of cyclohexyl hydroperoxide. During this decomposition reaction the ruthenium tetraarylporphyrin/cyclohexyl hydroperoxide system is capable of hydroxylating the solvent, i.e. cyclohexane or cyclopentane. A proposal for the mechanism is presented. The hydroxylating capacity of various ruthenium complexes is discussed.

Keywords: Cyclohexyl hydroperoxide; Decomposition; Hydroxylation; Porphyrins; Ruthenium

1. Introduction

Oxidation of cyclohexane by molecular oxygen to give cyclohexanol (CHOL) and cyclohexanone (CHON) is an important industrial process. This reaction is used to produce approximately 10^6 tons of cyclohexanol annually [1]. An intermediate in this reaction is cyclohexyl hydroperoxide (CHHP). In an earlier study the mechanism of decomposition of CHHP catalysed by manganese porphyrins has been discussed [2]. A previous study [3] showed that also ruthenium porphyrins exhibit high catalytic activity in the desired reaction. Therefore, we studied the decomposition of CHHP catalysed by ruthenium porphyrins more closely.

An excellent review by Mlodnicka and James [4] on the application of ruthenium porphyrins as catalysts in oxidation reactions has recently appeared. The first experiment with oxygen donors such as *tert*-butyl hydroperoxide, only led to complete decomposition of the porphyrin moiety [5] or to formation of the dimer, $[Ru^{IV}(P)X]_2O$ [3] [6]. Here, a distinction has to be made between complexes of sterically hindered porphyrin dianions such as TMP, and those of non-sterically hindered ones such as OEP and TPP. Collman et al. [6](b) proposed a mechanism of the reaction of molecular oxygen with

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[3] Abbreviations: P = (substituted)porphyrin dianion, TPP = 5,10,15,20-tetraphenylporphyrin dianion, OEP = 2,3,7,8,12,13,17,18-octaethylporphyrin dianion, TMP = 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrin dianion, TMFPP = 5,10,15,20-tetrakis(2-fluorophenyl)porphyrin dianion, TDFPP = 5,10,15,20-tetrakis(2,6-difluorophenyl) porphyrin dianion, TMCPP = 5,10,15,20-tetrakis(2-chlorophenyl) porphyrin dianion, TDCPP = 5,10,15,20-tetrakis(2,6-dichlorophenyl) porphyrin dianion.

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[1] This work is part of the thesis by C.B. Hansen, Utrecht, 1991.

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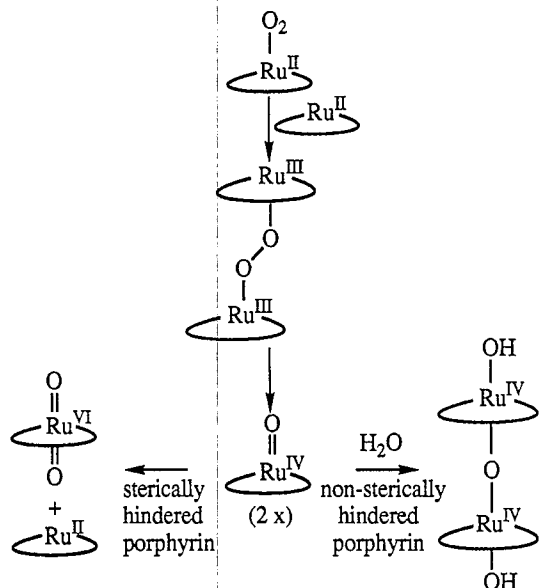
Scheme 1. Mechanism of the reaction between ruthenium(II) porphyrins and molecular oxygen proposed by Collman et al. [6](b).

ruthenium porphyrins, which is presented in Scheme 1.

After reaction of oxygen with a ruthenium(II) porphyrin, the dioxygen adduct formed reacts with a second ruthenium porphyrin molecule to form a μ-peroxo dimer. Homolytic cleavage of the O–O bond then leads to the formation of two oxoruthenium(IV) complexes. Depending on the steric properties of the porphyrin either a *trans*-dioxoruthenium(VI) complex or a μ-oxoruthenium(IV) dimer is formed. In addition to the steric properties of the porphyrin, the solvent also influences this choice; in alcoholic solvents it is possible to isolate *trans*-dioxo complexes of Ru(TPP) and Ru(OEP) [7].

Epoxidation of alkenes is possible with ruthenium(II) or with *trans*-dioxoruthenium(VI) porphyrins as catalysts [8–11]. Pyridine N-oxide [9] and molecular oxygen [8,10] have been used as oxygen donors. Groves et al. [10] proposed a mechanism for the epoxidation with molecular oxygen. According to this mechanism the Ru(II) in the complex is oxygenated to Ru(IV)O, which rapidly disproportionates to Ru(II) and Ru(VI)O$_2$. This dioxoruthenium complex is the epoxidizing agent.

On hydroxylation of alkanes catalysed by ruthenium porphyrins only a few reports could be found

in literature. James et al. used Ru^{III}(OEP)(PPh$_3$)Br in combination with iodosylbenzene for the hydroxylation of cyclohexane [12]. After 15 h, they found a total yield of CHOL, CHON and cyclohexyl bromide of 3.5% based on iodosylbenzene. They suggested the active oxidizing species, characterized by an ESR signal at $g = 2.00$, to be O=Ru^{IV}(OEP$^{+\cdot}$)Br and proposed that it is acting via free-radical reactions. After the reaction, an inactive green complex was isolated which was believed to be an O=Ru(OEP) species.

Hydroxylation of cyclohexane with N-methylimidazole complexes of Ru(OEP)(CO) and of Ru(TDFPP)(CO), applying *tert*-butyl hydroperoxide and sodium hypochlorite as oxygen donors, has been reported [13]. With *tert*-butyl hydroperoxide the CHON/CHOL ratio obtained with both porphyrins is similar. With the hypochlorite system only traces of hydroxylation products were detected.

