

# Transition-metal complexes for liquid-phase catalytic oxidation: some aspects of industrial reactions and of emerging technologies †

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This review presents recent developments in some important industrial processes. For homolytic systems, the similarities and specificities of the transformation of cyclohexane into adipic acid (*via* the formation and isolation of the cyclohexanol–cyclohexanone mixture) and of the process for the preparation of terephthalic acid (by oxidation of *p*-xylene) are analysed from a prospective viewpoint. Innovations in heterolytic chemistry are also presented. For example, the epoxidation of propene currently performed by the Arco–Lyondell method, which uses a molybdenum catalyst and *tert*-butyl hydroperoxide, is in competition with other systems involving recycling of the co-product, or the use of hydrogen peroxide as oxygen donor. Access to diphenols, from phenol and H<sub>2</sub>O<sub>2</sub>, is becoming more selective. New oxoperoxo complexes of titanium, rhenium, tungsten and molybdenum are presented with their potential for catalytic oxidation. Achievements of our group in the development of catalysts for C–C bond cleavage by dioxygen, and for epoxidations by H<sub>2</sub>O<sub>2</sub> are also given. Biomimetic oxidations and systems without metal catalysts feature among the innovations. These novel systems could compete with transition-metal-based chemistry for fine chemicals, but industry increasingly focuses research and development on fully inorganic systems, and there is little impact on the large scale of catalytic complexes with organic ligands.

## 1 Introduction

Homogeneous oxidation catalysis is used in many industrial scale procedures. These include the production of acetaldehyde from ethylene, of adipic acid from cyclohexane, of terephthalic acid from *p*-xylene and also that of propylene oxide by the epoxidation of propylene. The mechanisms of these reactions are fundamentally different and lead us to define three broad

areas of homogeneous catalysis oriented towards controlled selective oxidations.

The conversion of ethylene, C<sub>2</sub>H<sub>4</sub> into acetaldehyde, CH<sub>3</sub>CHO (the Wacker process) implies some of the fundamental concepts of palladium organometallic chemistry and two elementary redox processes. On the basis of experiments with deuterium-labelled ethylene it appears that the nucleophilic attack of water on ethylene coordinated to palladium is a key reaction for this purely heterolytic (non-radical) process. In this case, the involvement of dioxygen and an oxidant (copper(II) salts, heteropolyacids, “H<sub>3+n</sub>[PMo<sub>12-n</sub>V<sub>n</sub>O<sub>40</sub>]<sub>aq</sub>”, quinone, *etc.*) allows a stoichiometric reaction to be turned into a catalytic process. At present, this synthesis route is not so important as it was in the 1960s, due to the development of the Monsanto<sup>1</sup> and Cativa<sup>2</sup> processes leading directly to acetic acid. We have chosen not to develop this subject, even if the Wacker reaction still remains an important homogeneous catalytic route: it is closely related to the manufacture of vinyl acetate by heterogeneous catalysis and there are related challenging problems such as the selective oxidation of terminal olefins to methyl ketones. It is likely that using similar chemistry, an industrial process for the conversion of butenes to methyl ethyl ketone will be developed in the near future.

On the other hand, the oxidations of cyclohexane and *p*-xylene by dioxygen in air are chain reactions which imply organic free-radicals; these are considered as homolytic processes. In these systems, cobalt (III and II) and/or manganese (III and II) ions can catalyse the initiation steps. Reactions of this type, in which the organic substrates are directly oxidized by air or by pure dioxygen, are often classified as autoxidation processes.<sup>3</sup>

The conversion of propylene into its oxide implies the selective transfer of a peroxygen atom O(–I) by a heterolytic mechanism, without modification of the formal oxidation state (or oxidation number) of the metallic centre. This type of process has given rise to a new, creative chemistry for better tuned catalytic oxidation reactions. The origin of the oxygen atom is rarely dioxygen itself; another peroxygen atom-donor oxidant

† Dedicated to Professor William P. Griffith for his innovative and imaginative science.



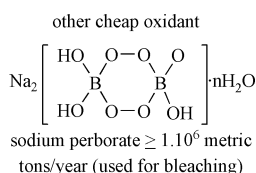
J.-M. Brégeault

*J.-M. Brégeault was born in 1939, in Paris. He graduated from I.P.E.S. and the Faculté des Sciences de Paris (Dr. ès Sciences in 1970 under the supervision of Professors G. Pannetier and P. Herpin). He was appointed assistant at the University of Orsay in 1961–1965 then, after serving in the army, at the Faculté des Sciences de Paris (1967–1987). He spent one year (1976) at Imperial College with Dr. William P. Griffith as an academic visitor. He was also a visiting scientist at the Commissariat à l'Energie Atomique and at the Institut Français du Pétrole with Drs Y. Chauvin, H. Mimoun and L. Saussine (1979–1980). He became Professor in 1988. His research interests include the design of heterogeneous catalysts based on controlled thermal treatments of hydroxohydrated precursors, homogeneous catalysis with early and late transition metals, model complexes (characterised by single-crystal X-ray diffraction and NMR), inorganic synthesis, applications of catalysis to environmentally friendly processes, thermodynamically uphill organic reactions and catalytic oxidations (with dioxygen, hydrogen peroxide or alkyl hydroperoxides as oxidant) on which he has published papers, patents, monographs and a book.*

**Table 1** Some oxygen-donor oxidants

Oxidant	Active oxygen (wt%)	By-product
H <sub>2</sub> O <sub>2</sub>	47.1	H <sub>2</sub> O
<i>t</i> -BuOOH	17.8	<i>t</i> -BuOH
HNO <sub>3</sub>	25.0	NO <sub>x</sub> , N <sub>2</sub> O, N <sub>2</sub>
N <sub>2</sub> O	36.4	N <sub>2</sub>
NaClO	21.6	NaCl
NaClO <sub>2</sub>	35.6	NaCl
NaBrO	13.4	NaBr
C <sub>5</sub> H <sub>11</sub> NO <sub>2</sub> <sup>a</sup>	13.7	C <sub>5</sub> H <sub>11</sub> NO
"KHSO <sub>5</sub> " <sup>b</sup>	10.5	KHSO <sub>4</sub>
NaIO <sub>4</sub>	29.9 <sup>c</sup>	NaI
PhIO	7.3	PhI

<sup>a</sup> *N*-Methylmorpholine *N*-oxide (NMO). <sup>b</sup> Stabilized and commercialized as the "triple salt": 2KHSO<sub>5</sub>·KHSO<sub>4</sub>·K<sub>2</sub>SO<sub>4</sub> (oxone®). <sup>c</sup> Assuming all 4 oxygen atoms are used.



must be used. This can be an organic hydroperoxide, ROOH, aqueous hydrogen peroxide, H<sub>2</sub>O<sub>2</sub> or performic, or peracetic acids, HC(O)OOH and CH<sub>3</sub>C(O)OOH, usually prepared via an equilibrium reaction. For most carboxylic acids, a strong acid catalyst must be added in order to achieve an acceptable rate of reaction. The *in situ* generation of percarboxylic acids has important applications in the production of epoxides without transition metal catalysts. Many medicines and intermediates in fine chemistry have functional groups which can be derived from epoxides. During the last 30 years, homogeneous oxidation catalysis has been used for the synthesis of epoxide intermediates and, to a lesser extent, of aldehydes or ketones. We cannot discuss in detail all the innovations and will present some examples with certain challenges which must be considered. Research in this area is very active, notably inspired by enzymatic transformations which are particularly selective.

Besides these oxidation reactions which have led to industrial processes, there are many other reactions for which catalytic systems have overall superiority, because of better economics, environmental constraints and the need for high selectivity. Much work is related to the "Green Chemistry" trend, aimed at converting often stoichiometric procedures generating large quantities of waste into simple catalytic processes without serious effluent problems, in the name of the principle of "atom economy".<sup>4</sup>

## 2 Different types of oxygen-donor oxidants

We have selected (Table 1) industrial oxygen-donating oxidants (hydrogen peroxide, *tert*-butyl hydroperoxide, nitric acid, *etc.*) and others, with more specific uses, like iodosylbenzene, PhIO, applied in very sophisticated oxidation systems with "fragile" catalysts, whose ligands are sensitive to oxidation.

