

Halogenated oxo- and peroxotitanium porphyrinates as sensitizers for the photooxygenation of olefinic compounds

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Abstract

A series of porphines, oxotitanium(IV) and peroxotitanium(IV) porphyrinates were tested as photosensitizers of the singlet oxygen ene reaction with cyclohexene and *cis*-cyclooctene. The relative order of activity is: $H_2(P) > O=Ti(P) \geq Ti(O_2)P$. Best stability is obtained for porphines or porphyrinate complexes with fluorine substituents. Oxotitanium(IV) porphyrinates are active in the decomposition of allylic hydroperoxides. The (photo)catalytic epoxidation occurs less readily than the thermal reaction at 82°C. Attempts of photocatalytic hydrogen peroxide activations lead to fast destruction of $O=Ti(P)$. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The catalytic oxidation of hydrocarbons derived from petrochemical feedstocks in the liquid or gas phase belongs to the most important methods in the chemical industry. The search

for new selective activation pathways using molecular oxygen or hydrogen peroxide is of current interest [1–3].

Photooxygenation reactions usually proceed very selectively at ambient temperatures using only light, oxygen and a sensitizer. Singlet oxygen is often the active species and a broad variety of compounds can be obtained starting from (hetero)aromatics, alkenes or alka-1,3-dienes [4–6].

Longer reaction times cause oxidative degradation of the used sensitizer dyes, such as rose bengale, methylene blue or H_2TPP . Quast et al. have shown the bleaching of *meso*-tetraphenylporphines to be dependent of the substituents of the macrocycle as well as the nature and concentration of the alkene applied. Especially during cyclohexene photooxygenation, complete

Abbreviations: OEP: octaethylporphinato; TMP: *meso*-tetrakis(2,4,6-trimethylphenyl)porphinato; TTP: *meso*-tetrakis(4-methylphenyl)porphinato; TPP: *meso*-tetraphenylporphinato; TP- PCl_4 : *meso*-tetrakis(4-chlorophenyl)porphinato; $TPPCl_8$: *meso*-tetrakis(2,6-dichlorophenyl)porphinato; $TPPF_8$: *meso*-tetrakis(2,6-difluorophenyl)porphinato; $TPPF_{20}$: *meso*-tetrakis(2,3,4,5,6-pentafluorophenyl)porphinato; (P): porphinato

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destruction of H_2TPP and H_2TPPF_{20} is observed. Under the same conditions, more than 30% of the initial H_2TPPCl_8 amount remained [7]. According to DiMugno et al., H_2TPPF_{20} is bleached only slightly during photooxygenation of allylic alcohols. Cyclohexene as substrate causes comparable decomposition of H_2TPPF_{20} and H_2TPP [8].

The physical separation of the sensitizer from the reaction products during the irradiation procedure using perfluorinated biphasic solvent systems [9–11] leads to an enhanced chemical stability of the sensitizer [8,12].

When transition metal porphyrinates with iron [13–20] and manganese [21–23], osmium [24], niobium [25,26] or molybdenum [27,28] as central atom are used as photocatalysts, they can cause oxygenation via a radical mechanism. Some oxovanadium and oxotitanium porphyrinates are reported to be singlet oxygen sensitizers [29,30].

To our knowledge, no systematic investigation concerning the influence of solvents or (halogen) substituents on the macrocyclus regarding the stability of oxotitanium porphyrinates and the selectivity during the photooxygenation of alkenes has been published.

We reported recently the syntheses of various new oxo- and peroxotitanium porphyrinates with perfluorinated or perchlorinated phenyl groups and the structure of $Ti(O)TPPF_{20}$ [31,32]. This paper shows the photooxygenation of cyclohexene and *cis*-cyclooctene with a series of titanium porphyrinate complexes as sensitizers. The influence of substituents and solvents on the porphyrinate stability and the selectivity of oxygenation will be shown in comparison to metal-free porphines.

2. Experimental

2.1. General

All solvents were dried, purified and stored under inert argon atmosphere. Cyclohexene was

dried with calciumhydride (Aldrich), distilled under argon and stored in the dark. *cis*-Cyclooctene was used with a purity of 95.5%. Cyclohexen-3-ol and cycloocten-3-ol were prepared by photooxygenation of cyclohexene or *cis*-cyclooctene and subsequent reduction with triphenyl phosphine or by reduction of cyclohexen-3-one (Fluka) with lithium aluminiumhydride (Merck). 2,3-Epoxy cyclohexanol was synthesized from cyclohexen-3-ol and *m*-chloroperbenzoic acid (Merck, 55%). *cis*-Cyclooctene-oxide, *trans*-cyclooctane-1,2-diol and $BF_3 \cdot Et_2O$ were purchased from Fluka.

Titanium tetrachloride (Fluka) was distilled from copper chloride under argon before use. Hydrogen peroxide (30%, Merck), *t*-butylhydroperoxide (3 mol/l in *i*-octane, Fluka), 2,3,5,6-tetrachlorobenzoquinone PCA (Fluka), 2,3-dichloro-5,6-dicyanobenzoquinone DDQ (Fluka), titanocene dichloride (Aldrich) and titanium acetylacetonate (Merck) were used as purchased.

The NMR spectra were recorded with a Bruker-AC300 spectrometer and the UV-Vis spectra with the Perkin-Elmer Lambda 14 spectrometer using toluene or dichloromethane as solvent. The IR spectra were measured with a Nicolet 510/P spectrometer in a KBr matrix. The Finnigan MAT 95 served for the detection of the SIMS spectra.