Furthermore, hydroxylation of adamantane, methylcyclohexane and ethylbenzene was observed by Hirobe et al. [14] using ruthenium porphyrins in combination with 2,6-dichloropyridine N-oxide and an acid such as HCl or HBr. The presence of the acid was necessary to obtain hydroxylation of the alkanes.

2. Results

2.1. Activity of the catalysts

Currently, insertion of ruthenium into porphyrins is carried out by the carbonyl method applying RuCl$_3$ [6,13,15], Ru$_3$(CO)$_{12}$ [5,7,16–20] or [RuCl$_2$(CO)$_3$]$_2$ [5] as ruthenium source. We applied Ru$_3$(CO)$_{12}$ as metal source, since the use of RuCl$_3$ or [RuCl$_2$(CO)$_3$]$_2$ has two disadvantages: (i) large quantities of carbon monoxide gas are required; (ii) chloride impurities can easily be formed [5]. Moreover, Ru$_3$(CO)$_{12}$ is less expensive than [RuCl$_2$(CO)$_3$]$_2$. Very recently, Tavares et al. [21] published a high yield preparation of
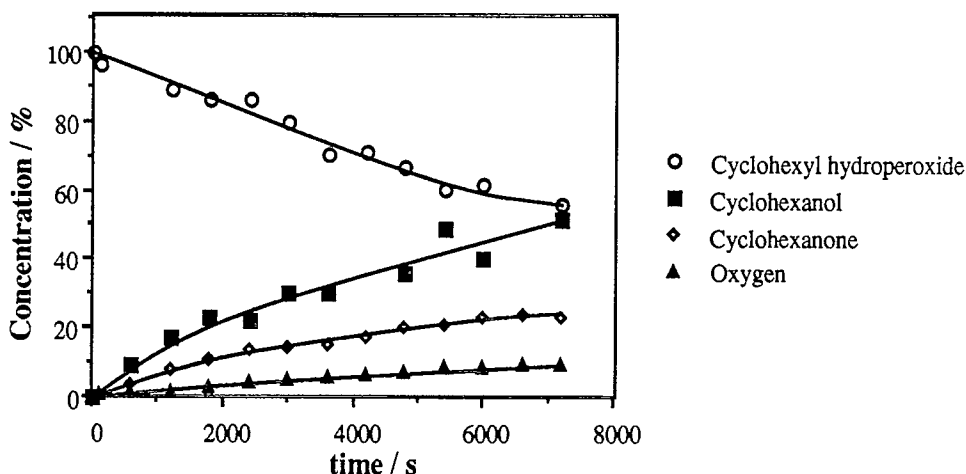
Fig. 1. Concentrations of CHHP, CHOL, CHON and oxygen expressed as mole percentage of the initial hydroperoxide concentration (150 mmol·dm^{-3}) plotted versus time for the Ru(TDCPP)(CO) (0.1 mmol·dm^{-3}) catalysed reaction.

Ru(TMP)CO by metallation of H$_2$TMP using Ru$_3$(CO)$_{12}$.

Several ruthenium porphyrins were synthesized and tested as catalysts in the decomposition of CHHP, viz. the sterically hindered Ru(TMCPP)(CO), Ru(TMP)'(CO) and Ru(TDCPP)(CO) and the non-sterically hindered Ru(TPP)(CO). The reactions were performed in cyclohexane as solvent at 25°C. In contrast to the experiments performed with manganese porphyrins described in Ref. [2], the reactions where performed without pyridine for the following reasons. (1) Addition of pyridine led to a decrease of the reaction rate and (2) the CHON/CHOL ratio remained the same. Probably, pyridine competes with the peroxide for coordination to the ruthenium.

The results obtained with Ru(TPP)(CO) were significantly different from those obtained with the sterically hindered ruthenium porphyrins. Applying Ru(TPP)(CO), an appreciably lower reaction rate was observed; the order in peroxide could not precisely be determined; it was approximately zero in the beginning of the reaction. The CHON/CHOL ratios, however, were similar for all porphyrins.

The concentrations of CHHP, CHON and CHOL in the Ru(TDCPP)(CO)-catalysed reaction are presented in Fig. 1 as a function of time. For the other sterically hindered catalysts,

Ru(TMP)(CO) and Ru(TMCPP)(CO) the same behaviour, the same CHON/CHOL ratio and essentially the same reaction rate were observed.

During the initial 40% conversion of the peroxide, its decomposition rate follows zero order behaviour as appears from the data in Fig. 1 and from data obtained in similar experiments with Ru(TMP)(CO) and Ru(TMCPP)(CO). Remarkably, although the concentration of ruthenium porphyrins decreases, the decomposition rate of the peroxide does not change dramatically. The order in catalyst was determined by plotting the decomposition rate versus catalyst concentration (Fig. 2). Since a linear correlation is obtained with a positive slope, it can be concluded that the decomposition of the peroxide is first order in catalyst.

2.2. Stability of the catalysts

For all ruthenium porphyrins, within 3 min after the addition of CHHP, the colour of the solution changed from orange to brown. This behaviour indicates a change in valence of the ruthenium. To collect more quantitative data, the catalyst solutions were monitored by UV/Vis spectroscopy.

