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Metalloporphyrins as catalysts in the decomposition of cyclohexyl hydroperoxide [☆]

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A series of metalloporphyrins with various metals were tested as catalysts in the decomposition of cyclohexyl hydroperoxide. The more active complexes are those of manganese(III), iron(III), chromium(III) and ruthenium(II). No relation could be found between the redox potentials of the catalysts and their activity.

Keywords: Metalloporphyrins; decomposition; cyclohexyl hydroperoxide; redox potential

1. Introduction

Oxidation of cyclohexane to cyclohexanol (chol) and cyclohexanone (chon) is an important industrial process. An intermediate in this oxidation is cyclohexyl hydroperoxide (chhp). In nature, oxidation of saturated hydrocarbons with molecular oxygen is catalysed very selectively by the enzyme cytochrome P-450. With isolated cytochrome P-450 also hydroperoxides can be used as oxygen donor. Therefore, an investigation of the usefulness of metalloporphyrins as catalysts in the decomposition of chhp seems worthwhile. From earlier work on the decomposition of chhp it is known that iron(III) and cobalt(II) porphyrins are able to decompose chhp [1], while also chromium(III) and manganese(III) porphyrins have been patented for this purpose [1]. Furthermore, a literature search revealed that manganese(III), osmium(II), iron(III) and cobalt(II) tetraphenylporphyrins are able to decompose cumyl hydroperoxide at 20°C with half-life times of the peroxide of 4320, 210, 1–2 and 0.3 min, respectively [2,3]. In contrast, the metal-free tetraphenylporphyrin as well as magnesium(II), copper(II), nickel(II), zinc(II), oxotitanium(IV) and oxovanadium(IV) tetraphenylporphyrins do not show any catalytic activity in the decomposition of cumyl hydroperoxide [2,3]. However, it has also

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been reported that oxotitanium porphyrins are capable of reaction with tert-butyl hydroperoxide, dibenzoyl peroxide and hydrogen peroxide [4–6]. Besides, reactions between oxomolybdenum(V) [7–11], oxorhenium(V) and oxotungsten(V) [11] porphyrins and hydrogen peroxide and/or tert-butyl hydroperoxide have been reported.

In order to answer the question which metals are to be preferred in the porphyrin core of a catalyst in the decomposition of chhp, metallotetraphenylporphyrins containing the following metals were tested: titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, molybdenum, ruthenium, tungsten and rhenium, while also the parent, metal-free tetraphenylporphyrin was tested for its catalytic activity. As porphyrin moiety, tetraphenylporphyrin (TPP) was used, because of both the ease of preparation of this ligand and the easy introduction of a metal in this porphyrin.

2. Experimental

The instrumentation and analytical procedures have been described earlier [12,13]. The decomposition reactions were carried out in a Schlenk tube, containing a N_2 atmosphere, thermostated at 25.0 ± 0.2°C. The tube was filled with 10.0 cm^3 of 0.158 mol dm^{-3} chhp solution in cyclohexane. 500 mm^3 of a 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 mm^3 was required for the gaschromatographic determination of the chol and chon concentrations and the second, 1.0 mm^3, was necessary for the spectroscopic determination of the chhp concentration. All reactions were at least carried out twice. Tetraphenylporphyrin was prepared according to the procedure described by Adler [14,15]. Mn(TPP)Cl, Cr(TPP)Cl, Fe(TPP)Cl and VO(TPP) were prepared by reaction of H_2(TPP) with $Mn(OAc)_2 \cdot 4H_2O$, $CrCl_2$, $FeCl_2 \cdot 4H_2O$ and $V(acac)_3$, respectively [16]. Ru(TPP)(CO) was synthesized from $Ru_3(CO)_{12}$ [17], Co(TPP) from $Co(OAc)_2 \cdot 4H_2O$, Cu(TPP) from $Cu(OAc)_2 \cdot H_2O$, Ni(TPP) from $NiCl_2 \cdot 6H_2O$ and Zn(TPP) from $Zn(OAc)_2 \cdot 2H_2O$ [18]. TiO(TPP) was obtained by a method described by Latour [19]. MoO(TPP)OMe, ReO(TPP)Br and WO(TPP)Br were kindly donated by Dr. G. Legemaat.

