Highly efficient cascade-oxygen-transfer from H_2O_2 to olefins mediated by halogenated carbonyl compounds and metalloporphyrins

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Abstract

The catalytic oxidation of cyclohexene with hydrogen peroxide promoted by manganese and iron porphyrins has been studied in the presence of halogenated carbonyl compounds as co-catalysts in a dichloromethane/water biphasic medium. The efficiency of the overall catalytic process is strictly related to the nature of the co-catalyst and to the high reactivity of its perhydrate form toward metalloporphyrins in forming an high valent oxo-pororphyrin derivative. Hydrogen peroxide fixation by hexafluoroacetone hydrate provides an useful system to hamper catalyst bleaching and/or oxidant decomposition. Thus, a complete olefin conversion into oxygenated products is accomplished with a very limited excess of oxidant respect to the organic substrate. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Aqueous solutions of hydrogen peroxide (H_2O_2) are cheap and safe sources of oxygen atoms and may be used as primary oxidant in catalytic oxidative processes [1]. At least in principle and when compared to other common oxidants, H_2O_2 is ideally suitable as it features the highest active oxygen content that can be transferred to a proper substrate and the side-product resulting from the oxygen transfer process is simply water. In spite of such advantages, H_2O_2 is scarcely employed when compared with a variety of hydroperoxides, in the selective oxidations of organic substrates. The problem arises from the fact that H_2O_2 is, like other hydroperoxides, relatively stable and requires either organic [2] or inorganic [3] promoters to be converted in a more reactive form. Unlike other hydroperoxides, H_2O_2 shows two major drawbacks which hamper its use. The first one is related to the presence of water which, under the experimental conditions generally required for H_2O_2 activation, may cause the hydrolysis of the reaction products, so that, for instance, oxiranes obtained using olefins as substrates are readily converted to diols. The second disadvantage is the free radical decomposition of H_2O_2 which frequently occurs in transition-metal-catalysed oxidations. For example, in the case of manganese and iron porphyrins catalysed oxidations by H_2O_2, the most desirable route is the heterolytic O–O bond cleavage leading to

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an high-valent metal–oxo-porphyrin complex. This reactive intermediate, in a subsequent step, may transfer the oxo–oxygen to a suitable substrate [4]. When metalloporphyrins are used as catalysts, two undesirable routes are often observed, namely the homolytic decomposition of H_2O_2 (Fenton-type route) [5,6] and the reaction of the metal–oxo-porphyrin intermediate with a second H_2O_2 molecule to produce molecular oxygen and water (catalase route) [7,8]. The first of these reactions causes the catalyst degradation due to the hydroxyl radical attack to the periphery of the porphyrin ligand [9] whereas the second one induces a fast decomposition of the primary oxidant [10]. For these reasons only few oxygenation reactions have been reported using H_2O_2 as a source of oxygen using metalloporphyrins as catalyst [11–17].

In this paper, we report the use of hexafluoroacetone hydrate, HFAH, and other halogenated analogs as co-catalyst for the oxygen transfer from H_2O_2 to olefins mediated by an activated manganese porphyrin. Although HFAH, and its superior homologues, is known to act as catalyst via formation of its perhydrate derivative, HFAPH, in the epoxidation of reactive olefins by H_2O_2 [18–20], it is here reported that its utilization in the presence of an appropriate metalloporphyrin allows to speed up reaction rates up to 100-fold and completely convert the olefin employing only a slight excess of H_2O_2 (10%). Furthermore, it has been shown that the ultimate oxygen transferring agent is a metal–oxo-porphyrin intermediate which is much more effective than HFAPH, thus, allowing to carry out, in perspective, a wider range of chemical oxidative transformation [21]. For comparison purposes, the investigation has been also extended to the use of an iron porphyrin and different activators.

2. Experimental

Free base porphyrins TDCPPH$_2$, TMPH$_2$, TPPH$_2$ and their corresponding manganese and iron complexes were synthesised following literature methods [22,23]. Hexafluoroacetone trihydrate 98%, hexachloroacetone 99%, trichloroacetaldehyde hydrate 99.5%, pyridine, 4-*tert*-butylpyridine, 4-CN-pyridine, hydrogen peroxide and *n*-decane were all commercially available products and used as received.

Perlauric acid was synthesised following literature method [24].