Again, the catalysts could be divided into non-sterically hindered and sterically hindered ones. For Ru(TPP)(CO) the Soret band at 413 nm had
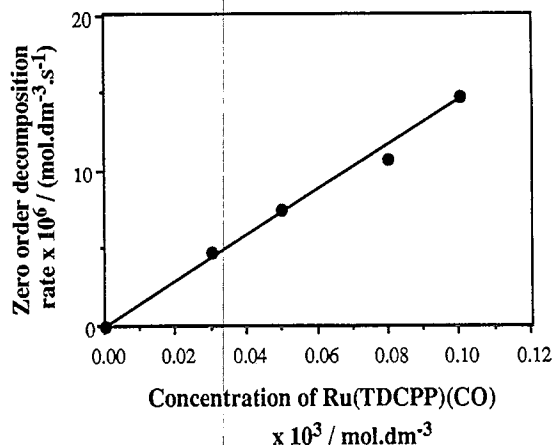
Fig. 2. Zero order decomposition rate of hydroperoxide versus concentration of Ru(TDCPP)(CO).

almost completely disappeared after 7 min, while a weak absorption at 395 nm was observed. This latter absorption is due to a μ-oxo-dimer [6]. The

extinction coefficient of this dimer has approximately the same value as that of the monomer [6](a). Thus, Ru(TPP)(CO) has almost completely disappeared and only a small percentage of it has been converted to the μ-oxo-dimer. Therefore, it may be concluded that almost all porphyrin had been destroyed.

For sterically hindered ruthenium porphyrins, such as Ru(TDCPP)(CO), within 3 min, formation of a new porphyrin complex was observed by UV/Vis spectroscopy through a red shift of the Soret band from 408 to 418 nm. Besides, the α-band had shifted from 528 nm to 515 nm. The change in the Soret band is presented in Fig. 3a. The newly formed porphyrin probably is the *trans*-dioxoruthenium(VI) porphyrin, which is obtained when sterically hindered ruthenium por-
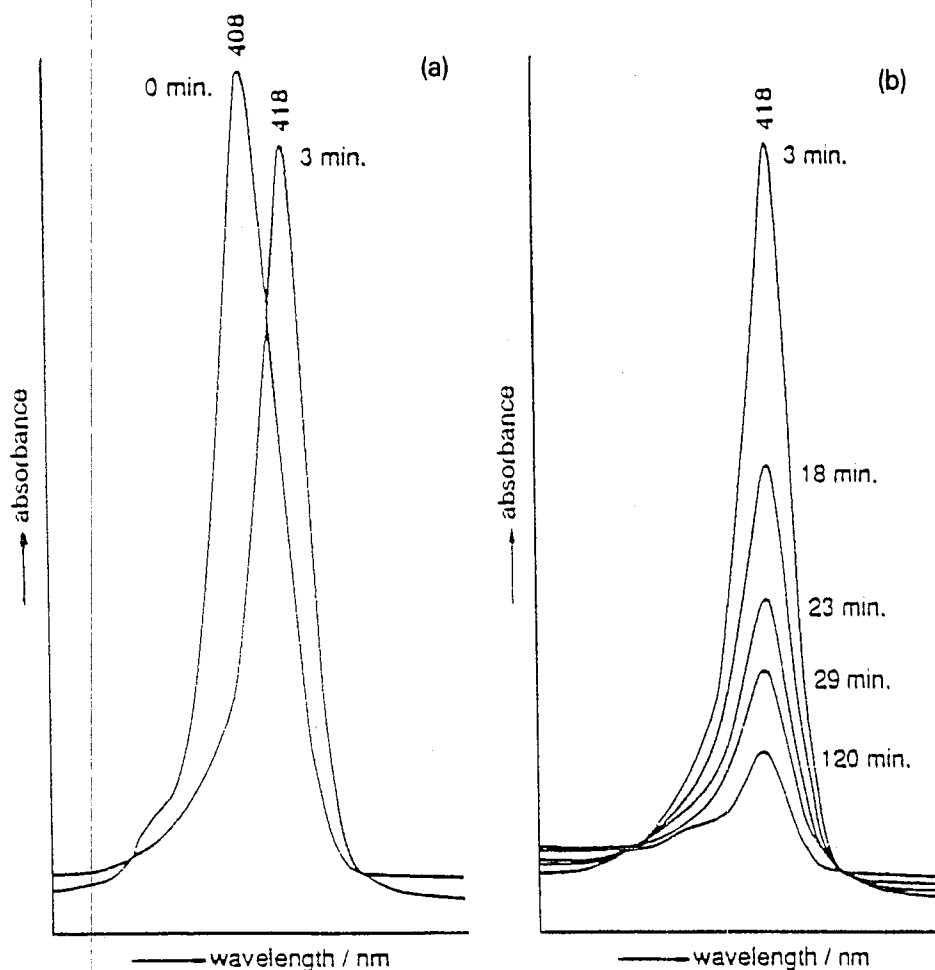

Fig. 3. Change of the Soret band in a solution of Ru(TDCPP)(CO) in cyclohexane after addition of CHHP as a function of time.

phyrins are treated with 3-chloroperoxybenzoic acid [11]. Similar results were obtained for Ru(TMP)(CO), although its conversion was completed more rapidly, viz. within 1 min.

During the reaction the intensity of the new absorption at 418 nm decreased with a rate second order in porphyrin indicating a dimerization process (Fig. 3b). Probably, dimerization of the porphyrin was followed by its destruction. The same behaviour was observed for the other ruthenium porphyrins, although the rates of destruction were different. An increase in stability was found in the sequence: TPP < TMCPP < TMP < TDCPP complex.

Attribution of the UV/Vis data to the *trans*-dioxoruthenium(VI) porphyrin was verified by separate synthesis of this complex. This synthesis was performed by titration of a dichloromethane solution of Ru(TDCPP)(CO) with a solution of 3-chloroperoxybenzoic acid as has been described by Groves et al. [11]. Approximately 2 moles of oxidant were required to obtain 1 mole of Ru(TDCPP)O_2. The isosbestic points at 380, 414, and 429 nm indicate that the conversion to Ru(TDCPP)O_2 occurs without a detectable intermediate. The UV/Vis spectral data of this synthesized complex were in agreement with those found during reaction. This observation leads to the conclusion that during reaction a sterically hindered ruthenium(II) porphyrin is rapidly converted into its *trans*-dioxoruthenium(VI) derivative.