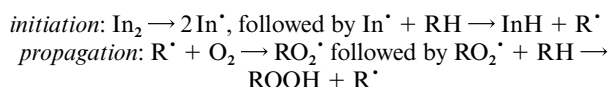
Economic factors and ecological constraints lead to a preference for oxidations involving dioxygen, hydrogen peroxide, alkyl hydroperoxides such as *t*-BuOOH (*tert*-butyl hydroperoxide – see Box 1). However, an oxidant such as concentrated nitric acid has been chosen for certain industrial processes (*vide infra*), even if it does not correspond, far from it, to an economy of matter and a chemistry which respects the environment in its initial design. It should be added that ozone, O<sub>3</sub>, as long as it is prepared and used on the site, leads to industrial productions worthy of interest (15000 tons/year of glyoxylic acid by DSM-Chemie Linz).<sup>5-7</sup>

### Box 1 Advantages of *tert*-butyl hydroperoxide, *t*-BuOOH, as oxidant for industrial synthesis

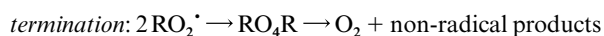
- good thermal stability (*t*<sub>1/2</sub> ≈ 520 h at 130 °C for a 0.2 M solution in C<sub>6</sub>H<sub>6</sub>)
  - fewer handling risks than 70% H<sub>2</sub>O<sub>2</sub> in water or CH<sub>3</sub>C(O)OOH
  - not very corrosive
  - leads to selective oxidations after activation by an appropriate transition metal complex (formation of alkylperoxy complexes – see Fig. 2).
  - very soluble in non-polar solvents
  - acid–base conditions close to neutrality
  - the co-product, after use of the peroxygen atom, is *tert*-butanol. This is easy to separate by distillation and can be recycled or used for other industrial processes (synthesis of methyl *tert*-butyl ether, MTBE).

#### Autoxidation mechanism: homogeneous systems for radical oxidation.<sup>3,8</sup>

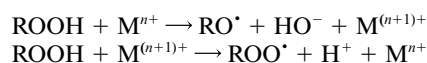
These reactions involve a large number of simultaneous and consecutive radical steps. The following elementary reactions must be considered:



(rate-controlling step)



In<sub>2</sub> is an organic radical initiator (no metal complex is involved). In certain cases a transition metal complex can take part in the initiation steps and be absolutely necessary. The following balance sheet generates R<sup>•</sup>: RH + M<sup>(n+1)+</sup> = R<sup>•</sup> + H<sup>+</sup> + M<sup>n+</sup>. Elementary Haber–Weiss reactions must also be taken into account:



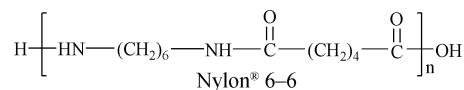
where the overall result is: 2 ROOH = RO<sup>•</sup> + ROO<sup>•</sup> + H<sub>2</sub>O, the M<sup>(n+1)+</sup>/M<sup>n+</sup> couple playing the role of catalyst.

Thus, there is another possibility for the propagation step: RO<sup>•</sup> + RH → ROH + R<sup>•</sup>. The redox potential of the M<sup>(n+1)+</sup>/M<sup>n+</sup> couple in the medium is then one of the most important factors.

## 3 Liquid-phase autoxidation: reactions induced by transition metal salts

### 3.1. Some specificities in the industrial production of adipic acid

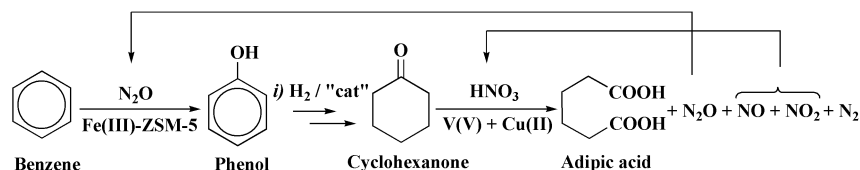
(an intermediate in the synthesis of Nylon® 6–6)



**3.1.1. Obtaining the cyclohexanol-cyclohexanone mixture: "olone".** The scheme (Fig. 1) presents the accepted mechanism<sup>8a</sup> for the first stage of this very important industrial process. This presentation is based upon the fundamentals of radical oxidation chemistry (see Box 1). Cyclohexyl hydroperoxide, C<sub>6</sub>H<sub>11</sub>OOH, is at the origin of chain reactions involving the C<sub>6</sub>H<sub>11</sub>O<sup>•</sup> and C<sub>6</sub>H<sub>11</sub>OO<sup>•</sup> radicals. The cyclohexanol-cyclo-



Scheme 1



Scheme 2 The route adopted by Solutia to recycle dinitrogen monoxide.<sup>12</sup>

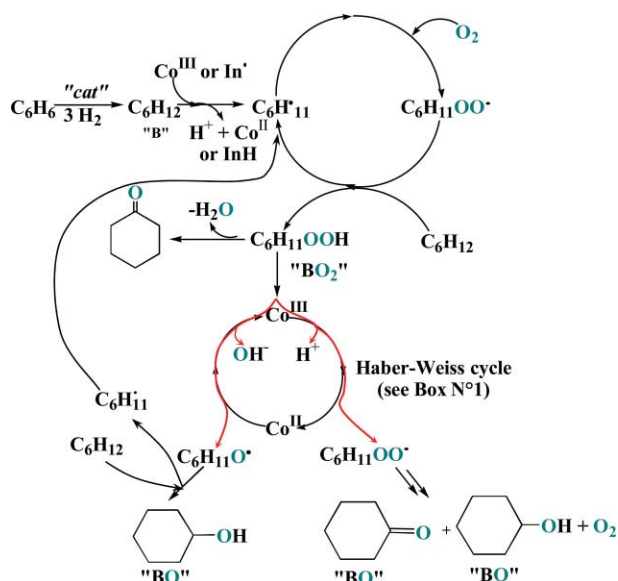


Fig. 1 Formation of cyclohexanol-cyclohexanone mixture by cyclohexane oxidation.

hexanone mixture being more easily oxidized than cyclohexane, the conversion must be limited ( $\approx 15\%$ ) to keep a good selectivity for olone (yield  $\approx 80\text{--}85\%$ ). A solution which is used, notably by DSM, is to optimize the cyclohexyl hydroperoxide content by running the first operation in passivated reactors coated with a dense, highly adherent layer of oxide and, of course, in the absence of transition metal complexes; this is followed by a decomposition oriented by the choice of the catalyst, making it possible to control the cyclohexanol/cyclohexanone ratio.<sup>3,9</sup>

**3.1.2. Obtaining adipic acid from the olone mixture (DuPont, BASF, Hüls, Rhodia, Solutia, Asahi, etc., 2–3 million metric tons per year).** The difficulties encountered in orienting the oxidation of cyclohexane to adipic acid,  $\text{HOOC}(\text{CH}_2)_4\text{COOH}$  (AA), have led to nitric acid oxidation of the olone mixture being used for the essential of the world production of this raw material. Vanadium(V) and copper(II) catalyse certain elementary steps, whether  $\text{HNO}_3$  is present or not, but the details of their catalytic role are not well known.<sup>10</sup> The precursors can be  $\text{NH}_4\text{VO}_3$  and  $\text{Cu}(\text{NO}_3)_2\text{aq}$ .<sup>8</sup> Air allows part of the nitrogen oxides to be recycled, mainly NO and  $\text{NO}_2$  which are reoxidized to  $\text{HNO}_3$ , but until recently dinitrogen monoxide was lost; whatever the case, this process remains semi-stoichiometric as regards  $\text{HNO}_3$  (see Scheme 1).

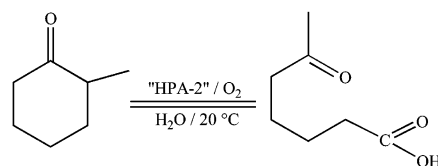
Moreover, since it is not obtained industrially by the direct oxidation of dinitrogen, but solely by the oxidation of ammonia, the dihydrogen necessary for the catalytic synthesis of  $\text{NH}_3$  is “lost” (formation of water) in the preparation of  $\text{HNO}_3$ ; the nitric acid oxidation of olone is not a process with “economy of raw materials and energy”. Since  $\nu_5$  is between 0.75 and 1.2, and  $\text{N}_2\text{O}$  contributes to the depletion of the ozone layer ( $\approx 0.30$  kg  $\text{N}_2\text{O}/\text{kg}$  AA), several improvements in the “nitric path” have been studied and some already applied on production sites in

the Western World. Certain companies have developed catalytic or thermal decomposition units to convert this gas into dioxygen and dinitrogen; other have opted for the incineration or the recycling of  $\text{N}_2\text{O}$  into nitric acid (Rhodia). Only the American company Solutia (ex-Monsanto) has opted for dinitrogen monoxide to oxidize benzene to phenol in the presence of ZSM-5 zeolites, cation-exchanged with Fe(III) (following a process developed at the Borekov Institute of Catalysis of Novosibirsk).<sup>11</sup> Several groups are working on the activation of  $\text{N}_2\text{O}$  by transition metal complexes and an economic way to prepare it. Highly active low-temperature catalysts will have to be developed.