Typically, the reactions were initiated by adding, under magnetic stirring, 50 µl of a 70% w/w aqueous solution of H_2O_2 (1.1 mmol) in a dichloromethane solution (2 ml) containing cyclohexene (1.0 mmol), the metalloporphyrin (0.00071 mmol), the nitrogen aromatic base acting as axial ligand of the catalyst (0.0068–0.17 mmol), the co-catalyst (0.007–0.18 mmol) and the appropriate GLC internal standard (*n*-decane, 0.26 mmol), in a jacketed reactor thermostated at 25°C. At appropriate time intervals, the stirring was suspended and 0.5 µl of the organic solution were withdrawn with a syringe and directly analysed by GL-chromatography on a SE-30 capillary column (0.25 mm i.d.). The concentration of the oxygenated products was measured on the basis of previously determined response factors. The identification of the reaction products was performed by comparison of the GLC data with those of authentic samples and by GC–MS analysis carried out with a Hewlett-Packard 5890 gas chromatograph, connected with a Hewlett-Packard 5970 mass selective detector, using a 15 m SE-30 capillary column, 0.25 mm i.d.

3. Results and discussion

3.1. The ultimate oxygen transferring agent in the cascade process

Preliminary experiments were addressed to the identification of the ultimate oxygen transferring agent operating in the catalytic process under investigation, by means of spectroscopic measurements.

First, we could establish that H_2O_2 alone does not transfer its oxygen to manganese 5,10,15,20-tetrakis-(2′,6′-dichlorophenyl)porphyrinate, Mn(TDCPP)Cl, under the experimental conditions adopted. In fact, even by suspending under magnetic stirring a 350-fold excess of H_2O_2 (0.7% w/w aqueous solution) to a mixture of 1.6×10^{-5} M Mn(TDCPP)Cl and 1.5×10^{-3} M 4-*tert*-butylpyridine, 4-*t*BuPy, acting as axial ligand, in dichloromethane at 25°C, no spectral change were observed in the region of the Soret band which occurs at 478 nm. After over 1 h, the spectrum showed a decrease in the intensity of the Soret band, without formation of new bands which might signal the
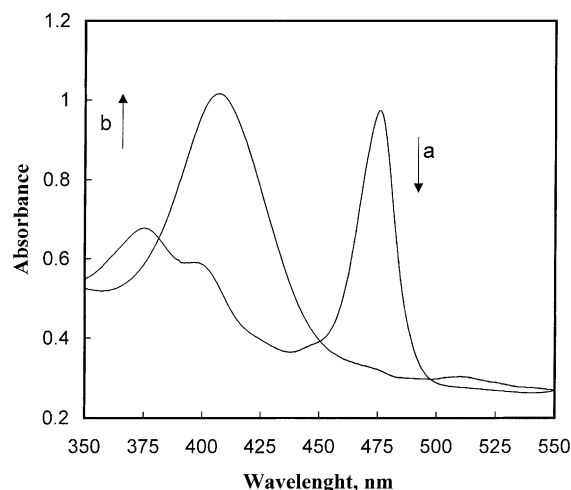
Fig. 1. (a) Spectrum of Mn(TDCPP)Cl (1.6×10^{-5} M) in the presence of 4-*tert*-butylpyridine (1.5×10^{-3} M) and H_2O_2 (formally 5.6×10^{-3} M), in dichloromethane at 25°C. (b) Spectrum of the reaction mixture upon addition of $(CF_3)_2CO \cdot 3H_2O$ (formally 0.1 M).

supporting the hypothesis of a manganese–oxo derivative formation [26]. This outcome indicates the possibility of performing efficient catalytic oxidative processes based on H_2O_2 as oxygen source, comparable to those realized with efficient but more expensive oxygen donors like peracids, iodosylbenzene, monopersulfate or ipochlorite [21]. In fact, by choosing the proper reaction conditions it is possible to convert the main part of H_2O_2 into HFAPH. This opportunity involves two relevant consequences concerning the efficiency of a catalytic process involving free H_2O_2. The first one is the suppression of undesirable side reactions. The second is the conversion of H_2O_2 in a more reactive form which can easily generate a manganese–oxo-porphyrin a well known efficient oxygen-transferring agent toward many substrates [27].