When the reciprocal of the concentration of ruthenium porphyrin, determined from Fig. 3b, is plotted versus time, Fig. 4 is obtained. From this figure, it can be concluded that, even when a correction is applied for the slight difference in extinction coefficient between Ru(P)(CO) and Ru(P)O_2, during the reaction the porphyrin concentration decreases rapidly with approximately second order kinetics and a rate constant of 79 ± 3 $dm^3 \cdot mol^{-1} \cdot s^{-1}$. Similar observations were reported by Groves et al. [11] who found only about 50% of the initially added porphyrin in the reaction mixture during the epoxidation of cyclooctene with molecular oxygen. Apparently, a new ruthenium compound is formed.

Further investigation of the catalyst was performed by IR spectroscopy. Ruthenium porphyrins show a strong absorption at 1000–1020 cm^{-1}. This absorption is called the oxidation state marker since the exact position depends on the valence of the ruthenium. For ruthenium complexes with TMP the state marker was found at 1003 cm^{-1} for ruthenium(II), at 1011 cm^{-1} for oxoruthenium(IV) and at 1019 cm^{-1} for *trans*-dioxoruthenium(VI) [22]. Similar behaviour was observed for the OEP and the TPP complexes by Che et al. [7].

Our IR experiments were carried out with Ru(TDCPP)(CO) which shows the state marker at 1008 and the carbonyl absorption at 1948 cm^{-1}. To a solution of Ru(TDCPP)(CO) in dichloromethane was added a large excess of pure CHHP (molar ratio Ru(TDCPP)(CO) to CHHP 1:30). Immediately after this addition, all absorptions of Ru(TDCPP)(CO) disappeared. In addition to the weak absorptions of CHOL and CHON, two new absorptions arose at 1019 and 825 cm^{-1}. These wavenumbers are equal to those observed for separately synthesized Ru(TDCPP)O_2.

From the UV/Vis and IR experiments it can be concluded that during the decomposition reaction sterically hindered ruthenium(II) porphyrins are rapidly converted into *trans*-dioxoruthenium(VI) porphyrins. Moreover, during the decomposition reaction of the hydroperoxide the ruthenium porphyrin complex is gradually destroyed.

2.3. trans-Dioxoruthenium porphyrin as catalyst

Since from the above mentioned experiments it was concluded that Ru(TDCPP)O_2 is an intermediate in the catalytic cycle, synthesized Ru(TDCPP)O_2 was used as catalyst in the decomposition of CHHP in cyclohexane as solvent. From these experiments it appeared that the initial decomposition rate of the peroxide amounted to approximately 75% of the rate obtained with the carbonyl complex. Thus, although at the beginning of the reaction a somewhat smaller amount of hydroperoxide was decomposed, this differ-
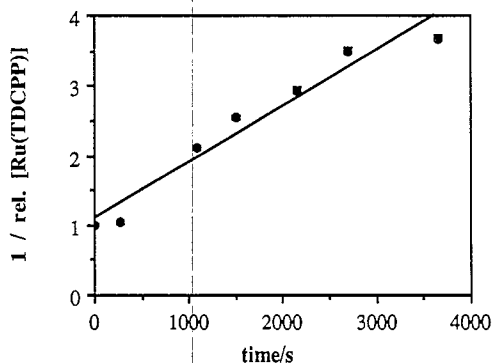
Fig. 4. Reciprocal concentration of Ru(TDCPP) plotted versus time.

ence between Ru(TDCPP)O_2 and Ru(TDCPP)(CO) catalysed reactions diminished after 2 h: no difference in concentration of peroxide, CHON and CHOL could be determined anymore. These results support the suggestion that the dioxo complex is present in the catalytic cycle. An explanation of the lower initial catalytic activity of the dioxo complex will be given in the discussion of the mechanism.

Are radicals involved?

In order to answer the question whether radicals are involved in the decomposition of the peroxide, a radical scavenger, galvinoxyl, (galvinoxyl:CHHP:catalyst = 380:1500:1) was added to the reaction mixture in cyclohexane. This addition caused the decomposition rate of the peroxide to decrease; the initial rate being 54% of the rate found without the addition of radical scavenger. For the formation of CHOL an induction period of approximately 50 min was observed. The amount of CHON formed during the first 2 h of reaction appeared to be too small to determine whether an induction period was involved. Probably, reaction intermediates, such as alkoxyl and/or peroxyl radicals, had been captured by the scavenger.

After longer periods, 2 and 48 h, the amounts of decomposed peroxide were similar with and without scavenger, but only 30 and 39%, respectively, of the ketone were formed, and 45 and 87%, respectively, of the alcohol. Thus, radicals seem to play a role in the decomposition reaction of the peroxide as well as in the formation of CHOL and CHON.

For a further investigation of the role of radicals in the reaction mixture ESR spectroscopy was applied. To a solution of Ru(TMP)(CO) in dichloromethane pure CHHP was added (CHHP:porphyrin = 1700:1). The initial solution of Ru(TMP)(CO) did not show ESR signals. After approximately 3 min a signal at $g = 2.0023$ appeared. The intensity of this signal increased for approximately 15 min; then the signal slowly disappeared. After 20 min a new signal arose at $g = 2.24$. This signal persisted during the remainder of the reaction. Neither signal showed a coupling pattern.