3. Results and discussion

Various metalloporphyrins were tested as catalyst in the decomposition of chhp. The results are presented in table 1. From table 1 it is clear that only Cr(TPP)Cl, Mn(TPP)Cl, Fe(TPP)Cl, Co(TPP), Ru(TPP)(CO) and ReO(TPP)Br catalyse the decomposition of chhp. These catalysts contain metals which are found in the centre of the periodic system, i.e. in groups VI, VII, VIII and IX. For

Table 1
Decomposition of chhp catalysed by various tetraphenylporphyrins [a]

Catalyst	Chhp decomposed (%)	Chon formed [b] (%)	Chol formed [b] (%)	Chon/chol
H_2(TPP)	0	–	–	–
TiO(TPP)	0	–	–	–
VO(TPP)	0	–	–	–
Cr(TPP)Cl	53	20	20	1.0
Mn(TPP)Cl	50	23	24	1.0
Fe(TPP)Cl	67	43	23	1.9
Co(TPP)	16	4	14	0.3
Ni(TPP)	0	–	–	–
Cu(TPP)	0	–	–	–
Zn(TPP)	0	–	–	–
MoO(TPP)(OCH_3)	0	–	–	–
Ru(TPP)(CO)	89	32	54	0.6
WO(TPP)(Br)	0	–	–	–
ReO(TPP)(Br)	19	7	7	1.0

[a] Conditions: [chhp] = 0.150 mol dm^{-3}, [catalyst] = 0.1 mmol dm^{-3} in c-C_6H_{12}/CH_2Cl_2 (20 : 1) at 25°C for 48 h.

[b] Based on initial concentration of chhp.

metalloporphyrins containing metals positioned more to the left (groups IV and V) or more to the right (groups X, XI and XII) in the periodic system no activity was found. Further study, aimed at finding an explanation of the results presented in table 1, was preceded by an investigation of the stability of these metalloporphyrins. Therefore, during the reaction the catalyst was monitored by UV/Vis spectroscopy. It appeared that on basis of their catalytic behaviour the tested metalloporphyrins can be divided into three groups: catalytically active, stoichiometrically active and inactive. Catalytically active are Mn(TPP)Cl, Fe(TPP)Cl, Co(TPP), Cr(TPP)Cl, Ru(TPP)(CO) and ReO(TPP)Br, stoichiometrically active are Zn(TPP), MoO(TPP)(OCH_3) and WO(TPP)Br and inactive are H_2(TPP), TiO(TPP), VO(TPP), Ni(TPP) and Cu(TPP).

In order to increase our understanding of the catalytic activity of the metalloporphyrins tested, their redox potentials were determined by cyclic voltammetry (table 2). The oxidation or reduction of the metalloporphyrin can take place on two sites: on the metal itself or on the porphyrin ring. An asterisk indicates that the oxidation or reduction occurred mainly on the metal.

Manassen et al. [34,43] observed a correlation between the catalytic activity of metalloporphyrins in the oxidative dehydrogenation of cyclohexadiene and the oxidation potential of the metalloporphyrin. The catalytic activity increased when the oxidation potential decreased. Besides, for a given potential, a catalyst which undergoes a metal centred oxidation, exhibited higher catalytic activity than one

Table 2
Redox potentials of various metalloporphyrins versus SCE[a]. An asterisk indicates that oxidation or reduction occurs on the metal. For comparison literature references when available are given.

Catalyst	Oxidation potentials (V)			Reduction potentials (V)			Refs.
H_2(TPP)	0.92	1.15		−1.28			[20,21]
TiO(TPP)	1.07	1.31		−1.17	−1.57		
VO(TPP)	1.04	1.25		−1.16	−1.55		
Cr(TPP)Cl	0.40*	0.60	0.81	−1.28*			
Mn(TPP)Cl	1.03			−0.41*			[22]
Fe(TPP)Cl[b]	1.03*			−0.41*	−1.25*		[23–27]
Co(TPP)	0.89	1.14		−0.92*	−1.29		[25,29,30]
Ni(TPP)	0.91*	1.00		−1.28			[28,31,32]
Cu(TPP)	0.89	1.14		−1.41			[28,33,35]
Zn(TPP)	0.68	0.99		−1.52			[33,34,36]
MoO(TPP)(OCH_3)[c]	1.11			−0.82*	−1.14	−1.43	[37–40]
Ru(TPP)(CO)	0.74	1.16*		−1.55			[20,30,41,42]
WO(TPP)(Br)	0.76	1.08		−1.01*	−1.42		
ReO(TPP)(Br)[d]	0.77	1.10		−1.04*	−1.45		

[a] Conditions: 0.5 mmol dm^{-3} porphyrin, 0.1 mol dm^{-3} tetra(*n*-butyl)-ammonium perchlorate in CH_2Cl_2 at 25°C; sweep rate 100 mV s^{-1}.