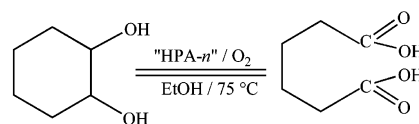
This year, Solutia is planning to convert the phenol obtained in this way into cyclohexanol/cyclohexanone by hydrogenation, the conventional oxidation of which by  $\text{HNO}_3$  into adipic acid produces the  $\text{N}_2\text{O}$  necessary for the hydroxylation of benzene<sup>12</sup> (see Scheme 2).

**3.1.3. Dioxygen (or air) for C–H activation and C–C bond cleavage.** To overcome the disadvantages related to the use of  $\text{HNO}_3$ , the oxidation of the olone mixture by dioxygen would be the ideal solution. For example, in the presence of vanadium- and molybdenum-based heteropolyacids, “ $\text{H}_{3+n}[\text{PMo}_{12-n}\text{V}_n\text{O}_{40}]_{\text{aq}}$ ”, denoted HPA- $n$ , or copper salts, cyclohexanone gives adipic acid in 72% yield at atmospheric pressure of dioxygen and a temperature of  $110^\circ\text{C}$ .<sup>10a</sup>

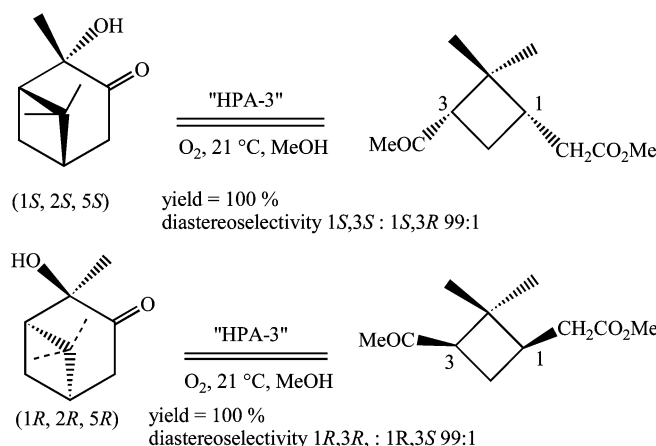
The oxidative properties of an HPA- $n$  such as “ $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]_{\text{aq}}$ ” are being extensively investigated in our group, for the cleavage of cyclic ketones, of vicinal diols, of  $\alpha$ -ketols, etc. in the presence of dioxygen under mild conditions.<sup>10</sup> For example, 2-methylcyclohexanone is cleaved at room temperature in the presence of dioxygen to form 6-oxoheptanoic acid with 90% selectivity at 96% conversion, thus with “atom economy” and high selectivity according to:



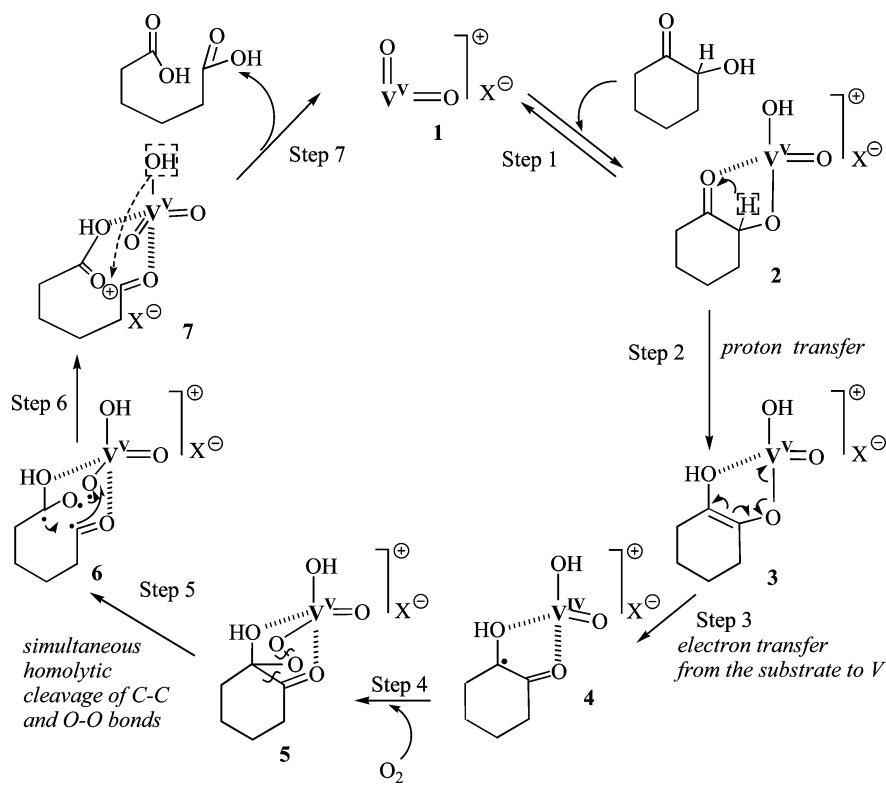
The oxidative cleavage of 1,2-cyclohexane-diol occurs at  $75^\circ\text{C}$  in ethanol and dioxygen atmosphere, and adipic acid ethylester is obtained with 90% selectivity at 62% conversion.



These reactions are of practical interest and are traditionally achieved using stoichiometric oxidants such as periodates, lead tetraacetate, etc. causing the formation of polluting residues which can be avoided by these HPA catalysts and even by some less sophisticated mononuclear species. Because of their high



**Scheme 3** Oxidative cleavage of a carbon-carbon bond at ambient temperature in fine chemistry ("HPA-3"  $\equiv$  " $\text{H}_6[\text{PMo}_9\text{V}_3\text{O}_{40}]\cdot 11\text{H}_2\text{O}$ ").<sup>13</sup>



**Scheme 4**

reactivity and structural flexibility, catalysts based on heteropoly compounds are of considerable interest and are potentially quite promising for the synthesis of intermediates and fine chemicals.


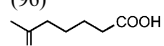

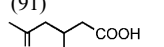

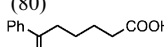




This particularly regioselective homolytic reaction can also be used in fine chemistry to valorize natural products derived from pine at ambient temperature<sup>13</sup> (see Scheme 3) or at 60 °C,<sup>14</sup> for the conversion of (–)-2-isopropyl-5-methylcyclohexanone [(–)-menthone] to (+)-3,7-dimethyl-6-oxooctanoic acid. These syntheses illustrate novel catalytic possibilities for preparing a chiral synthon from a natural product.

Some Fe(III),<sup>10</sup> Ce(IV),<sup>10,15</sup> Ru(II) and Ru(III)<sup>16</sup> complexes and monomeric vanadium species:  $\text{VOSO}_4\cdot 5\text{H}_2\text{O}$ ,  $[\text{VO}(\text{acac})_2]$ ,  $[n\text{-Bu}_4\text{N}]\text{VO}_3$ ,  $[\{\text{Ph}_3\text{SiO}\}_2\text{VO}_2]^-$ , *etc.* lead to conversions as good as the heteropolyacids, HPA-*n*, but with lower yields of  $\alpha,\omega$ -diacids, keto-acids, *etc.*<sup>16</sup> Thus, the redox and acid properties of HPA-*n* (*n* = 2–9) are better tuned.<sup>17</sup> Moreover, they are readily obtained from inexpensive reagents:  $\text{V}_2\text{O}_5$ ,  $\text{MoO}_3$ ,  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{O}_2$ .<sup>18,19</sup> The oxidative systems described with these precursors can be considered as models of dioxxygenases.<sup>17</sup> In view of the fact that monomeric vanadium species give the

same chemistry as polyoxometalates, it does not seem that cooperation of adjacent V centres is needed with  $\alpha$ -hydroxy ketones and  $\alpha$ -diols. A mechanism is depicted in Scheme 4 for the C–C bond cleavage of 2-hydroxycyclohexanone (enol form). We believe these results can help us to understand parent systems for linear alkane and cyclohexane oxidation under study in our group and the effects of promoters in these homogeneously catalysed reactions, particularly in relation to the activation of C–H and C–C bonds.