In the literature it is known that a ruthenium(II) porphyrin radical cation shows an ESR signal at $g = 2.00$ [23] and that an oxoruthenium(IV) porphyrin radical cation shows a strong ESR signal also at $g = 2.00$ [12](b). Ruthenium(III) porphyrin radical cations show a sharp ESR signal at $g = 2.008$, but this signal is accompanied by a broad signal at $g = 2.35$ [24]. Assuming a similarity in behaviour between ruthenium(III) octaethylporphyrin and Ru^{III}TMP, a ruthenium(III) species is excluded [24]. Therefore, the signal at $g = 2.0023$ may be attributed to a ruthenium(II) or (IV) radical cation. The absence of an absorbance of these species in the UV/Vis spectrum may be due to a low concentration or to their low extinction coefficients (approximately 30% of the coefficient of a non-radical ruthenium porphyrin). The signal at $g = 2.24$ probably belongs to an inorganic ruthenium complex since, to the best of our knowledge, no ruthenium porphyrin complexes are known that give a signal at $g = 2.24$.

2.4. Formation of CHON

In the manganese porphyrin-catalysed system CHON was formed directly from the peroxide and not by oxidation of CHOL [2]. The question can be raised of which route was followed in the formation of CHON in the ruthenium system. To answer this question experiments similar to those described for the manganese system were performed. At the beginning of the reaction 3,3,5,5-tetramethylcyclohexanol was added (CHHP :

alcohol = 1 : 1). Only after 40 min reaction time was the formation of 3,3,5,5-tetramethylcyclohexanone observed. After 48 h approximately 10% of the added alcohol was converted to the ketone. The formation of ketone from the alcohol at longer reaction times was confirmed by an experiment with cyclohexanol-d_{12} (CHHP : alcohol = 1 : 1) added initially. After 48 h only 12% of the formed ketone consisted of cyclohexanone-d_{10}. Apparently, in the beginning of the reaction alcohol is not oxidized to ketone.

Another indication for the direct formation of CHON in the beginning of the reaction is derived from a plot of the concentration of CHON versus time; see Fig. 1. The slope of the curve, when extrapolated to zero time, does not converge towards zero, thus indicating that at least part of the CHON is formed directly from the peroxide.

From these experiments it can be concluded that during the first 40 min of the reaction almost all CHON is formed directly from the peroxide. Furthermore, thereafter, a complex capable of oxidizing CHOL is present in the reaction mixture.

2.5. Hydroxylation

When the decomposition of CHHP catalysed by Ru(TMP)(CO) is performed in cycloheptane as solvent instead of cyclohexane, oxidation of the solvent yields 16% of cycloheptanol and 30% of cycloheptanone after 48 h. Both percentages are based on the initial amount of peroxide. Similar results were obtained when the reaction was performed in cyclopentane.

When various amounts of galvinoxyl were added to the reaction mixture (galvinoxyl : CHHP : catalyst = 380 : 1500 : 1 and 1500 : 1500 : 1) after 48 h approximately the same amount of cyclopentanone was formed, but the amount of cyclopentanol appeared to be only 45 and 20%, respectively, of the commonly formed amount of cyclopentanol. Thus, radicals seem to play a role in the hydroxylation.

When the hydroxylation of the solvent was monitored, an induction period of approximately 20 min was observed. By UV/Vis spectroscopy it was concluded that the catalyst is destroyed during reaction and that after 30 min no more than 25% of a porphyrin catalyst is present. Although the catalyst is destroyed no decrease in decomposition rate of the peroxide is observed. These data may suggest that the hydroxylating agent is not a porphyrin complex. This suggestion was supported by the following observation. When, after 24 or 48 h, the catalyst was separated from the reaction mixture and examined with ^{1}H NMR spectroscopy, no signals of phenyl or pyrrole protons could be found. Since after 24 h the reaction was still going on, apparently a non-porphyrinic ruthenium complex was the active catalyst. Our experiments suggest that in the reports on hydroxylation mentioned in the introduction [12–14], ruthenium porphyrins might not be involved. In none of these reports has a convincing characterization of the active complex been given.

In order to obtain information about the hydroxylating agent several ruthenium complexes were tested in the decomposition of CHHP. The results are presented in Table 1. From this table it may be concluded that only for the ruthenium complexes having ruthenium with a valence of two or three, results were obtained similar to those for the porphyrin complexes. Moreover, the ligand of the ruthenium has to be easily exchangeable. Therefore, the active hydroxylating catalyst may be a ruthenium(II) or (III) complex with easily exchangeable ligands.

In order to obtain further information on the hydroxylating agent, a solution of Ru(TMP)(CO) was added to a solution of CHHP (molar ratio of Ru(TMP)(CO) to CHHP, 1500 : 1) and after 24 or 48 h, all volatile compounds were removed from the reaction mixture, leaving a brownish/black oil. The obtained oil was submitted to several analyses. With ^{1}H NMR only signals belonging to CHHP could be found. The signals of the peroxy hydrogen and of the α-hydrogen were shifted upfield from 8.6 to 4.9 ppm and from 3.9 to 3.6 ppm, respectively. These shifts will be due to coordination of the hydroperoxide to ruthenium. The presence of the ruthenium was confirmed by neutron activation analysis. Fur-

Table 1
Decomposition of CHHP in cyclohexane catalysed by several ruthenium complexes after a reaction time of 48 h expressed in molar percentages

Catalyst	CHHP decomposed/%	CHON formed/%	CHOL formed/%	Hydroxylation/% [a]
$Ru_3(CO)_{12}$ [b]	12	2	9	0
$RuCl_3$ [b]	0	0	0	0
Ru^{IV} on Al_2O_3	16	12	3	0
Ru^{IV} on SiO_2	0	0	0	0
$RuO_2 \cdot xH_2O$	0	0	0	0
Ru red [c]	0	0	0	0
$RuCl_2 \cdot 4DMSO$	82	32	77	33
$Ru(acac)_3$	87	37	64	17
$Ru(TPP)(CO)$	89	32	54	0
$Ru(TMCPP)(CO)$	97	47	79	30
$Ru(TDCPP)(CO)$	89	51	81	48
$Ru(TMP)(CO)$	92	53	79	43

[a] Hydroxylation = {(CHOL formed + CHON formed − CHHP decomposed)/CHHP decomposed} × 100%.
[b] After a reaction time of 2 h.
[c] Ru red = $[(NH_3)_5RuORu(NH_3)_4ORu(NH_3)_5]Cl_6 \cdot 4H_2O$.

thermore, this oil was examined by UV/Vis spectroscopy, but no absorption maxima were present from 300 to 800 nm. Other analytical methods such as ESR, FAB/MS, TGA/MS and IR spectroscopy gave no indication about the origin of this ruthenium compound.