2.2. Synthesis of porphyrinates

The free porphines H_2TPP , H_2TMP , H_2TTP , H_2TPPCl_4 and $H_2TPP(OMe)_{12}$ were prepared according to the conditions of the Rothmund synthesis [33–38]. H_2OEP was provided by Midcentury. The porphine H_2TPPF_{20} was synthesized from 2,3,4,5,6-pentafluorobenzaldehyde and pyrrole in the presence of boron trifluoride-diethyl ether and subsequent oxidation with *p*-chloroanile or 2,3-dichloro-5,6-dicyanobenzoquinone under equilibrium conditions [39]. By a similar procedure, H_2TPPF_8 [40] and H_2TPPCl_8 [41] can be obtained.

The reaction of the porphines with titanium tetrachloride in dry toluene under argon atmosphere and subsequent hydrolysis with dilute mineral acid yields oxotitanium porphyrinates [31,32,42]. After chromatography on silica, the oxotitanium porphyrinates were reacted with an excess of aqueous hydrogen peroxide in dichloromethane. The light sensitive peroxotitanium(IV) porphyrinates were obtained after chromatography [31,32,43].

2.3. Photochemical procedures

All photoreactions were carried out in a 45-ml Pyrex™ photoreactor (3 cm in diameter) equipped with a magnetic stirrer, a gas supply and a heat exchanger in the reaction mixture. The with water cooled light source was placed outside of the reactor at a distance of 5 cm. Different high-pressure mercury lamps (TQ 150, TQ 150 Z1 or TQ 150 Z2, Hereus Noble-light) were used. When hydrogen peroxide or *t*-butylhydroperoxide were used as oxidant, the oxygen stream was replaced by an argon supply. Excess hydrogen peroxide and water were removed after the irradiation by adding small amounts of manganese dioxide and molecular sieve as a drying agent.

The mixture of the olefin, the solvent(s), the catalyst and *n*-decane as internal standard was stirred for half an hour in the dark, while oxygen was bubbled through the mixture with a constant stream of 10 l/h. Before and during the irradiation, samples from the reactor were withdrawn and analysed by gas chromatography and thin layer chromatography. At the end of the irradiation, the reaction mixture was reduced by the addition of triphenyl phosphine or lithium aluminium hydride in anhydrous diethylether and was also gas chromatographically analysed.

2.4. Thermal procedures

In a Schlenk tube, the weighted amounts of the olefin, the catalyst, *n*-decane and *t*-butylhydroperoxide were heated in 4 ml of toluene

under argon. After 20 or 60 h, the reaction mixture was cooled and analyzed by GC and TLC.

3. Results and discussion

3.1. Syntheses of titanium porphyrinates

The syntheses of the oxotitanium(IV) porphyrinates starts from the free porphines and titanium tetrachloride in toluene according to Fig. 1. Derivatisation with aqueous hydrogen peroxide of the pure compound dissolved in dichloromethane yields the light-sensitive peroxotitanium(IV) porphyrinates [31,32,42,43]. Good yields, ranging from 80% to 92% in both reaction steps, can be reached by this method. Table 1 and Fig. 2 respectively show the abbreviations and the structures of the synthesized complexes used as catalysts for the activation of oxygen, *t*-butylhydroperoxide or hydrogen peroxide.

3.2. Photooxygenation reactions with dioxygen

The catalytic activity of the synthesized titanium(IV) porphyrinates was evaluated during the photooxygenation of cyclohexene 10a and *cis*-cyclooctene 10b with dioxygen as oxidant. The observed products are shown in the Fig. 3.

3.2.1. Influence of the titanyl group and the substituents at the porphine core

The photooxygenation of cyclohexene and *cis*-cyclooctene using different tetraarylpor-

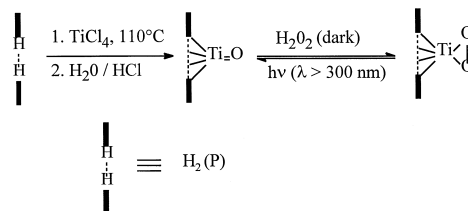


Fig. 1. Syntheses of (per)oxotitanium(IV) porphyrinates: H₂(P)-free porphine.

Table 1
Titanium(IV) porphyrinates and abbreviations

R ₁	R ₂	M: Ti=O	M: Ti(O ₂)
H	Phenyl <u>1a</u>	Ti(O)TPP <u>1b</u>	Ti(O ₂)TPP <u>1c</u>
H	2,6-Dichlorophenyl <u>2a</u>	Ti(O)TPPCl ₈ <u>2b</u>	Ti(O ₂)TPPCl ₈ <u>2c</u>
H	2,4,6-Trimethylphenyl <u>3a</u>	Ti(O)TMP <u>3b</u>	Ti(O ₂)TMP <u>3c</u>
H	2,3,4,5,6-Pentafluorophenyl <u>4a</u>	Ti(O)TPPF ₂₀ <u>4b</u>	Ti(O ₂)TPPF ₂₀ <u>4c</u>
H	4-Methylphenyl <u>5a</u>	Ti(O)TTP <u>5b</u>	
H	4-Chlorophenyl <u>6a</u>	Ti(O)TPPCl ₄ <u>6b</u>	Ti(O ₂)TPPCl ₄ <u>6c</u>
H	2,6-Difluorophenyl <u>7a</u>	Ti(O)TPPF ₈ <u>7b</u>	Ti(O ₂)TPPF ₈ <u>7c</u>
Et	H <u>8a</u>	Ti(O)OEP <u>8b</u>	Ti(O ₂)OEP <u>8c</u>
H	H ₂ T(3,4,5-(OMe) ₃)PP <u>9a</u>	Ti(O)T(3,4,5-(OMe) ₃)P <u>9b</u>	