[b] For Fe(TPP)Cl a reduction potential was found at −0.07 V but this potential is due to the reduction of Fe(TPP)(ClO_4) [24].

[c] For MoO(TPP)(OCH_3) a reduction potential was found at 0.03 V but this potential is due to the reduction of MoO(TPP)(ClO_4) [39].

[d] For ReO(TPP)Br a reduction potential was found at −0.18 V but this potential will be due to the reduction of ReO(TPP)(ClO_4).

that undergoes oxidation on the porphyrin ring. In view of Manassen's results an attempt was made to find a correlation between the redox potential and the catalytic activity of metalloporphyrins. Therefore, the catalytic activity (here defined as percentage of hydroperoxide decomposed after 48 h) was plotted versus the first oxidation potential as well as versus the first reduction potential of the metalloporphyrin. In both cases scattered points were obtained. Limitation of the plots to either metal-centred or ring-centred oxidation potentials did not lead to an acceptable correlation. Remarkably, a correlation seems to exist between catalytic activity and the difference between reduction and oxidation potential except for Ru(TPP)(CO). The chemical meaning of such a correlation is not clear; it might well be a fortuitous one.

The absence of either of these correlations may be explained in the following way. Various investigations indicate that catalytic activity of e.g. manganese and iron porphyrin complexes in the presence of oxygen donors involves the sequence $Mn^{III}(TPP)^+ \rightarrow O{=}M^V(TPP)^+ \rightarrow M^{III}(TPP)^+$. Since in the present experiments Mn(TPP)Cl and Fe(TPP)Cl are always present in their $M^{III}(TPP)^+$ state, the first step of the sequence probably is the rate determining one. Formally, the overall process of this step involves a two-electron donation by the metal. Assuming that the other catalysts of tables 1 and 2 show similar behavior, the absence of any correlation might be due to the following reasons: (i) the metal centred oxidation potentials have to be compared; (ii) the oxidation potentials are one electron potentials; (iii) a reduction instead of an oxidation is rate determining.

Of the several metalloporphyrin complexes tested as catalysts in the decomposition of chhp, only the porphyrin complexes of chromium, manganese, iron, cobalt, ruthenium, and rhenium are catalytically active. The highest activity is obtained with ruthenium porphyrin, although its stability is very low. The best selectivity (chon/chol = 1.9) is obtained for the iron porphyrin. Taking into account the selectivity, stability and reactivity of the catalysts manganese, iron, chromium and ruthenium porphyrins appear to be the better choice.

An explanation for the absence or presence of catalytic activity cannot yet be given. A correlation exists neither with oxidation nor with reduction potential.

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References

[1] T. Matsuda, K. Sakai, M. Takahashi, T. Sato and A. Yashima, Japanese Patent 60-126237 (1985).
[2] D. Mansuy, J.F. Bartoli, J.C. Chottard and M. Lange, Angew. Chem. 92 (1980) 938.
[3] D. Mansuy, J.F. Bartoli, J.C. Chottard and M. Lange, Angew. Chem. Int. Ed. 19 (1980) 909.
[4] R. Guilard, J.M. Latour, C. Lecomte, J.C. Marchon, J. Protas and D. Ripoll, Inorg. Chem. 17 (1978) 1228.
[5] H.J. Ledon and F. Varescon, Inorg. Chem. 23 (1984) 2735.
[6] O. Bortolini, F. di Furia and G. Modena, J. Mol. Catal. 33 (1985) 241.
[7] H.J. Ledon, P. Durbut and F. Varescon, J. Am. Chem. Soc. 103 (1981) 3601.
[8] H.J. Ledon, F. Varescon and P. Durbut, *Chem. Uses Molybdenum*, Proc. Int. Conf. 4 (1982) 319.
[9] M. Inamo, S. Funahashi, Y. Ito, Y. Hamada and M. Tanaka, Chem. Lett. (1985) 19.
[10] G. Legemaat, W. Drenth, M. Schmidt, G. Prescher and G. Goor, J. Mol. Catal. 62 (1990) 119.
[11] G. Legemaat, Thesis, Utrecht, The Netherlands (1990).
[12] C.B. Hansen, G.J. Hoogers and W. Drenth, J. Mol. Catal. 79 (1993) 153.
[13] C.B. Hansen, G. Mul, R.B.J. Tabor and W. Drenth, Rec. Trav. Chim. Pays Bas, accepted.
[14] A.D. Adler, F.R. Longo and W. Shergalis, J. Am. Chem. Soc. 86 (1964) 3145.