Also, the catalytic activity of the isolated oil was tested. The yield of hydroxylation product was in the same range as obtained in the porphyrin experiments, except for the cyclopentanone/cyclopentanol ratio which was 0.9 instead of 1.9.
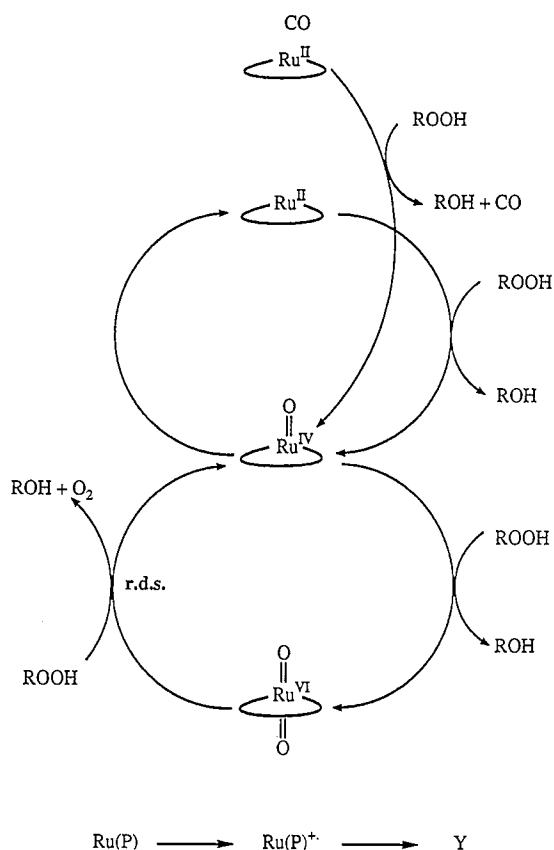
3. Discussion

Compared to the reaction of manganese porphyrins (Ref. [2]), for the reaction between ruthenium tetraarylporphyrins and CHHP a completely different reaction mechanism has to be proposed. Reasons for this difference are (i) addition of pyridine decreases, instead of increases, the reaction rate and (ii) a dioxo compound, instead of a monooxo compound, plays a dominant role.

At first sight our results are in agreement with a mechanism resembling that proposed by Collman et al. [6](b) as presented in Scheme 1. Also in our reaction, for non-sterically hindered porphyrins the formation of a μ-oxo-dimer and for sterically hindered porphyrins the formation of a *trans*-dioxoruthenium(VI) porphyrin has been observed. When this mechanism of Collman et al. [6](b) is compared with that proposed by Groves et al. [10] for the epoxidation of alkenes with molecular oxygen and a sterically hindered *trans*-dioxoruthenium(VI) porphyrin, it is found that these mechanisms are based on the same principle, viz. oxidation of a ruthenium(II) porphyrin complex via an oxoruthenium(IV) species to a *trans*-dioxoruthenium(VI) porphyrin complex. Since formation of the latter complex has undoubtedly been found in our reaction, the mechanism presented in Scheme 2 is proposed for the reaction between CHHP and ruthenium(II) porphyrins.

The first step in this mechanism will be the simultaneous oxidation of the ruthenium(II) porphyrin complex and ejection of the carbonyl ligand, as has been shown by IR spectroscopy. Since the gas formed has not been analyzed, the ejection of CO as CO_2 instead of as CO cannot be excluded. CHHP will oxidize the ruthenium(II) porphyrin complex to oxoruthenium(IV) porphyrin under formation of CHOL. Groves et al. proposed that this oxoruthenium(IV) porphyrin rapidly disproportionates into a *trans*-dioxoruthenium(VI) porphyrin and a ruthenium(II) porphyrin, since the oxidation of Ru(TMP)(CO) with iodosylbenzene or peroxy acids afforded the

Scheme 2. Mechanism proposed for the formation of CHOL from the reaction between CHHP and ruthenium(II) tetraarylporphyrins.

During the first period of the reaction the *trans*-dioxoruthenium(VI) porphyrin is clearly present. Therefore, reduction of this complex will be the rate determining step in this catalytic cycle. From the experiment with 3,3,5,5-tetramethylcyclohexanol it appeared that *trans*-dioxoruthenium(VI) porphyrin does not react with CHOL under formation of CHON. Also reaction with cyclohexane has to be ruled out since hydroxylation of the similar compound cyclopentane started only after approximately twenty minutes, whereas the *trans*-dioxoruthenium(VI) porphyrin is almost immediately present in the reaction mixture. Thus, the *trans*-dioxoruthenium(VI) complex has to react with another peroxide molecule under formation of molecular oxygen and CHOL. The formation of molecular oxygen was indeed observed; see Fig. 1. The oxoruthenium(IV) complex may subsequently be either oxidized or reduced. Actually, since the catalyst is present as a *trans*-dioxoruthenium(VI) complex the oxoruthenium(IV) porphyrin will mainly be oxidized by CHHP. Thus, the ruthenium porphyrin catalytic cycle will be a ruthenium(IV) ruthenium(VI) one.