phines as photosensitizers results in the selective formation (> 94%) of the corresponding allylic hydroperoxides 11a and 11b (Table 2). Nearly no by-product formation occurs. Cyclohexene and *cis*-cyclooctene show similar reactivities. With the partial fluorinated porphine H₂TPPF₈ 7a, the best results with respect to stability and hydroperoxide yield are obtained. The porphines H₂TPP 1a, H₂TMP 3a and H₂TPPCl₈ 2a, which were reported to be superior sensitizers [7], exhibit lower, but still good yields. H₂TPP 1a is not stable in the presence of cyclohexenyl-hydroperoxide 11a. After 6 h of irradiation, nearly total porphine bleaching was observed. The low hydroperoxide yields obtained with the porphine H₂TPPF₂₀ 4a are surprising because the quantum yield should increase with the fluorine and especially with the chlorine content of the porphine core [44]. According to product yield and stability, the following order of sensitizer quality was found: 7a >> 3a ~ 2a >> 4a ~ 1a.

Oxotitanium(IV) porphyrinates (Tables 3 and 4) exhibit lower yields than the corresponding

tetraarylporphines. Small amounts of the corresponding peroxotitanium(IV)–tetraarylporphyrinates are formed during the irradiation (TLC). The allylic hydroperoxides 11a and 11b are the main products with selectivities from 38 to 77%. Major side products are the allylic alcohol 12a/12b, the α,β-unsaturated ketone 13a/13b and the epoxide 14a/14b. In a few cases, the 1,2-epoxycyclohexan-3-ol 15a could be detected in small amounts.

The best results of stability and activity can be obtained with oxotitanium(IV) tetraarylporphyrinates disubstituted in the 2,6 position of the aryl group. Fluorine and chlorine substituents are more suitable than methyl groups. Especially, Ti(O)TPPF₂₀ 4b catalyses the decomposition of the hydroperoxides and exhibits further enhanced epoxidation activity. The introduction of the titanyl group enhances the catalytic performance of H₂TPPF₂₀ 4a significantly. The *para*- or unsubstituted oxotitanium(IV) tetraarylporphyrinates are completely destroyed during the irradiation. The following order of sensitizer quality was found: 7b ~ 4b > 2b > 3b > 1b > 5b > 6b > 8b ~ 9b.

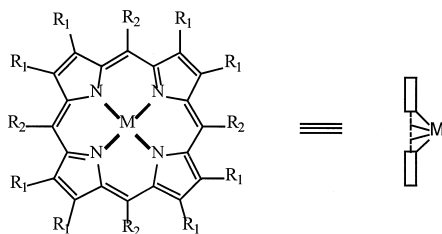


Fig. 2. Structure of (per)oxotitanium(IV) porphyrinates.

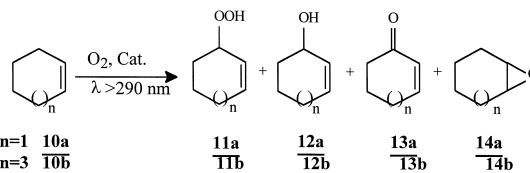




Fig. 3. Product spectra of the photooxygenation of cyclic olefins.

Table 2

Photooxygenation of cyclohexene **10a** and *cis*-cyclooctene **10b** with different tetraarylporphyrines

Cat.	n(Cat.) [mmol]	n(10a) [mmol]	n(10b) [mmol]	ϑ [°C]	Time [h]	Yield [%]	TOF [h ⁻¹]	S [%]	
									
1a	0.036	19.7	-	18	6.0 ^a	31.8	28.2	97	-
2a	0.019	20.9	-	15	8.3	26.4	35.3	96	-
3a	0.019	19.9	-	13	8.1	31.2	40.4	97	-
3a	0.019	-	22.3	15	8.1	31.7	46.1	-	97
4a	0.019	20.0	-	13	8.7	16.6	20.7	99	-
4a	0.037	-	23.1	14	8.0	15.7	12.1	-	94
7a	0.019	20.6	-	15	8.4	37.0	49.1	97	-
7a	0.018	-	22.3	15	8.1	56.1	88.7	-	94

^a Porphine was destroyed.
TQ 150 Z2, 40 ml CH₂Cl₂.






3.2.2. Influence of the catalyst concentration

The amount of the hydroperoxide decomposition during the irradiation depends on the aryl substituents and the concentration of the used

oxotitanium porphyrines. The influence of the concentration on the reaction was investigated in the case of Ti(O)TPP **1b** as catalyst (Fig. 4). With increasing catalyst concentration, signifi-

Table 3





Photooxygenation of cyclohexene **10a** with different oxotitanium porphyrines

Cat.	n(10a) [mmol]	ϑ [°C]	Yield [%]	TOF [h ⁻¹]	S [%]				
									
6b	19.7	12	11.0	9.6	58	14	12	10	4
8b	19.6	11	10.0	9.0	48	25	11	9	5
9b	20.5	13	9.3	9.2	58	14	15	9	3
1b	19.0	16	16.5	13.8	70	12	10	8	0
2b^a	20.6	25	13.4	23.0	73	10	9	6	0
3b	20.3	25	19.7	18.1	60	22	12	5	0
4b	20.1	25	26.0	23.5	56	21	10	13	0
7b	20.4	19	27.6	25.4	77	7	6	5	4

^a 0.020 mmol.
0.037 mmol Catalyst, TQ 150 Z2, 6.1 h, 40 ml CH₂Cl₂.