3.2. The oxidation of cyclohexene using H_2O_2 and HFAH

3.2.1. In the absence of additives

Choosing cyclohexene, here dubbed CH, as a model substrate, the oxidation reactions hereafter described were carried out in dichloromethane at 25°C under magnetic stirring, in the presence of 1.1 H_2O_2 equivalent (70% w/w aqueous solution) and 0.18 HFAH equivalent. The resulting reaction medium was, therefore, a 1/0.025 v/v dichloromethane/water mixture. The reaction evolution was monitored by GLC analysis of solution samples taken at appropriate time to determine the concentrations of the various oxidation products formed, namely

bleaching of the manganese porphyrin. By contrast, when the experiment was carried out in the presence of 0.1 M HFAH, the spectroscopic analysis of the reaction mixture revealed the almost immediate disappearance of the Mn(TDCPP)Cl Soret band and the appearance of a new broad band centered at 408 nm indicating the formation of a Mn(V) derivatives, as shown in Fig. 1 [25].

The same species adsorbing at 408 nm was also formed from Mn(TDCPP)Cl, in the presence of 4-*t*BuPy, when perlauric acid was added, thus,

Table 1
Oxidation of cyclohexene (1.0×10^{-3} mol) by H_2O_2 (1.1×10^{-3} mol) in the presence of $(CF_3)_2CO \cdot 3H_2O$ (1.8×10^{-4} mol), in dichloromethane (2 ml) at 25°C

Run	Catalyst ($\times 10^7$ mol)	Axial ligand ($\times 10^5$ mol)	V_0 ($\times 10^5$ M s^{-1})	Maximum CH conversion (%)	CH oxide selectivity (%)	2-CH-1-olo selectivity (%)	2-CH-1-one selectivity (%)	1,2-CH-diol selectivity (%)
1	–	–	8.5	60	86	–	–	14
2	–	4-*t*BuPy, 17	2.8	62	100	–	–	–
3	Mn(TDCPP)Cl, 7.1	–	8.5	70	84	1.2	1.2	13.6
4	Mn(TDCPP)Cl, 7.1	4-*t*BuPy, 17	210	100	93	–	7	–
5	Mn(TDCPP)Cl, 7.1	4-*t*BuPy, 3.4	290	100	90	6.4	3.6	–
6	Mn(TDCPP)Cl, 7.1	4-*t*BuPy, 0.68	130	94	89	5.0	2.0	4
7	Mn(TDCPP)Cl, 7.1	Pyridine, 3.4	120	100	90	2.5	7.5	–
8	Mn(TDCPP)Cl, 7.1	3-CN-Py, 3.4	17	75	77	2.0	1.5	19.5
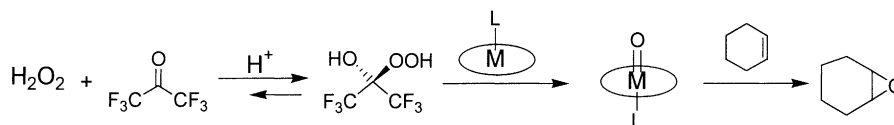
Scheme 1.

cyclohexene epoxide, 2-cyclohexen-1-olo, 2-cyclohexen-1-one and *trans*-1,2-cyclohexanediol. The pertinent results are reported in Table 1.

Under the experimental conditions of run 1, the maximum CH conversion observed is 60%, with a reaction rate of $8.5 \times 10^{-5} \, M \, s^{-1}$ and the products being the epoxide (86%) and the *trans*-diol (14%).

3.2.2. In the presence of 4-tert-butylpyridine (4-tBuPy)

Addition of 0.17 equivalent (relative to the olefin) of 4-*t*BuPy, which is normally essential for the occurring of a catalytic process based on manganese porphyrins, induces a three-fold decrease of the reaction rate (run 2). This outcome is probably due to an increased basicity of the reaction medium and to a related left-shift of the equilibrium relative to the formation of HFAPH, according to Scheme 1.

However, the selectivity of the reaction is quite remarkable, the only product being the oxirane. Again, this may be related to the increase in basicity which slows down the acid-catalysed ring opening of the oxirane formed.

3.2.3. In the presence of manganese 5,10,15,20-tetrakis(2′,6′-dichlorophenyl)porphyrinate Mn(TDCPP)Cl and nitrogen axial ligands

Addition of 7.1×10^{-4} equivalents of Mn(TDCPP)Cl relative to the olefin (in the absence of *t*BuPy) has virtually no effect on the reaction (run 3). The only detectable effect of the manganese complex is the formation of trace amounts of 2-cyclohexen-1-olo and 2-cyclohexen-1-one arising from the allylic hydroxylation of the olefin [28]. On the other hand, manganese porphyrins in the absence of a suitable nitrogen axial ligand are known to be mostly inert toward oxidants [29–31]. This is fully confirmed by the results obtained when the reaction was carried out in the presence of both Mn(TDCPP)Cl and 4-*t*BuPy (run 4). The reaction rate increases up to 100-fold (compare runs 5 and 2) and leads to a complete olefin conversion. It is noteworthy that the reaction rates reach up to 218 turnovers per minute. The relative yields in epoxide are, in each case when 4-*t*BuPy is used, larger than 90% and only minor amounts of 2-cyclohexen-1-olo and 2-cyclohexen-1-one were detected among the products.