A very exciting development was the activation of dioxygen by the copper(II/I) system.<sup>10a</sup> Little attention has been devoted to performing catalytic oxidations in ionic liquids. One of these, "ethylammonium nitrate"<sup>20,21</sup> (an ionic liquid at RT) with copper chloride dihydrate and a phase transfer agent,  $\text{Q}^+\text{Cl}^-$  is excellent for preparing  $\alpha$ -chloroketones and in some cases,  $\alpha$ -hydroxy ketones, from the parent carbonyl compounds.<sup>22,23</sup> The oxidative cleavage of open-chain ketones was observed as a side-reaction. An oxidation carried out identical experimental conditions (but in the absence of  $\text{Q}^+\text{Cl}^-$ ) transforms benzylic ketones to acids and substituted cycloalkanones to the corresponding oxo-acids almost quantitatively.<sup>22</sup> *To the best of our*

**Table 2** Catalytic oxidation of substituted cycloalkanones by “Cu(II)–AcOH–H<sub>2</sub>O–O<sub>2</sub>” system at 60 °C (from ref. 24)<sup>a</sup>

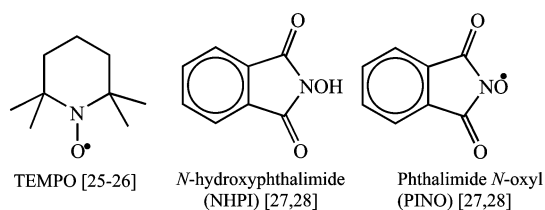
Entry	Substrate	t/h	mmol O <sub>2</sub> /mmol subst.	Conv. <sup>b</sup> (%)	Product (yield (%)) <sup>c</sup>
1		4	0.90	98	(96) 
2		6	0.72	95	(91) 
3		4	0.90	92	(80) 
4		24	0.98	80	(77) 
5		24	1.0	90	(85) 

<sup>a</sup> Catalyst: Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (1.2 mmol); solvent: AcOH–H<sub>2</sub>O (9:1 mL); substrate: 16–20 mmol; O<sub>2</sub> stream (14 L h<sup>-1</sup>) or reactor vessel equipped with a gas burette system; temperature: 60 °C. <sup>b</sup> Percentage of substrate consumed. <sup>c</sup> Yield determined by GC.

knowledge, this is the first report of a transition metal-catalysed oxidation in an ionic liquid. Other procedures were tested with expensive ionic liquids.<sup>10a</sup> Though these offer the promise of new technologies, much investment will be required to market them.

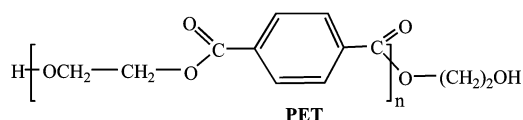
Less demanding procedures can be developed with water as a solvent or with acetic acid/water mixtures. It must be emphasized that copper(II) nitrate is catalytically more active than the acetate: the nitrate may contribute to the homolytic reaction. Subsequent cleavage of the resulting oxo-acids synthesized from  $\alpha$ -substituted cycloalkanones does not occur under these conditions. Table 2 shows that the molar ratio of oxygen uptake to substrate is about 1, which suggests that a single oxidation cleavage process is involved; *i.e.* a dioxxygenase-like system.<sup>17</sup> Such a catalytic oxidation takes advantage of the remarkable ability of copper(II) to react in a low Brønsted acidic medium, especially in inexpensive solvents,<sup>24</sup> and synergic effects can be developed as for many homolytic processes (*vide infra*).<sup>8</sup>

With catalytic reactions of this type, we could replace the polluting and non-recyclable stoichiometric oxidants and use the dioxygen of air. At present, even if the processes for the direct oxidation of cyclohexane to adipic acid have not yet led to large-scale industrial plants, nevertheless, some promising systems can be remarked upon. We would mention those involving radical catalysts such as 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) for the oxidation of alcohols<sup>25,26</sup> or that (PINO, Scheme 5) generated by *N*-hydroxyphthalimide<sup>27,28</sup> and new bimetallic catalysis systems. For the moment, we are short of information about the fate of initiators in oxidizing media: although it was claimed that NHPI is stable enough to oxidative degradation to be used in many industrial processes, there is a good deal of scepticism about this. (An alternative for the future, in the framework of heterolytic processes implies cyclohexene, obtained by a controlled catalytic hydrogenation of benzene (Asahi), and its oxidation by hydrogen peroxide catalysed by peroxy complexes of tungsten – *vide infra*.)<sup>4</sup>

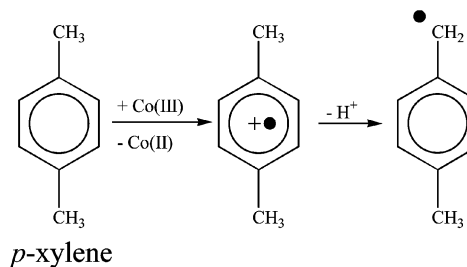
**Scheme 5** Radical initiators being studied.

### 3.2. Industrial synthesis of terephthalic acid

This is an intermediate in the preparation of poly(ethylene terephthalate), PET, one of the raw materials of the synthetic fiber industry.<sup>29–32</sup>



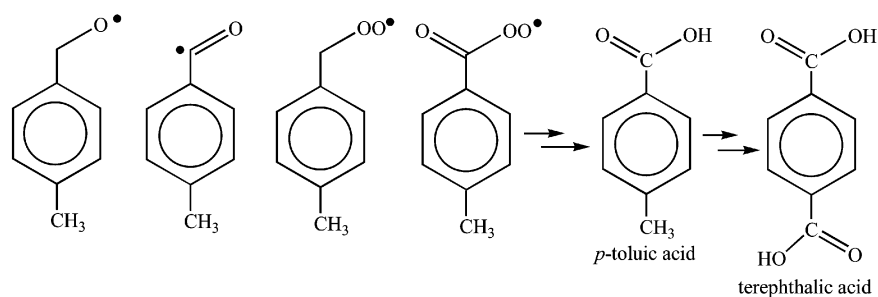
For the synthesis of the olone mixture (Fig. 1) the reaction can be initiated by means of an organic radical R<sup>•</sup>, but also by M<sup>(n+1)+</sup> (Co(III), for example). Nevertheless, for derivatives of methylbenzene, such as xylenes and particularly *p*-xylene, initiation by Co(III) is obligatory with the intermediate formation of a radical-cation:



Among the initial products one finds *p*-methylbenzaldehyde and the corresponding alcohol. Under the chosen conditions, these are oxidized to *p*-toluic acid and, in the final stage, to terephthalic acid *via* a large number of alkoxy and peroxy radicals (Scheme 6).

It must be emphasized that the oxidation of the second methyl group is much more difficult. At the industrial level two types of process have been adopted: Mid-Century/BP-Amoco and Enichem-Montedipe/Dow-Inca (more than 21 million metric tons per year) and Dynamit Nobel/Hercules (more than 4 million metric tons with BASF, DuPont, Witten, *etc.*). In the first case, the solvent is acetic acid; the catalysis system involves cobalt(III), manganese(III) and bromide ions. The reaction conditions are quite demanding (at least 200 °C; 1.5 MPa). The Br<sup>•</sup> and <sup>•</sup>CH<sub>2</sub>CO<sub>2</sub>H radicals are involved in the catalytic process; the final product is very pure terephthalic acid but “cutting-edge technology” is required.<sup>8,29–32</sup>

The second process is carried out without solvent, with Co(III) and Mn(III) and without Br<sup>-</sup> ions, therefore without Br<sup>•</sup>. The conditions are less demanding (160 °C; 0.7 MPa) but the



Scheme 6

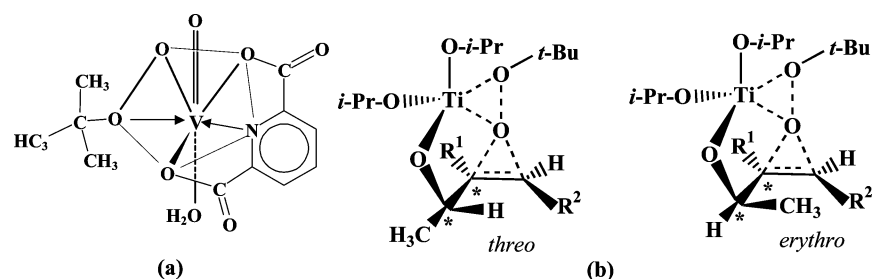


Fig. 2 Complex  $[VO(OOt-Bu)(dipic)H_2O]$  proposed as a model that shows the mode of interaction between an organic hydroperoxide and V(v) (ref. 33) and analogy with a proposed transition structure for diastereoselective epoxidation of chiral allylic alcohols by titanium *tert*-butylhydroperoxo complexes (ref. 34).

isolated monoacid (*p*-toluic acid) is more difficult to oxidize than the initial substrate. It has to be converted to the methyl ester. Under these conditions it is the co-oxidation of the ester and of *p*-xylene which leads to the diester with monomethyl terephthalate as intermediate. Recent discoveries concerning  $CO_2/O_2$  mixtures, showing that carbon dioxide plays the role of co-oxidant, can according to preliminary tests, improve the yields. These complex systems are still being studied intensively,<sup>31a</sup> as are processes designed to effect oxidations such as that of *p*-xylene to terephthalic acid *under supercritical or near supercritical* conditions for water at 375–420 °C and 240–280 MnBr<sub>2</sub>.<sup>31b,c</sup> Compared to existing industrial processes, the reaction may have the potential for a significant increase in energy efficiency and a substantial reduction in waste. There appear to be no reports of large-scale experiments. Safety problems have to be considered.