[15] A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour and J. Korsakoff, J. Org. Chem. 32 (1967) 476.

[16] A.D. Adler, F.R. Longo, F. Kampas and J. Kim, J. Inorg. Nucl. Chem. 32 (1970) 2443.

[17] D.P. Rillema, J.K. Nagle, L.F. Barringer and T.J. Meyer, J. Am. Chem. Soc. 103 (1981) 56.

[18] J.H. Fuhrop and K.M. Smith, *Porphyrins and Metalloporphyrins*, ed. K.M. Smith (Elsevier, Amsterdam, 1975) p. 757.

[19] P. Fournari, R. Guilard, M. Fontesse, J.M. Latour and J.C. Marchon, J. Organomet. Chem. 110 (1976) 205.

[20] G.M. Brown, F.R. Hopf, J.A. Ferguson, T.J. Meyer and D.G. Whitten, J. Am. Chem. Soc. 95 (1973) 5939.

[21] K.M. Kadish and M.M. Morrison, J. Am. Chem. Soc. 98 (1976) 3326.

[22] L.J. Boucher and H.K. Garber, Inorg. Chem. 9 (1970) 2644.

[23] R.H. Felton, G.S. Owen, D. Dolphin, A. Forman, D.C. Borg and J. Fajer, Ann. NY Acad. Sci. 206 (1973) 504.

[24] A. Wolberg, Isr. J. Chem. 12 (1974) 1031.

[25] J. Manassen, Isr. J. Chem. 12 (1974) 1059.

[26] K.M. Kadish, G. Larson, D. Lexa and M. Momenteau, J. Am. Chem. Soc. 97 (1975) 282.

[27] K.M. Kadish, J. Electroanal. Chem. 168 (1984) 261.

[28] A. El-Kasmi, D. Lexa, P. Maillard, M. Momenteau and J.M. Savéant, J. Am. Chem. Soc. 113 (1991) 1586.

[29] F.A. Walker, D. Beroiz and K.M. Kadish, J. Am. Chem. Soc. 98 (1976) 3484.

[30] K.M. Kadish and X. Mu, Pure Appl. Chem. 62 (1990) 1051.

[31] D. Dolphin, T. Niem, R.H. Felton and I. Fujita, J. Am. Chem. Soc. 97 (1975) 5288.

[32] K.M. Kadish and M.M. Morrison, Inorg. Chem. 15 (1976) 980.

[33] R.H. Felton and H. Linschitz, J. Am. Chem. Soc. 88 (1966) 1113.

[34] A. Wolberg and J. Manassen, J. Am. Chem. Soc. 92 (1970) 2982.

[35] R.A. Binstead, M.J. Crossley and N.S. Hush, Inorg. Chem. 30 (1991) 1259.

[36] D.W. Clack and N.S. Hush, J. Am. Chem. Soc. 87 (1965) 4238.

[37] Y. Matsuda, S. Yamada and Y. Murakami, Inorg. Chem. 20 (1981) 2239.

[38] K.M. Kadish, T. Malinski and H.J. Ledon, Inorg. Chem. 21 (1982) 2982.

[39] T. Malinski, P.M. Hanley and K.M. Kadish, Inorg. Chem. 25 (1986) 3229.

[40] T. Suzuki, T. Imamura, T. Sumiyoshi, M. Katayama and M. Fujimoto, Inorg. Chem. 29 (1990) 1123.

[41] D.P. Rillema, J.K. Nagle, L.F. Barringer and T.J. Meyer, J. Am. Chem. Soc. 103 (1981) 56.

[42] X.H. Mu and K.M. Kadish, Langmuir 6 (1990) 51.

[43] J. Manassen and A. Bar-Ilan, J. Catal. 17 (1970) 86.