Runs 4–8 of Table 1 show the results of some experiments aimed at establishing the effects of the concentration and of the nature of the nitrogen aromatic bases on the overall catalytic process. Runs 4–6 indicate that the reaction rates depend on the 4-*t*BuPy concentration in a non-monotonous way. In fact, the maximum initial rate is observed with an axial ligand/Mn(porphyrin) ratio of 50 (run 5) whereas at higher (250) and lower (10) ratios (respectively, runs 4 and 6) the initial velocity is significantly lower. The apparent bell-shaped rate-(base) profile may be the result of two effects acting in opposite ways as the base concentration increases. The first one leading to a rate increase is the expected result of the larger concentration of the "effective catalyst", namely the manganese complex bearing the nitrogen axial ligand. The second effect, responsible for the rates drop, is likely related to the increase in basicity of the reaction medium, and hence, a decrease of HFAPH concentration (see above and Scheme 1) and a slower formation of the oxo–manganese derivative.

Remarkable effects on the reaction rates were observed on changing the nitrogen aromatic base. Runs 5, 7 and 8 indicates that the basicity of the nitrogen base plays a relevant role in activating the manganese porphyrin toward the formation of the oxo–manganese complex. Furthermore, an increase in basicity induces a significant higher selectivity toward epoxide formation due to the resulting slower acid-catalysed hydrolysis of the oxirane.

Table 2 shows the results of experiments revealing the effect of other relevant parameters such as co-catalyst concentration, co-catalyst nature and metalloporphyrin nature, on reaction rates and selectivities.

Table 2
Oxidation of cyclohexene (1.0×10^{-3} mol) by H_2O_2 (1.1×10^{-3} mol) in the presence of various metalloporphyrins (7.1×10^{-7} mol), 4-*tert*-butylpyridine (3.4×10^{-5} mol) and various halogenated carbonyl compounds, in dichloromethane (2 ml) at 25°C

Run	Catalyst	Co-catalyst ($\times 10^{-5}$ mol)	V_0 ($\times 10^5$ M s^{-1})	Maximum CH conversion (%)	CH oxide selectivity (%)	2-CH-1-olo selectivity (%)	2-CH-1-one selectivity (%)	1,2-CH-diol selectivity (%)
9	Mn(TDCPP)Cl	(CF$_3$)$_2$CO, 3.6	110	100	85	3.5	9.5	2
10	Mn(TDCPP)Cl	(CF$_3$)$_2$CO, 0.7	74	80	87	7	4	2
11	Mn(TDCPP)Cl	(CCl$_3$)CHO, 18.1	100	65	68	10	4	3[a]
12	Mn(TDCPP)Cl	(CCl$_3$)$_2$CO, 18.1	32	78	31	9	4	9[b]
13	Mn(TPP)Cl	(CF$_3$)$_2$CO, 18.1	69	80	71	6	21	2
14	Mn(TMP)Cl	(CF$_3$)$_2$CO, 18.1	190	100	80	9	11	–
15	Fe(TDCPP)Cl	(CF$_3$)$_2$CO, 18.1	94	100	96	2.6	1.4	–
16	Fe(TDCPP)Cl	(CF$_3$)$_2$CO, 18.1[c]	27	90	96	4	–	–
17	Fe(TDCPP)Cl	(CF$_3$)$_2$CO, 18.1[d]	120	98	96	2.6	1.4	–
18	Fe(TDCPP)Cl	(CF$_3$)$_2$CO, 18.1[e]	19	24	75	5.5	5.5	14

[a] Plus 15% of *trans*-2-chlorocyclohexanol.

[b] Plus 47% of *trans*-2-chlorocyclohexanol.

[c] In the presence of 1.7×10^{-4} mol of 4-*tert*-butylpyridine.

[d] In the presence of 6.8×10^{-6} mol of 4-*tert*-butylpyridine.

[e] In the absence of 4-*tert*-butylpyridine.