#### 4 Epoxidation of propylene and of other alkenes

Propylene epoxide cannot be obtained by a heterogeneously catalysed procedure similar to that applied to ethylene,<sup>8</sup> since over-oxidation is in this case predominant. This product at the root of the synthesis of polyether polyols used for the production of polyurethane foams, and also much used for the synthesis of propylene glycol for the elaboration of unsaturated polyester resins.

The world production, which we estimate to be greater than 5 million metric tons per year, is increasing by more than 5% annually. Up until 1970–80 this epoxide was produced from chlorohydrin essentially by stoichiometric routes;<sup>8</sup> at present catalytic routes are the most important. The oxidants are *tert*-butyl hydroperoxide,  $(CH_3)_3C(OOH)$ , or ethylbenzene hydroperoxide,  $C_6H_5CH(CH_3)(OOH)$ . Much progress results from the fact that the old chlorohydrin routes have been abandoned and that the new alkyl hydroperoxide systems are *catalytic and highly selective*, but it remains to commercialize or recycle the alcohol co-product. Thus, the 1-phenylethanol obtained as a co-product from the ethylbenzene hydroperoxide reaction is dehydrated to produce styrene; *tert*-butyl alcohol, co-produced from *tert*-butyl hydroperoxide, can be blended with gasoline to inhibit engine knock or dehydrated to make isobutylene for

conversion to methyl *tert*-butyl ether, also a gasoline blending component.

#### 4.1. Processes using alkyl hydroperoxides<sup>8</sup> (Arco process, became Lyondell-Chemical)

A peroxygen atom is rarely transferred from an alkyl hydroperoxide, ROOH, to an olefinic substrate without activation by a metallic centre. This can be achieved by different metal complexes of the left or the right of the Periodic Table ( $M = Ti(IV)$ , V(v), Mo(vi) or Co(III), Pd(II), Pt(III), Pt(IV), etc.). Fig. 2 depicts to representative model complexes.<sup>33,34</sup> The transfer of peroxygen atom to an olefinic substrate with  $d^0$  metal complexes can give epoxides or ketones, depending on the metal. Fig. 3

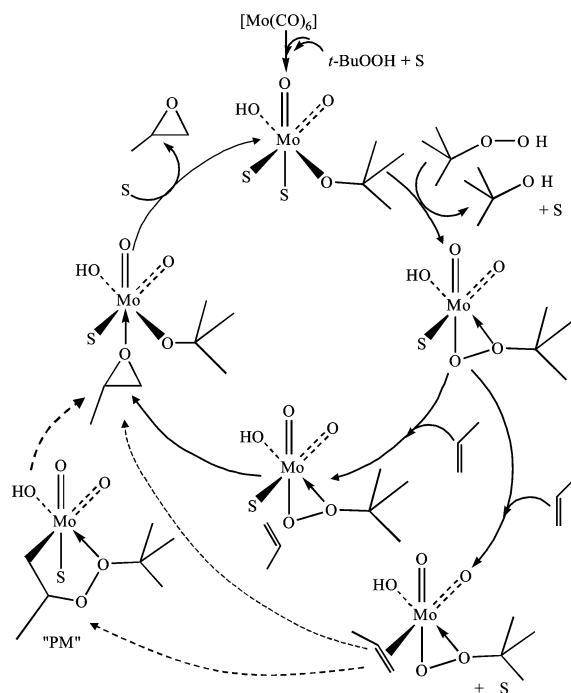
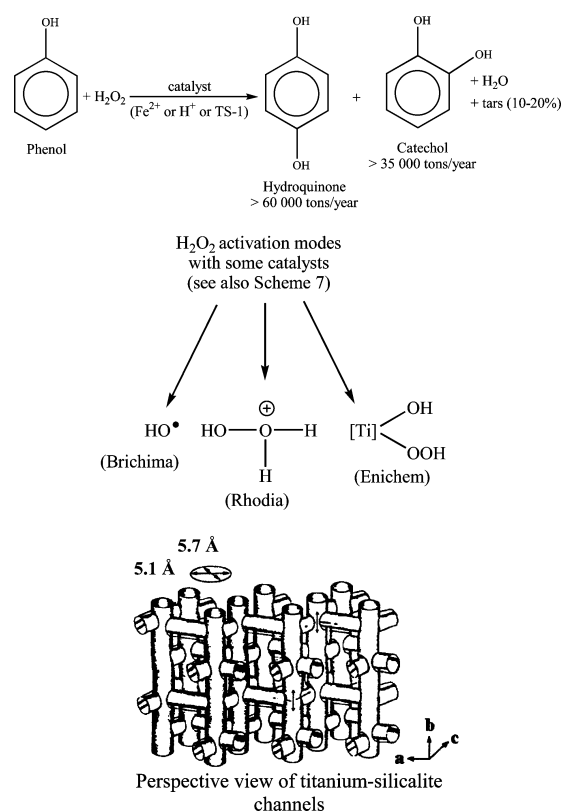


Fig. 3 Catalytic cycle for the molybdenum (vi)-catalysed epoxidation of propene by *tert*-butyl hydroperoxide (S: *tert*-butanol or solvent) (see ref. 8).

## Box 2 Titanium silicalite: a microporous catalyst resulting from the synergy of homogeneous and heterogeneous catalysis<sup>39,86</sup>

Titanium silicalite, TS-1, is a microporous solid with MFI structure (analogous to that of ZSM-5 zeolite) with channels 5.1–5.7 Å in diameter. It is a hydrophobic molecular sieve, in contrast to Ti(IV)/SiO<sub>2</sub> which is hydrophilic. It has been synthesized by Enichem, and is used, amongst other things, for the selective oxidation of phenol to catechol/hydroquinone. The efficient activation of H<sub>2</sub>O<sub>2</sub> by titanium(IV) (formation of [Ti]–OOH) leads to a phenol conversion higher (25%) than that of other processes (Brichima and Rhodia). The hydroquinone/catechol ratio is about 1. Very high performances on the epoxidation of propylene with H<sub>2</sub>O<sub>2</sub>/TS-1 must be obtained before industrial reactors can be built (secondary reactions: epoxide opening, ether formation, TS-1 deactivation, *etc.*). Many companies (Lyondell, Sumitomo, Dow, BASF, Enichem, Bayer, Degussa) are working on this process. Degussa has claimed major improvements with 98% H<sub>2</sub>O<sub>2</sub> conversion and 90% propylene oxide yield.