Table 4

Photooxygenation of *cis*-cyclooctene **10b** with different oxotitanium porphyrinates

Cat. n(10b)	θ [mmol]	t [°C]	t [h]	Yield [%]	TOF [h ⁻¹]				
						S [%]	S [%]	S [%]	S [%]
5b	21.2	15	8.2	12.9	9.0	72	7	8	13
3b	21.2	14	8.5	24.5	16.9	66	12	11	11
2b	20.5	25	8.4	35.3	24.0	76	10	6	8
4b	21.2	25	8.0	44.7	32.8	38	27	21	13

0.036 mmol Catalyst, TQ 150 Z2, 40 ml CH₂Cl₂.

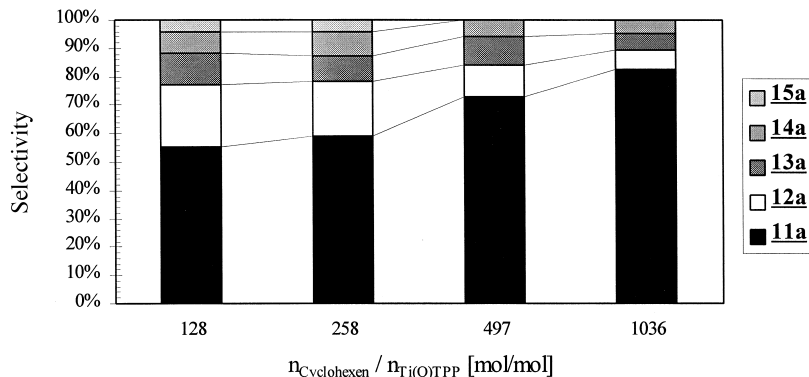
cant amounts of the allylic alcohol **12a** could be detected. In the dark, no further decomposition occurred at room temperature. This is in agreement with published results [45]. The overall yields increased only slightly with the amount of catalyst and varied between 15 and 17% after an irradiation time of 4 h. These results indicate a photochemically induced hydroperoxide decomposition.

3.2.3. Peroxotitanium(IV) porphyrinates as catalysts

The peroxotitanium porphyrinates are known to be photosensitive [31,32]. They release singlet dioxygen during irradiation (Fig. 5) [46,47]. The irradiation of cyclohexene in benzene or ethyl acetate in the presence of Ti(O₂)TPP and

oxygen yields mainly cyclohexenone. The turnover frequency is less than 0.4 mol/(mol × h). No formation of hydroperoxides was reported.

During the course of this investigation, the formation of peroxotitanium porphyrinates could be observed when cyclohexene and *cis*-cyclooctene were photooxygenated with oxotitanium(IV) porphyrinates as catalysts. The peroxotitanium(IV) porphyrinates Ti(O₂)TPPCl₈ **2c**, Ti(O₂)TMP **3c**, Ti(O₂)TPPF₂₀ **4c** and Ti(O₂)-TPPF₈ **7c** were therefore tested as catalysts as well. The catalytic performance is, in general, lower in comparison to the corresponding oxotitanium porphyrinates. The selectivity to the hydroperoxide ranges from 80 to 85%. During the irradiation, most of the peroxo complex is con-

Fig. 4. Photooxygenation of 19.3 mmol **10a** with different concentrations of **1b** (4 h, TQ 150 Z2, 40 ml CH₂Cl₂).

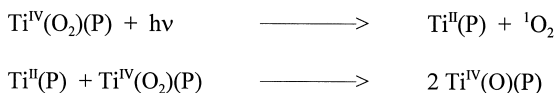


Fig. 5. Photodeoxygenation of peroxotitanium porphyrinates (P) = TPP, T(*m*-TP).

verted to the corresponding oxo complex. The stabilities of the peroxy catalysts are nearly as high as the oxo complexes (Fig. 6). In the case of *cis*-cyclooctene 10b as substrate, only small differences in yield and selectivity were measured (Table 5).

3.2.4. Variation of the solvents and influence of additives

It became obvious during the course of these investigations that the catalyst activities differ with the solvent used. Best results could be obtained in benzene or toluene, whereas in dichloromethane, the yield was reduced by almost 50%. A faster catalyst decomposition occurred in dichloromethane. The solvent, therefore, significantly influences the course of the reaction.

Fig. 7 shows some results using pure dichloromethane and acetonitrile as cosolvent (50%). Although both solvents show similar singlet oxygen lifetimes, the turnover numbers increase (7–25%) by adding acetonitrile. The selectivity to the hydroperoxide 11a increases from about 60% to 70–80% as well. An enhanced catalyst stability because of the axial

coordination at the oxotitanium moiety could be the reason (Fig. 9). In ethanolic solution, for example, an equilibrium between Ti(O)TPP 1b and (EtOH)Ti(O)TPP exists, whereas no coordination occurs in chloroform or toluene [48]. Mono- or disubstituted amines show only a weak coordination and triethylamine or DMSO do not act at all as ligands [49]. The effect of axial coordination with (methyl) imidazole during the photooxygenation of manganese and molybdenum is well-documented [21–23,50].

Because the catalysts Ti(O)TMP 3b and Ti(O)TPPF₂₀ 4b are more sensitive to a change in the reaction medium, a detailed investigation of the influence of additives on their activity and selectivity was undertaken. The results are summarized in Fig. 8. Addition of imidazole increases the product yield and the selectivity of hydroperoxide formation. The irradiation of Ti(O)TMP 3b with imidazole causes an additional absorption in the UV–Vis spectrum at 433 nm ($\log \epsilon = 5.1$). As in the case of acetonitrile, axial coordination may be the reason for this (Fig. 9).