Unfortunately, the porphyrin-catalysed decomposition of the peroxide will not be the only mechanism playing an important role in the reaction under investigation. There are three major observations which are not accounted for in the mechanism presented in Scheme 2. The first is the disappearance of at least 30% of the porphyrin in the beginning of the reaction. The second is the observed hydroxylation of the solvent and the last is the direct formation of ketone from peroxide.

Although it is possible to convert a ruthenium(II) porphyrin into its dioxo complex in 100% yield by titration with two equivalents of 3-chloroperoxybenzoic acid in dichloromethane, in our catalytic experiments at least 30% of the porphyrin had disappeared before conversion into the dioxo complex. The same phenomenon has been observed by Groves et al. [10]. An, as yet unknown ruthenium complex, X, is formed. Thus, after oxidation of the ruthenium(II) carbonyl compound, two ruthenium complexes are present,

Ru(P) ——→ Ru(P)⁺· ——→ Y

trans-dioxoruthenium(VI) porphyrin without observable intermediates [10]. Indeed, with two equivalents of 3-chloroperoxybenzoic acid or 20 equiv. of CHHP, this conversion is possible without visible intermediates and with clear isosbestic points. In contrast to Groves et al. we propose that the oxoruthenium(IV) porphyrin does not disproportionate under our conditions, but that it is rapidly oxidized by a second molecule of peroxide to the *trans*-dioxoruthenium(VI) porphyrin. As ruthenium(IV) complexes were not detected by UV/Vis, IR or ^{1}H NMR spectroscopy, the concentration of oxoruthenium(IV) porphyrin will be extremely low. Thus, disproportionation, which would require reaction between two molecules of oxoruthenium(IV) porphyrin, is highly unlikely. Since the reaction of Ru-dioxo with CHOL or cyclohexane is excluded, its reaction with ROOH is conceivable. This reaction, moreover, is supported by the formation of molecular oxygen and CHOL.

viz. *trans*-dioxoruthenium(VI) porphyrin and X. The question can be asked whether X is catalytically active in the decomposition of the hydroperoxide. We believe it is, because *trans*-dioxoruthenium(VI) porphyrin by itself has an initial activity that amounts to 75% of that of the mixture of *trans*-dioxoruthenium(VI) porphyrin and X.

In the course of the reaction the concentration of *trans*-dioxoruthenium(VI) porphyrin decreases. This compound is slowly converted into an inorganic ruthenium compound, Y. During this conversion the rate of decomposition of the hydroperoxide does not change appreciably. Thus, compound Y has to have catalytic activity.

A major question is: what is the structure of Y and along which route is it formed? We have a few indications that its formation probably proceeds via a radical cationic porphyrin complex. In the first place, the decomposition rate of the peroxide is reduced when a radical scavenger is added. The second indication is the ESR signal at $g = 2.0023$ which can be ascribed to a ruthenium radical cation compound. The intensity of this signal is highest during the period in which the porphyrin is destroyed. The third indication is that the destruction of the porphyrin is almost negligible when the reaction is performed in dichloromethane instead of cyclohexane. The destruction rate constant of the porphyrin in dichloromethane is 0.250 ± 0.012 mol$^{-1} \cdot$ dm$^3 \cdot$ s^{-1}, whereas in the reaction mixture this rate constant is 79 ± 3 mol$^{-1} \cdot$ dm$^3 \cdot$ s^{-1} [25]. The explanation could be that dichloromethane has slight radical trapping character. Unfortunately, the influence of the radical scavenger, galvinoxyl, on the destruction of the porphyrin could not be examined by UV/Vis spectroscopy, because of the intense colour of galvinoxyl. Finally, for phthalocyanines destruction via radical cations has already been proposed [26]. Thus, it may well be that X is a ruthenium(II) or an oxoruthenium(IV) radical cation, that gradually disintegrates to one or more inorganic compound(s), called Y:

$$Ru(P) \rightleftharpoons Ru(P)^{+\cdot} \rightarrow Y$$

Another route for the destruction of ruthenium porphyrins has been proposed by James et al. [27]. They found that when Ru(OEP)(PPh$_3$)$_2$ was reacted with molecular oxygen the black solid RuO$_2$ and the metal free porphyrin were formed. This destruction was suggested to occur via formation of a μ-oxo-dimer under the influence of traces of water. Since in our system the presence of neither metal free porphyrin nor RuO$_2$ could be demonstrated, this destruction mechanism does not play a significant role in our reaction. Besides, our destruction products, X and Y, are catalytically active, whereas RuO$_2$ is not.

Theoretically the active catalyst may also be an impurity in the ruthenium porphyrin. This is unlikely, since the purity of porphyrins was accurately examined and the most likely ruthenium impurity, Ru$_3$(CO)$_{12}$, showed almost no catalytic activity.

An induction period was observed for the hydroxylation reaction. This observation suggests compound Y to be capable of hydroxylation. From our results, it may tentatively be concluded that this ruthenium complex will be a mononuclear ruthenium complex with easily exchangeable ligands.

As already has been mentioned, in the beginning of the reaction CHON is formed directly from peroxide. It was suggested that radical species play a role in the formation of the ketone. This radical may be an alkoxyl radical, formed by homolytic cleavage of a peroxide molecule by the porphyrin.

4. Experimental

The instrumentation, materials, decomposition reactions and analytical procedures have been described elsewhere [2,3,25,28]. Ru red, RuO$_2 \cdot x$H$_2$O and Ru(acetylacetonate)$_3$ were obtained from Strem. RuCl$_2 \cdot$4DMSO was a gift of J.M. Valk (Utrecht University) and Ru^{IV} on Al$_2$O$_3$ or SiO$_2$ were a gift of T. Koerts (Technical University of Eindhoven).