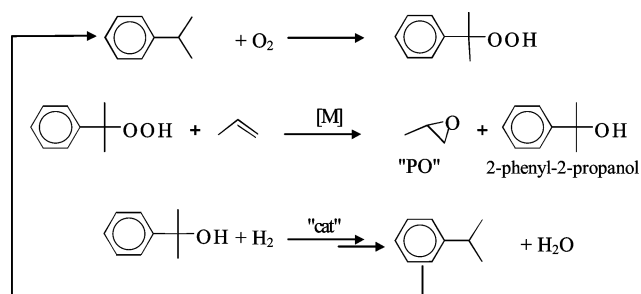
**Table 3** Hydroxylation of phenol by H<sub>2</sub>O<sub>2</sub> (comparison of four industrial processes)

Characteristics of the process	Rhodia ( <i>France &amp; USA</i> ) HClO <sub>4</sub> /H <sub>3</sub> PO <sub>4</sub> /+ ? (acid catalysis)	Brichima Fe <sup>2+</sup> /Co <sup>2+</sup> (homolytic system)	Enichem ( <i>Italy</i> ) “TS-1” titanium silicalite	NCL ( <i>India</i> ) Metallo-silicate
Phenol conversion (%)	5	10	25	20–25
Yield/H <sub>2</sub> O <sub>2</sub> converted (%)	70	50	70	75
Diphenol selectivity (%)	90	80	90	>90
Catechol/hydroquinone (%)	1.4	2.3	1	1.6
Tars (%)	10	20	<12	

shows the catalysis cycle corresponding to the industrial process with propene. The chosen precursor, here [Mo(CO)<sub>6</sub>], has been oxidized to give a *cis*-dioxo molybdenum(vi) complex.<sup>8</sup> Note that the molybdenum retains its formal oxidation state of (+vi). The interaction between the olefin and activated peroxygen atom is at the origin of the transfer; coordination of the olefin at the Mo centre cannot be totally ruled out, and the formation of a *peroxometallacycle*, denoted “PM” (Fig. 3), has been suggested by some experts! However, for functionalized olefins with electron-donating groups (allylic alcohols, *etc.*), these latter are preferentially associated with the M centre (Fig. 2(b)); no school of thought then considers that the metal–olefin bond is involved in the oxidation mechanism. Whatever the details of the mechanism, the process developed by Arco leads to a world production of well over 2 million metric tons per year. A transposition to heterogeneous catalysis has been developed by Shell Chemicals with a catalyst based on titanium(IV) on amorphous silica. Certain authors present this catalyst as the parent of titanium silicalite, TS-1 (see Box 2), better adapted to working with hydrogen peroxide than with alkyl hydroperoxides as oxidants to prepare propylene oxide.

### 4.2. Recent progress involving cumene hydroperoxide and the field of enantioselective epoxidation

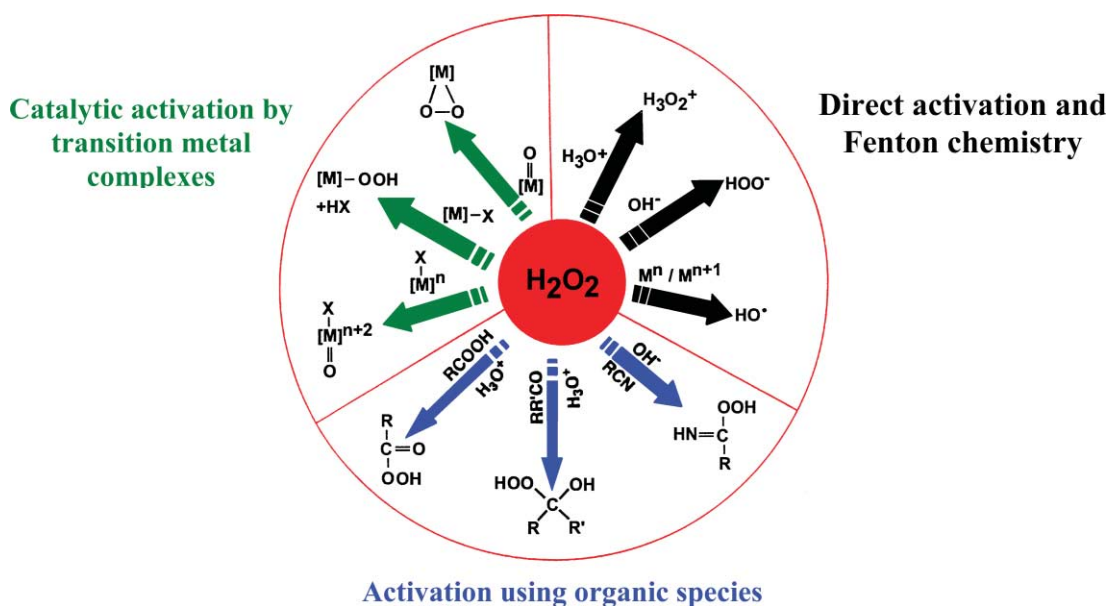
The Sumitomo process, by including a transformation of the tertiary alcohol, 2-phenyl-2-propanol, obtained as co-product, allows the cumene (isopropylbenzene) to be recycled. Fig. 4 shows the reactions involved. This route is at the commercial



**Fig. 4** Sumitomo process with cumene recycling.

stage (March 2003, Chiba-Japan, 200 kton/year). Used in the breakthrough process is a proprietary titanium-based epoxidation catalyst, which produces PO at a markedly high yield ratio.

For enantioselective syntheses of epoxides from alkyl hydroperoxides and their recent applications, leading references and work are well known.<sup>35,36</sup> In the field of fine chemicals, hydrolytic kinetic resolution (HKR procedure) for the joint productions of chiral epoxides and chiral 1,2-diols<sup>37</sup> (or  $\alpha$ -amino alcohols) are certainly worth comparing with osmium-catalysed asymmetric dihydroxylation (“K<sub>2</sub>[OsO<sub>2</sub>(OH)<sub>2</sub>]-*t*-BuOH–NMO–H<sub>2</sub>O–quinine derivatives” system)<sup>35</sup> for direct dihydroxylation of olefins. Systems must be designed for direct catalytic enantioselective epoxidation and for practical applications.



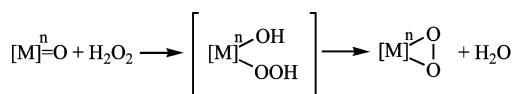
**Scheme 7** Activation of hydrogen peroxide: great possibilities some of which are used for synthetic purposes on the industrial scale.

### 4.3. Recent progress involving hydrogen peroxide

Procedures for selective oxidation and particularly epoxidation correspond to about 30% of the hydrogen peroxide consumption of the chemical industry. Many involve *peracids* and are little used because of safety problems. For this reason the search continues for *active catalysts in not only homogeneous but also heterogeneous systems* to perform controlled, selective oxidations with hydrogen peroxide without the intermediary of peracids.<sup>8,38</sup>

As previously, with alkyl hydroperoxides, the peroxygen atom of  $\text{H}_2\text{O}_2$  cannot be transferred unless it is activated in a peracid, a dioxirane or a transition metal complex (see Scheme 7) or perhaps in the polyoxides of hydrogen  $\text{HO}_n\text{H}$  ( $n > 2$ ).<sup>39</sup>

**4.3.1. Inorganic analogues of peracids: metal-peroxo and hydroperoxo systems.** Scheme 8 give a synthesis route for the oxo complex/peroxo complex reaction which is well known with  $d^0$  metal compounds:

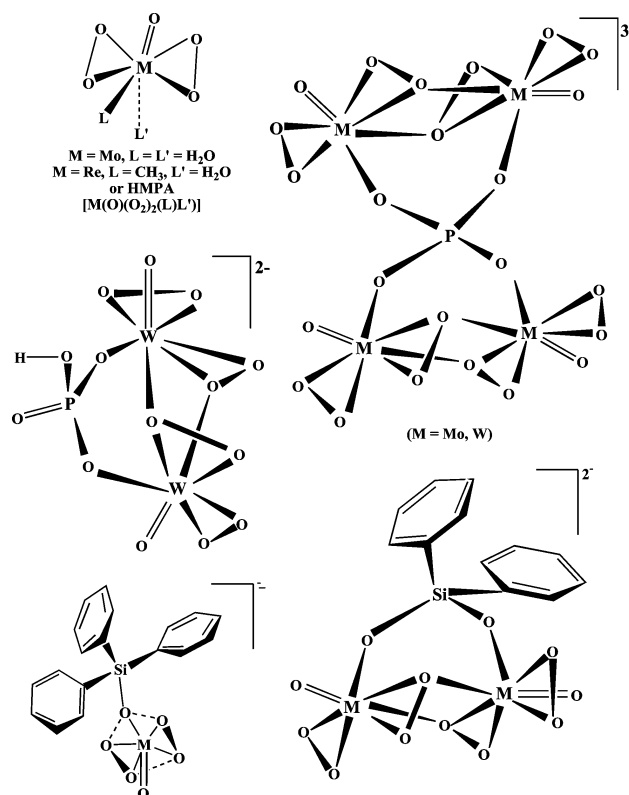


**Scheme 8**

Neither homogeneous nor heterogeneous Ti(IV)/ $\text{SiO}_2$  catalysts are effective with  $\text{H}_2\text{O}_2$  as the oxygen donor; Ti( $\text{O}_2$ ) species are seriously inhibited by water.