DABCO quenches the reaction effectively. The addition of titanium complexes reduces the product formation and the hydroperoxide formation drastically. This may be the consequence of radical formation, e.g., C₅H₅ and Ti(η^5 -Cp)Cl₂, which can react with chlorinated solvents to yield Ti(η^5 -Cp)Cl₃ and further radicals [51,52]. In the presence of excess TBHP, the activity of Ti(O)TPPF₂₀ 4b is significantly lower and the

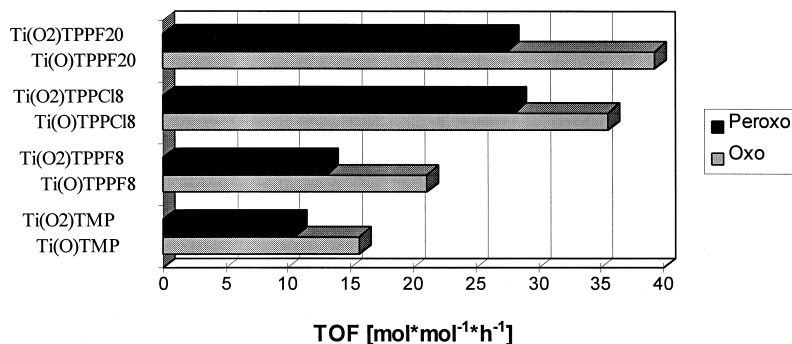






Fig. 6. Photooxygenation of cyclohexene 10a (20.1 ± 0.4 mmol). Comparison between the activity of oxo- and peroxotitanium porphyrinates (8 h, 40 ml dichloromethane, TQ 150 Z2, 2b/2c and 4b/4c: 0.019 mol; 3b/3c and 7b/7c: 0.036 mmol).

Table 5

Photooxygenation of 22.5 mmol *cis*-cyclooctene **10b** using peroxy complexes Ti(O)₂P as catalysts

Cat	Yield [%]	TOF [h ⁻¹]				
			S [%]	S [%]	S [%]	S [%]
7b	39.7	58.9	82	6	7	5
7c	39.3	58.1	92	1	3	5

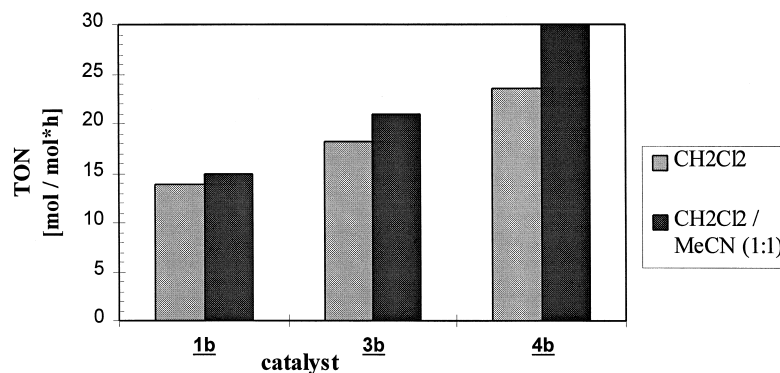
0.019 mmol Catalyst, TQ 150 Z2, 8.1 h, 40 ml CH₂Cl₂, 16°C.

hydroperoxide **11a** is formed selectively. In general, the hydroperoxide decomposition increases with increasing concentration.

3.2.5. Activation of hydrogen peroxide and *t*-butylhydroperoxide

Because of the above discussed titanium porphyrinates reactivity, one can postulate a new way of hydrogen peroxide activation according to Fig. 10. A mixture of 3.6×10^{-5} mol O=Ti(P), 20.5 mmol cyclohexene **10a**, 1.1 g H₂O₂ (30%, 9.5 mmol), 30 ml CH₂Cl₂ and 10 ml CH₃CN was, therefore, stirred under argon at 15°C for 1 h before the irradiation with the high-pressure mercury lamp TQ 150 Z2 was started. A rapid bleaching of the catalyst oc-

curred. Within 4 h of irradiation, the complexes Ti(O)TPPF₂₀ **4b**, Ti(O)TMP **5b** and Ti(O)TP-PCl₄ **6b** were completely destroyed. The porphyrinate Ti(O)TPPF₈ **7b**, on the other hand, was stable for 6 h. The product formation was low with a total yield between 2 and 5%. Hydroperoxide **11a** (50%) and ketone **13a** (30%) were the main products present in the reaction mixture, together with alcohol **12a** and epoxide **14a**. The desired activation path for hydrogen peroxide was not possible under these reaction conditions, but there must be another oxidising species which is responsible for the rapid catalyst bleaching (hydroxyl radicals; OH, for example). However, all light with wavelenghts shorter than 290 nm were filtered off by Pyrex™ glass. No significant direct hydrogen peroxide

Fig. 7. Activity of different catalyst (0.037 mmol) during the photooxygenation (6 h) of cyclohexene **10a** (20 mmol).