4.1. (5,10,15,20-Tetraphenylporphyrinato)(carbonyl)ruthenium(II), Ru(TPP)(CO)

This compound was prepared in 83% yield according to the procedure described by Rillema et al. [29] by reaction of $H_2(TPP)$ with $Ru_3(CO)_{12}$. ^{1}H NMR ($CDCl_3$, δ/ppm): 8.6 (s, 8H, β-pyrrole), 7.2 (s, 20H, phenyl). UV/Vis (CH_2Cl_2, λ/nm (log (ϵ/dm^3·mol^{-1}·cm^{-1}))): 413 (5.30), 532 (4.20), 565 (3.53). IR (KBr, $\tilde{\nu}$/cm^{-1}): 1944 (s, CO), 1009 (s, Ru^{II}N$_4$). The UV/Vis wavelengths are identical to those published by Rillema et al. [29]. The CO wavenumber is listed in Ref. [29] as 1922 cm^{-1}, in Ref. [30] as 1930 cm^{-1} and in Ref. [30] as 1945 cm^{-1} after oxidation.

4.2. (5,10,15,20-Tetrakis(2,4,6-trimethylphenyl)porphyrinato)(carbonyl)ruthenium(II), Ru(TMP)(CO)

This compound was prepared in 82% yield by a method analogous to the method used by Rillema et al. [29]. ^{1}H NMR ($CDCl_3$, δ/ppm): 8.49 (s, 8H, β-pyrrole), 7.26 (s, 8H, 3,5-phenyl), 2.61 (s, 12H, 4-methyl), 1.93 (s, 24H, 2,6-methyl). UV/Vis (CH_2Cl_2, λ/nm (log (ϵ/dm^3·mol^{-1}·cm^{-1}))): 412 (5.28), 529 (4.27). IR (KBr, $\tilde{\nu}$/cm^{-1}): 1942 (s, CO), 1010 (s, Ru^{II}N$_4$). FAB/MS (m/z): 910 (M$^{+\cdot}$), 882 (M$-$CO$^{+\cdot}$).

4.3. (5,10,15,20-Tetrakis(2-chlorophenyl)porphyrinato)(carbonyl)ruthenium(II), Ru(TMCPP)(CO)

This compound was also prepared by a method analogous to the method described by Rillema et al. [29]. The yield amounted to 80%. UV/Vis (CH_2Cl_2, λ/nm (log (ϵ/dm^3·mol^{-1}·cm^{-1}))): 410 (5.24), 527 (4.24).

4.4. (5,10,15,20-Tetrakis(2,6-dichlorophenyl)porphyrinato)(carbonyl)ruthenium(II), Ru(TDCPP)(CO)

Again, a modification of the method described by Rillema et al. [29] was used; yield 84%. ^{1}H NMR ($CDCl_3$, δ/ppm) : 8.45 (s, 8H, β-pyrrole), 7.7 (m, 12H, 3,4,5-phenyl). UV/Vis (CH_2Cl_2, λ/nm (log (ϵ/dm^3·mol^{-1}·cm^{-1}))): 228 (4.49), 412 (5.30), 528 (4.26), 558 (sh, 3.75). IR (CH_2Cl_2, $\tilde{\nu}$/cm^{-1}): 1948 (s, CO), 1008 (s, Ru^{II}N$_4$).

4.5. (5,10,15,20-Tetrakis(2,4,6-trimethylphenyl)porphyrinato)(dioxo)ruthenium(VI), Ru(TMP)(O$_2$)

For the preparation of this compound a modification of the procedure described by Groves et al. [11] was used. Very recently an improved method was described by Tavarès et al. [21]. Ru(TMP)(CO) was oxidized by titrating a 1×10^{-3} mol·dm^{-3} solution in dichloromethane with a 4.2×10^{-3} mol·dm^{-3} solution of 3-chloroperoxybenzoic acid solution in dichloromethane. The titration was monitored with UV/Vis spectroscopy. After completion of the reaction, the solvent was removed by rotary evaporation. The impure product was brought on a basic alumina column and eluted with hexane/chloroform (1:1 v/v). After chromatography the product was recrystallized from toluene/acetonitrile (2:1 v/v), and dried at room temperature under reduced pressure (0.01 mmHg) for 6–8 h. Yield 70%. It has to be remarked that *trans*-dioxoruthenium(VI) porphyrins are sensitive to decomposition, especially in acidic medium [11]. ^{1}H NMR data are in agreement with Ref. [11]. UV/Vis (CH_2Cl_2, λ/nm (log (ϵ/dm^3·mol^{-1}·cm^{-1}))): 421 (5.45), 515 (4.38).

4.6. (5,10,15,20-Tetrakis(2,6-dichlorophenyl)porphyrinato)(dioxo)ruthenium(VI), Ru(TDCPP)(O$_2$)

This complex was prepared according to the procedure described above in 63% yield. UV/Vis (CH_2Cl_2, λ/nm (log (ϵ/dm^3·mol^{-1}·cm^{-1}))): 419 (5.41), 515 (4.14). IR (CH_2Cl_2, $\tilde{\nu}$/cm^{-1}): 1019 (s, Ru^{VI}N$_4$), 825 (O=Ru=O). IR (KBr, $\tilde{\nu}$/cm^{-1}): 1019 (s, Ru^{VI}N$_4$), 824 (O=Ru=O). Ref. [11] reported O=Ru=O at 821 cm^{-1}. FAB/MS

(m/z): 1022 $(M+H)^{+\cdot}$, 1005 $(M-O)^{+\cdot}$, 990 $(M-2O+H)^{+\cdot}$. The isotopic pattern of the $(M+H)$ peak matches the pattern generated by a computer, calculated from known natural isotope relative abundances.

Acknowledgements

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