Compared to titanium derivated for homogeneous systems, vanadium, molybdenum, tungsten and rhenium oxoperoxo species are more reactive and lead to catalysis systems. A major breakthrough was the simultaneous discovery of two basic model peroxo complexes which were isolated in 1969 from aqueous hydrogen peroxide–molybdenum(VI) systems. Simple molybdates, “ $\text{H}_2\text{MoO}_4$ ” or “ $\text{MoO}_3 \cdot \text{H}_2\text{O}$ ” can be used for the synthesis of oxodiperoxo neutral species,  $[\text{MoO}(\text{O}_2)_2\text{L}_1\text{L}_2]$  (see Fig. 5 and refs. 40 and 41) or anionic complexes “(AmH) $\text{H}_2$ – $[\text{PO}_2(\text{Mo}_2\text{O}_{11})_2 \cdot 2\text{Am}]$ ”<sup>42</sup> (Am = 2-aminopyridine) with  $\{\text{Mo}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}$  moieties (see Fig. 5 and refs. 42 and 43). Analogues with tungsten(VI) compounds and  $\text{H}_2\text{O}_2$  were subsequently discovered and structurally characterized.<sup>44,45</sup>

The addition of phosphate, arsenate or sulfate to some peroxo species, as well as the use of polyoxometalate species such as the Keggin dodecatungstophosphate anion of  $\text{H}_3[\text{PW}_{12}\text{O}_{40}]_{\text{aq}}$  gave with aqueous  $\text{H}_2\text{O}_2$  highly effective systems for several oxidation procedures.<sup>39,45–59</sup> It was suggested<sup>46</sup> and then con-

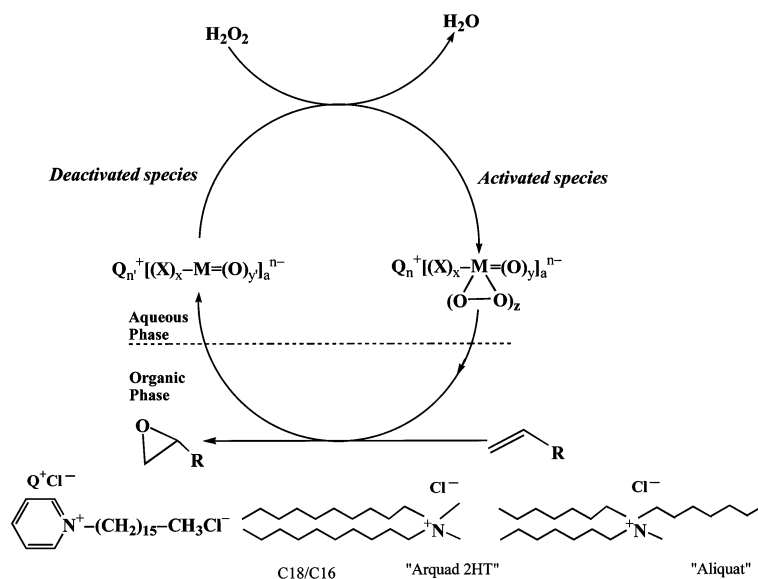


**Fig. 5** Some model oxodiperoxo complexes for the transfer of peroxygen atom (see text for references).

vincingly proved,<sup>47,48</sup> that the heteropolyanions involved in alkene epoxidation were only a precursor of the true catalysis complexes (e.g.  $[\text{PO}_4\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}_2]^{3-}$ , denoted “ $\text{PW}_4$ ”<sup>45</sup> and  $[\text{HPO}_4\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}]^{2-}$ , denoted “ $\text{PW}_2$ ”<sup>48</sup> etc.). The investigations on the mechanism of epoxidation<sup>47,48</sup> under Venturello’s conditions<sup>45</sup> ( $[\text{MO}_4]^{2-}/[\text{PO}_4]^{3-}/[\text{H}_3\text{O}]^+/\text{H}_2\text{O}_2\text{-H}_2\text{O}/$  phase transfer catalyst (PTC)/organic solvent/60 °C) and under Ishii’s conditions<sup>57,59</sup> ( $[\text{H}_3[\text{PM}_{12}\text{O}_{40}]_{\text{aq}}/\text{H}_2\text{O}_2\text{-H}_2\text{O}/$ PTC/organic solvent/60 °C) (M = Mo or W), indicate that the two catalysis systems involve common oxoperoxo anions, despite the fact that each group patented its particular set of catalyst precursors as novel chemistry.

Since then, additional studies nicely support these results.<sup>60–62</sup> From the <sup>31</sup>P NMR study of cyclohexene oxidation by  $\text{H}_2\text{O}_2$  catalysed by  $\text{H}_3[\text{PMo}_{12-x}\text{W}_x\text{O}_{40}]$  precursors in tri-*n*-butylphos-





Scheme 9 Principle of phase transfer catalysis with anionic oxoperoxo species.

phate, it has been demonstrated that various active peroxy species,  $[\text{PO}_4\{\text{M}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}]^{2-}$ , i.e. "PM<sub>4</sub>", with "PM<sub>2</sub>" (M = Mo and/or W) with different M/W ratios are formed. The catalytic performance depends of the  $x : (12 - x)$  ratio.<sup>61</sup> As opposed to these data, several cases of oxoperoxo metalates related, or not, to the Keggin structure have been reported,<sup>63-66</sup> but most of them may be precursors of active mono- to tetranuclear oxoperoxo species, drastic conditions ( $[\text{H}_2\text{O}_2]/[\text{W}] \approx 8000$ ;  $\text{H}_2\text{O}_2$  70%) are necessary to degrade  $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]_{\text{aq}}$ ,<sup>47</sup> and to generate oxoperoxo species.

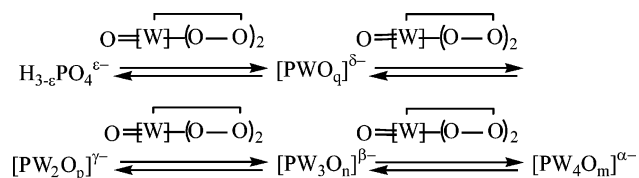
The structures of four model oxoperoxo anionic species with d<sup>0</sup> metals for "Phase Transfer Catalysis", (PTC) are presented in Fig. 5. Several companies have patented the use of mono- or polynuclear oxoperoxo tungsten complexes very similar or even identical to those described (Fig. 5). Complexes with different assembling anions have been isolated and characterized by several European teams (Germany, France, Great Britain, Italy, etc.).<sup>39,60</sup> The catalysed epoxidation reaction can be carried out in a homogeneous system, or in a two-phase system, or even by phase transfer catalysis (Scheme 9), and the catalyst can be recycled after precipitation of a partially "deperoxidized" entity [Degussa-Hüls, the second producer in the world of hydrogen peroxide ( $\geq 430000$  tons/year), is working on procedures which use  $\text{H}_2\text{O}_2$  for the preparation of propylene epoxide]. Several companies are working on tungsten-based catalysts; these processes are not yet developed and technically proven, although W(VI) oxoperoxo species are used for N-oxidation. The Holy Grail in propylene oxide technology is direct oxygen-based manufacture (or a direct  $\text{H}_2 + \text{O}_2$  process to generate  $\text{H}_2\text{O}_2$  and/or hydroperoxy species), but much work remains to be done.

The procedure described to isolate salts of  $[\text{HPO}_4\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}]^{2-}$  has been reconsidered and patented to prepare catalyst precursors to convert olefins, especially propylene, to epoxide ( $\approx 52\%$  conversion of  $\text{H}_2\text{O}_2$  with 77% selectivity to epoxide).<sup>67</sup> Several patents claim the use of "PW<sub>4</sub>", "PW<sub>2</sub>" and analogues.