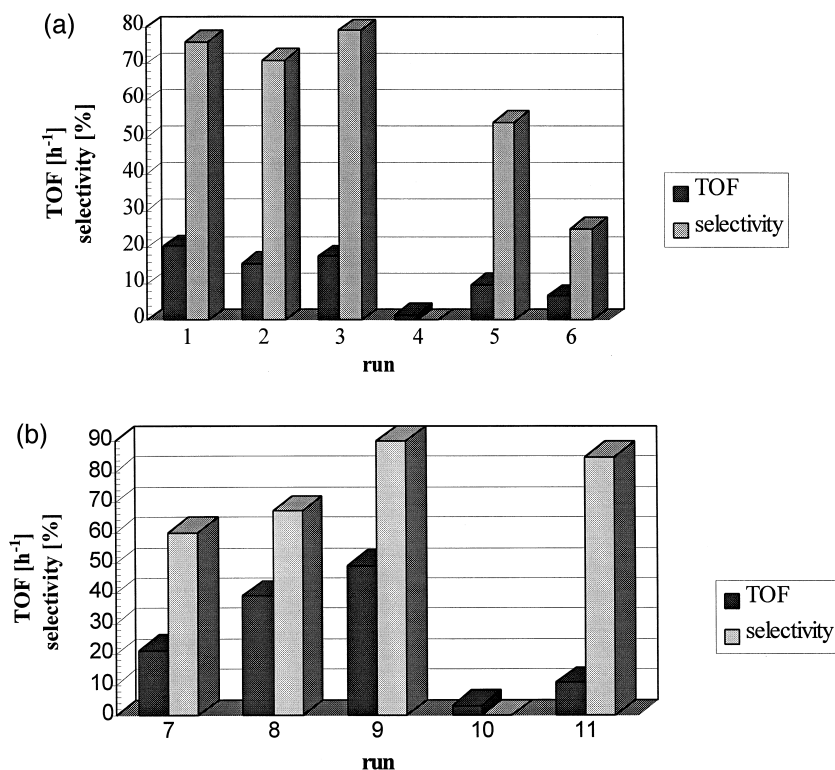


Fig. 8. (a) Influence of additives on the catalyst activity and selectivity to the hydroperoxide 11a during the photooxygenation of cyclohexene 10a (20.5 ± 0.3 mmol) with Ti(O)TMP 3b as catalyst in 40 ml CH₂Cl₂ (8 h, TQ 150 Z2): *run 1*: 0.018 mmol 3b; *run 2*: 0.036 mmol 3b; *run 3*: 0.037 mmol 3b/0.21 mmol Imidazol; *run 4*: 0.037 mmol 3b/0.15 mmol DABCO; *run 5*: 0.037 mmol 3b/0.16 mmol Ti(O)acac₂; and *run 6*: 0.037 mmol 3b/0.16 mmol Cp₂TiCl₂. (b) Influence of additives on the catalyst activity and selectivity to 11a during the photooxygenation of cyclohexene 10a (20.1 ± 0.4 mmol) with Ti(O)TPPF₂₀ 4b as catalyst in 40 ml CH₂Cl₂ (8 h, TQ 150 Z2): *run 7*: 0.036 mmol 4b; *run 8*: 0.019 mmol 4b; *run 9*: 0.019 mmol 4b/0.21 mmol Imidazol; *run 10*: 0.019 mmol 4b/0.21 mmol DABCO; and *run 11*: 0.037 mmol 4b/20.2 mmol TBHP.

splitting can, therefore, occur. It is obvious that the Ti^{II}(P) moiety is oxidised by hydrogen peroxide with loss of the porphyrinate ligand.

Addition of *t*-butylhydroperoxide to the photooxygenation of cyclohexene decreases the overall yield with a reduced decomposition of the hydroperoxide 11a in the case of Ti(O)TPPF₂₀ 4b as catalyst, which is stable under these circumstances for 8 h. In the dark, at ambient temperature, no decomposition of the hydroperoxide 11a occurred. Ti(O)P does not



Fig. 9. Acetonitrile and imidazole as axial ligands: (P) = TMP, TPPF₂₀.

catalyse the epoxidation of *cis*-cyclooctene 10b with TBHP in dichloromethane at 40°C. If the temperature is raised to 82°C, selective formation of the epoxide 14b occurred (Table 6). During the reaction, partial formation of the corresponding peroxy complexes takes place (TLC). No catalyst bleaching could be observed. The porphyrinate ligand has only a mi-

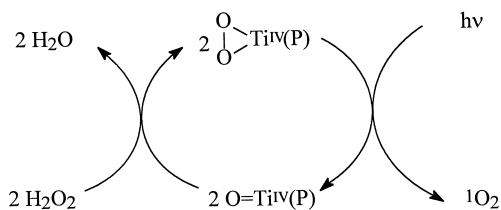


Fig. 10. Photocatalytic activation of hydrogen peroxide.

Table 6
Thermal epoxidation of *cis*-cyclooctene 10b with TBHP in toluene

Catalyst	<i>n</i> (Catalyst) [mmol]	<i>n</i> (<u>10b</u>) [mmol]	<i>n</i> (TBHP) [mmol]	Conversion (<u>10b</u>) [%]	TON [mol/mol]	Yield (<u>11b</u>) [%]	S (<u>11b</u>) [%]
<u>5b</u>	0.021	2.3	2.3	9	8	8.1	90
<u>6b</u>	0.020	2.5	3.1	12	12	10.1	84
<u>3b</u>	0.020	2.7	3.0	12	14	10.8	90
<u>4b</u>	0.020	2.8	3.0	10	12	8.8	88

82°C, 20 h.

nor influence on the catalyst activity. The best result is reached with Ti(O)TMP 3b. After a reaction time of 60 h, the conversion reached 30% without loss of selectivity. The relative reactivities of the cyclic olefins during the epoxidation with the system TBHP/Ti(O)TPP 1b were described by Agarwal [53]. A big excess of the olefin, with respect to the TBHP ($n_{\text{1b}}/n_{\text{TBHP}}/n_{\text{Olefin}} = 1/10/50$), was used because of catalyst deactivation through the for-

mation of Ti(O)₂TPP 1c. In contrast, the phenyl substituted O=Ti(P) 3b–6b show better catalytic performances.