The co-catalyst concentration appears to play a key role in determining the reaction rate of the overall oxidative process. In fact, a decrease in HFAH concentration, being all the other parameters unchanged, produces a steady rate decrease (runs 5, 9 and 10), indicating that HFAPH is involved in the rate determining step of the catalytic process.

3.2.4. Substituting HFAH with other halogenated carbonyl compounds

Other halogenated carbonyl compounds such as trichloroacetaldehyde, TCAA (run 11), and hexachloroacetone, HCA (run 12), show a much less pronounced catalytic effect respect than that observed employing HFAH. In fact, the initial rate increases by a factor of 35 in the case of TCAA and 11 in the case of HCA. Moreover, the chlorinated carbonyl compounds here used as co-catalyst are apparently not stable under the oxidative conditions employed. In fact, the kinetic profile of the reaction shows an initial burst in epoxide formation, followed by a slower reaction comparable to that of the blank experiment. The degradation of chlorinated co-catalyst is confirmed by GLC analysis. The epoxide selectivity in runs 11 and 12 is significantly lower than that observed in reactions employing HFAH as the result of chlorination of the oxirane leading to the corresponding chlorohydrin.

3.2.5. Substituting Mn(TDCPP)Cl with other metalloporphyrins

The Mn(TDCPP)Cl is known as one of the most resistant metalloporphyrins under oxidative conditions, particularly when H_2O_2 is present as primary oxidant [11–14]. Therefore, we checked the catalytic activity of few other fainter ganese porphyrins, namely 5,10,15,20-tetrakis(2′,4′,6′-trimethylphenyl)manganeseporphyrinate, Mn(TMP)Cl and 5,10,15,20-tetrakis-(phenyl)manganeseporphyrinate, Mn(TPP)Cl. Both the manganese porphyrins tested show a remarkable catalytic effect. In particular, in the case of Mn(TMP)Cl (run 14) a complete cyclohexene conversion and reaction rates close to those observed with Mn(TDCPP)Cl were observed. Mn(TPP)Cl, one of the most fragile first generation metalloporphyrins, affords 80% cyclohexene conversion before being bleached (run 13). Both these manganese porphyrins lead to a significantly higher allylic oxidation than in the case of Mn(TDCPP)Cl. In fact, 2-cyclohexen-1-olo and 2-cyclohexen-1-one account for 27% of the oxygenated products in the case of Mn(TPP)Cl and 20% in the case of Mn(TMP)Cl vis-a-vis the overall 10% observed in the presence of Mn(TDCPP)Cl.

Finally, the catalytic activity of an iron porphyrin, namely Fe(TDCPP)Cl, was briefly investigated (runs 15–18). Iron porphyrins usually display a lower catalase activity than the corresponding manganese

complexes [1]. However, since even their oxygenase activity and stability in the presence of H_2O_2 are significantly lower, the overall catalytic efficiency in epoxidations is generally poor [1]. Run 18 indicates that even in the absence of 4-*t*BuPy, Fe(TDCPP)Cl exhibits some catalytic activity. In fact, the initial velocity is higher than in the case of the analogue manganese porphyrin (run 3). However, under these experimental conditions the catalyst bleaching occurs quickly so that the maximum cyclohexene conversion results quite low. On the other hand, the catalyst stability and activity drastically increase when small amounts of 4-*t*BuPy are present (run 17). In fact, with a ratio 4-*t*BuPy/catalyst of 10 (run 17) and 50 (run 15), the cyclohexene conversion is quantitative and the initial rates are close to those observed in the case of Mn(TDCPP)Cl. There are two interesting differences worth of noticing. In the case of the iron complex, there is a more pronounced dependence of initial velocities from 4-*t*BuPy concentration than in that of the manganese analog. In fact, by passing from a 4-*t*BuPy/catalyst of 50 to 240, the initial rate is reduced by a factor of three whereas in the case of the manganese complex it is reduced only by a factor of 1.4. This outcome is probably related to the well known ability of iron porphyrins to bind two molecules of nitrogen base, thus, reducing the probability of forming the iron–oxo complexes [32]. Furthermore, Fe(TDCPP)Cl in this catalytic system is remarkably selective; as shown by the data of runs 15–17 ciclohexene epoxide is formed with a selectivity of 96% and only traces of products arising from allylic oxidation are detected.

In conclusion, we have shown that HFAH plays a key role in the catalytic efficiency of a cascade-oxygen-transfer process using hydrogen peroxide as primary oxidant and a metalloporphyrin as catalyst.

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