3.2.6. Mechanism

The titanium porphyrinate-catalyzed photooxygenation of cyclohexene 10a and *cis*-cyclooctene 10b results in the formation of hydroperoxide. Singlet oxygen is produced via the well-known energy transfer mechanism from

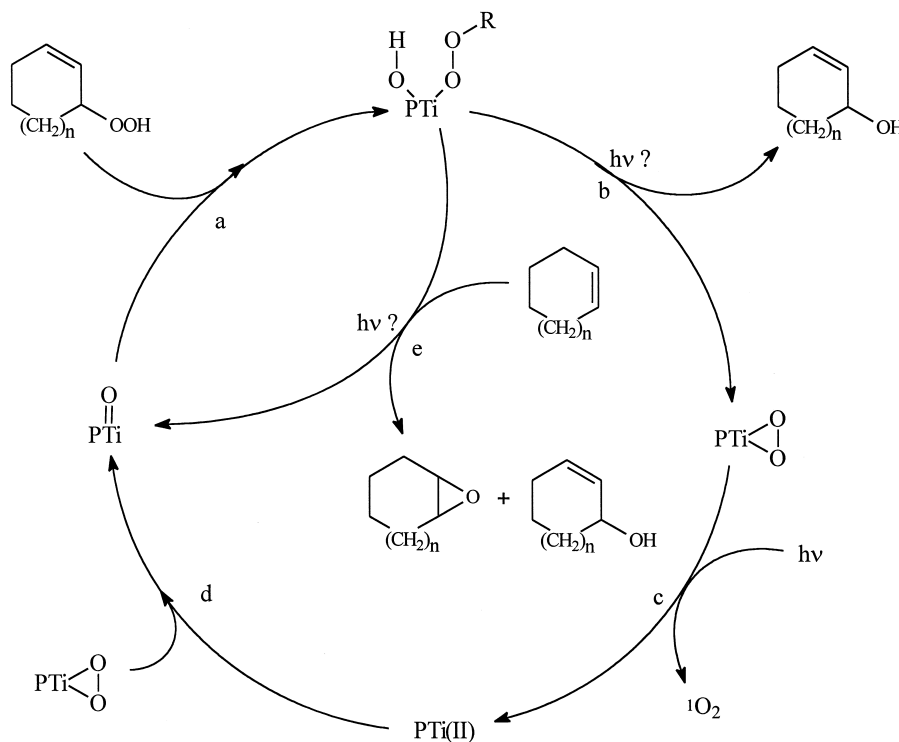


Fig. 11. (Photo)catalytic mechanism of titanium-catalyzed decomposition of allylic hydroperoxide.

excited porphyrinate to dioxygen. The product yields and the selectivity towards hydroperoxide formation are lower than in the case of free porphine bases. This indicates lower quantum yields and a (photo)catalytic property of the titanyl group. Fig. 11 shows a summary of possible hydroperoxide decomposition routes. The oxotitanium porphyrinate can be transformed to *cis*-hydroxy-alkylperoxytitanium(IV) porphyrinates, peroxotitanium(IV) porphyrinates and titanium(II) porphyrinates. The pathways b and e could be the rate-determining steps in this sequence. The epoxide formation occurs only for high catalyst concentrations and especially, when titanium porphyrinates with halogen substituents on the phenyl ring were used. *N*-oxides as intermediates, which were postulated during the photolyses of peroxotitanium porphyrinates in ethanolic solution [54], could also be responsible for the epoxide formation and catalyst decomposition. However, doting the reaction mixture with photolabile titanium complexes also indicates an influence of impurities on catalyst bleaching.

4. Summary

In a comparative study, the significant influence of substituents, oxotitanium and peroxotitanium groups on *meso*-tetraarylporphines in the course of the photosensitized singlet oxygen ene reaction could be demonstrated. Free porphines show the best catalytic activity. Good yields of the allylic hydroperoxides starting from cyclohexene and *cis*-cyclooctene can be obtained. *meso*-(2,6-Difluorophenyl)porphine is the sensitizer of choice for singlet oxygen. The replacement of hydrogen by oxotitanium or peroxotitanium group causes a reduction of the singlet oxygen production and an enhanced (photocatalytic) hydroperoxide decomposition. Complexes with fluorinated ligands are superior sensitizers. The photochemical epoxidation activity of Ti(O)TPPF₂₀ **4b** at room temperature is still lower than the epoxidation at elevated tem-

peratures in the dark. The synthesis of a teflon porphyrinate Ti(O)TPPF₂₈ could lead to preparative useful epoxide yields and a stable complex for photochemical activation of hydrogen peroxide.

References

- [1] R.A. Sheldon, G. Franz, Ullmann's Encyclopedia of Industrial Chemistry, Vol. A18, Verlag Chemie, Weinheim, 1991, p. 261.
- [2] L.I. Simandi, Dioxygen Activation and Homogeneous Catalytic Oxidation, Amsterdam, 1991.
- [3] R.A. Sheldon, J. Dakka, Catal. Today 19 (1994) 215.
- [4] M. Prein, W. Adam, Angew. Chem. 108 (1996) 519.
- [5] M. Prein, W. Adam, Angew. Chem. Int. Ed. Engl. 35 (1996) 495.
- [6] A.A. Frimer (Ed.), Singlet Oxygen, Vol. 2, CRC Press, Boca Raton, FL, 1985.
- [7] H. Quast, T. Dietz, A. Witzel, Liebigs Ann. Chem. (1995) 1495.
- [8] S.G. DiMagno, P.H. Dussault, J.A. Schultz, J. Am. Chem. Soc. 118 (1996) 5312.
- [9] M. Vogt, PhD thesis, RWTH, Aachen, 1991.
- [10] I.T. Horvath, J. Rabai, Science 266 (1994) 72.
- [11] I.T. Horvath, J. Rabai, US Patent 5463082, 1995.
- [12] R.D. Chambers, G. Sandford, A. Shah, Synth. Commun. 26 (1996) 1861.
- [13] D.N. Hendrichson, M.G. Kinnaird, K.S. Suslick, J. Am. Chem. Soc. 109 (1987) 1243.
- [14] A. Maldotti, R. Amadelli, C. Bartocci, V. Carassiti, E. Polo, G. Varani, Coord. Chem. Rev. 125 (1993) 143.
- [15] A. Maldotti, C. Bartocci, R. Amadelli, E. Polo, P. Battioni, D. Mansuy, J. Chem. Soc., Chem. Commun. (1991) 1487.
- [16] Y. Ito, Oxid. Commun. 15 (1992) 149.
- [17] M.W. Peterson, D.S. Rivers, R.M. Richman, J. Am. Chem. Soc. 107 (1985) 2907.
- [18] T. Berthold, D. Rehorek, H. Hennig, Z. Chem. 26 (1986) 183.
- [19] C.R. Guest, K.D. Straub, J.A. Hutchinson, P.M. Rentzepis, J. Am. Chem. Soc. 110 (1988) 5276.
- [20] L. Weber, G. Haufe, D. Rehorek, H. Hennig, J. Chem. Soc., Chem. Commun. (1991) 502.
- [21] L. Weber, J. Behling, G. Haufe, H. Hennig, J. Prakt. Chem. 334 (1992) 265.
- [22] L. Weber, J. Behling, G. Haufe, H. Hennig, J. Am. Chem. Soc. 116 (1994) 2400.
- [23] H. Hennig, J. Behling, R. Meusiger, L. Weber, Chem. Ber. 128 (1995) 229.
- [24] S. Mosseri, P. Neta, P. Hambright, D.Y. Sabry, A. Harriman, J. Chem. Soc., Dalton Trans. (1988) 2705.
- [25] Y. Matsuda, S. Sakamoto, H. Koshima, Y. Murakami, J. Am. Chem. Soc. 107 (1985) 6415.
- [26] Y. Matsuda, H. Koshima, K. Nakamura, Y. Murakami, Chem. Lett. (1988) 625.
- [27] L. Weber, G. Haufe, D. Rehorek, H. Hennig, J. Mol. Catal. 60 (1990) 267.

- [28] H.J. Ledon, M. Bonnet, D. Galland, *J. Am. Chem. Soc.* 103 (1981) 6209.
- [29] E.M.K. Mansour, P. Maillard, P. Krausz, S. Gaspard, C. Giannotti, *J. Mol. Catal.* 41 (1987) 361.
- [30] C.J. Boreham, J.-M. Latour, J.-C. Marchon, *Inorg. Chim. Acta* 45 (1980) L69.
- [31] P.E. Esser, U. Englert, W. Keim, *Chem. Ber.* 129 (1996) 833.
- [32] P.E. Esser, PhD thesis, RWTH, Aachen, 1995.
- [33] G.H. Barnett, M.F. Hudson, K.M. Smith, *J. Chem. Soc., Perkin Trans. 1* (1975) 1401.
- [34] G. H. Barnett, M.F. Hudson, K.M. Smith, *Tetrahedron Lett.* (1973) 2887.
- [35] J.B. Kim, J.J. Leonard, F.R. Longo, *J. Am. Chem. Soc.* 94 (1972) 3986.
- [36] J. Dalton, L.R. Milgrom, S.M. Pemberton, *J. Chem. Soc., Perkin Trans. 2* (1980) 370.
- [37] W.J. Albery, P.N. Bartlett, C.C. Jones, L.R. Milgrom, *J. Chem. Res., Synop.* (1985) 364.
- [38] R.W. Wagner, D.S. Lawrence, J.S. Lindsey, *Tetrahedron Lett.* 28 (1987) 3069.
- [39] H. Volz, S. Schneckenburger, *J. Prakt. Chem., Chem.-Ztg.* 335 (1993) 283.
- [40] A.W. van der Made, E.J.H. Hoppenbrouwer, R.J.M. Nolte, W. Drenth, *Rec. Trav. Chim. Pays-Bas* 107 (1988) 15.
- [41] J.S. Lindsey, R.W. Wagner, *J. Org. Chem.* 54 (1989) 828.
- [42] P. Fournari, R. Guilard, M. Fontesse, J.-M. Latour, J.-C. Marchon, *J. Organomet. Chem.* 110 (1976) 205.
- [43] R. Guilard, J.-M. Latour, C. Lecomte, J.-C. Marchon, J. Protas, D. Ripoll, *Inorg. Chem.* 17 (1978) 1228.
- [44] V.A. Ganzha, G.P. Gurinovich, B.M. Dzhagarov, G.D. Egorova, E.I. Sagn, A.M. Shu'iga, *J. Appl. Spectrosc.* 50 (1989) 402.
- [45] C.B. Hansen, W. Drenth, *Catal. Lett.* 20 (1993) 359.
- [46] .
- [47] P. Bergamini, S. Sostero, O. Traverso, P. Deplano, L.J. Wilson, *J. Chem. Soc., Dalton Trans.* (1986) 2311.
- [48] M. Hoshino, M. Imamura, S. Watanabe, Y. Hama, *J. Phys. Chem.* 88 (1984) 45.
- [49] T. Ozawa, A. Hanaki, *Inorg. Chim. Acta* 141 (1989) 49.
- [50] L. Weber, G. Haufe, D. Rehorek, H. Hennig, *J. Mol. Catal.* 60 (1990) 267.
- [51] R.W. Harrigan, G.S. Hammond, H.B. Gray, *J. Organomet. Chem.* 81 (1974) 79.
- [52] Z.-T. Tsai, C.H. Brubaker, *J. Organomet. Chem.* 166 (1979) 199.
- [53] D.D. Agarwal, *J. Ind. Chem. B* 31 (1992) 517.
- [54] M. Hoshino, K. Yamamoto, L.P. Lillis, T. Chijimatsu, J. Uzawa, *Inorg. Chem.* 32 (1993) 5002.