A catalytic system consisting of sodium tungstate dihydrate, ( $\alpha$ -aminoalkyl)phosphonic acid and methyltriocylammonium hydrogensulfate,  $\text{Q}^+\text{HSO}_4^-$ , has been described for the epoxidation of olefins using 30% hydrogen peroxide to promote these tungsten-based systems.<sup>68</sup> The reaction proceeds in toluene in high yield or *without solvents* under *entirely halide-free conditions*. Lipophilic ammonium hydrogensulfate and an (amino-methyl) phosphonic acid are crucial for the high reactivity, as is the pH of the aqueous phase which must be maintained below 3 throughout the reaction. Note that (i) the (aminomethyl) phosphonic acid decomposes under the reaction conditions to form

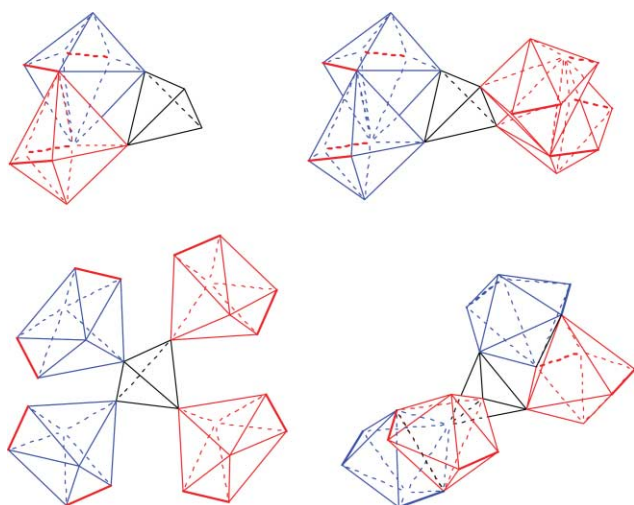
mainly  $\text{H}_3\text{PO}_4$  and/or  $[\text{HPO}_4]^{2-}$ ; (ii) the P : W ratio corresponds to that for the synthesis<sup>48</sup> of  $[\text{HPO}_4\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}]^{2-}$ , and there is a "deficiency" of  $\text{Q}^+$  ( $\text{Q}^+ : \text{P} \approx 0.5$  instead of 2 for "PW<sub>2</sub>"). The dramatic effects of the nature of  $\text{Q}^+$ , of the assembling ligand X, of the pH of the aqueous phase, of the W : X ratio, etc. have been analysed in detail.<sup>48,69,70</sup> It must be stressed that most of the experiments are run in the range 70–100 °C and there are limitations which also exist with rhenium(VII)-based systems (*vide infra*).

Procedures with tungsten might be more interesting than those involving expensive catalysts. It all depends on the price of hydrogen peroxide and the performance of the catalysts. Several groups have proposed mechanistic models of peroxy oxygen atom-to-olefin transfer,<sup>60</sup> mainly with mononuclear oxodiperoxo species. With tetranuclear complexes "PW<sub>4</sub>", "PMo<sub>4</sub>", etc.,<sup>60,70,71</sup> and probably with dinuclear parents such as "PW<sub>2</sub>" and analogues,<sup>60</sup> <sup>31</sup>P NMR gives evidence for dynamic systems at room temperature with Mo/W interchange<sup>60</sup> and fluxionality of the "PMo<sub>4-x</sub>W<sub>x</sub>" species.<sup>60,71</sup> These interconversion processes (Fig. 6), which imply breaking of the peroxy-bridged dimetallic moieties,  $\{\text{M}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}$ , into mononuclear  $\{\text{MO}(\text{O}_2)_2\}$  units with several equilibria summarized by:



This could explain the activity of these oxodiperoxo species in catalytic epoxidation.<sup>60,71</sup> These data compare well with those involving equimolar mixtures of  $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]_{\text{aq}}$  and  $\text{H}_3[\text{PW}_{12}\text{O}_{40}]_{\text{aq}}$  in pure water<sup>72,73</sup> (pH  $\approx 1.8$ ; 20 °C) where all "PW<sub>12-x</sub>Mo<sub>x</sub>" species are present after a short time (1 h). Thus, we can explain why the Keggin anions are degraded in the presence of  $\text{H}_2\text{O}_2$ , which would react with mononuclear  $\{\text{MO}_x\}$  oxo species to generate  $\{\text{MO}(\text{O}_2)_2\}$  moieties. The oxodiperoxo unit can be re-coordinated by an assembling ligand, here  $\text{PO}_4^{3-}$ . These results illustrate the contribution of NMR studies (<sup>31</sup>P and even <sup>183</sup>W) to a better understanding of homogeneous or two-phase systems;<sup>47,48</sup> solid-state NMR results on their heterogeneous counterparts are more puzzling.

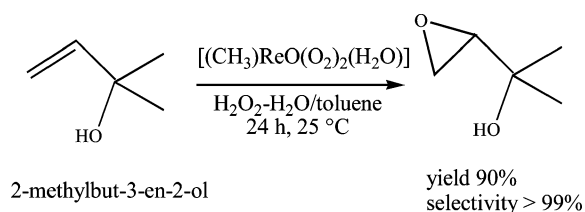
**4.3.2. A two-phase system: "CH<sub>3</sub>ReO<sub>3</sub> (MTO)/H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>O/solvent" for epoxidation of acid-sensitive epoxides.** A precursor



**Fig. 6** A schematic representation of the array of peroxy species:  $O = [W]-(O-O)_2/[PW_xO_3]^{2-}$  ( $x = 1-4$ ) likely to exist in fast and very complex equilibria. This makes it difficult to identify the kinetically active species (here  $x = 2$  or  $4$ ) [see refs. 48, 60 and 70].

based on alkyl oxo-metal chemistry is *methylrhenium(vii) oxide*  $[(CH_3)Re(O)_3]$ , MTO;<sup>74</sup> this has been proposed for epoxidation in homogeneous media with aqueous (acidic) hydrogen peroxide and *tert*-butanol mixtures.<sup>75</sup> The reaction proceeds via  $\eta^2$ -peroxorhenium intermediates  $[(CH_3)Re(O)(O_2)(L')]$  (Fig. 5).<sup>76</sup> The Lewis acidity of the complexes and the Brønsted acidity of the medium lead to subsequent reactions, mainly related to the acid-catalysed hydrolysis of the epoxide(s). PTC systems<sup>77,78</sup> and a two phase system were studied in order to avoid these undesired processes.<sup>77</sup> PTC involving onium salts (*vide supra*), for which there are dramatic effects of the nature of the cation  $Q^+$ , of the assembling ligands ( $PO_4^{3-}$ ,  $AsO_4^{3-}$ ,  $SO_4^{2-}$ ,  $O_2^{2-}$ ,  $R_2SiO_2^{2-}$ ,  $R_3SiO^-$ , etc.), of the ratio  $Q^+ : M$  where  $M = Mo, W$ , etc. is only efficient in terms of conversion and selectivity if the operating conditions are carefully optimized. With strong oxidants the alkylammonium salts, which are not environmentally benign, have to be renewed, probably because they are oxidatively degraded, as are many organic ligands in catalytic oxidation systems.<sup>78</sup> Basically, a two phase system with aqueous and organic phases is simpler than phase transfer catalysis systems involving onium salts: *the use of a two-phase medium may make it possible to suppress subsequent reactions with or without the controlled addition of tertiary amines as "proton sponges"*.<sup>70,79</sup>

Results on 2-methyl-3-buten-2-ol show that the homogeneous system "MTO/ $H_2O_2$ -*t*-BuOH" leads to mediocre results (epoxy-alcohol yield of 10% with a selectivity of 20%). For this demanding substrate, we observed the formation of 3-methyl-2-buten-1-ol, of 3-methyl-2-butenal and their oxidation products as well as ethers. A two-phase system leads to remarkable improvements for substrates and/or epoxides very sensitive to Brønsted and/or Lewis acidity,<sup>39,77,79,80</sup> as is the case here (Scheme 10).



**Scheme 10**

The improvement is due to the fact that the oxidiperoxo complex can be present in the organic phase and be regenerated in the aqueous phase. The addition of "proton sponge" (*e.g.*

**Table 4** Epoxidation of limonene with supported "PW<sub>2</sub>" species at RT

Catalyst	Substrate conversion (%)	Yield of 1a + 1b (%)	Yield of 2 (%)
PW <sub>2</sub> /Amberlyst A26®	95	94	Trace
Q'PW <sub>2</sub> /SiO <sub>2</sub>	100	95	0
Q <sub>2</sub> PW <sub>2</sub>	90	72	14

PW<sub>2</sub>:  $[HPO_4\{W_2O_2(\mu-O_2)_2(O_2)_2\}]^{2-}$ ; Q' = (*n*-Bu<sub>4</sub>N); QCl = Arquad 2HT®; Amberlyst A26® is a macroreticular resin (see ref. 70).

bipyridine) can be profitable,<sup>79</sup> even if the gradual oxidation of these amines to *N*-oxides may complicate these systems. However, the "MTO/ $H_2O_2$ - $H_2O$ /chlorinated solvent or toluene" system cannot be used to epoxidize olefins substituted with too bulky groups (sensitivity to steric effects due to substituents on the carbon  $\alpha$  to the double bond,  $-SiR_2R'$  groups, etc.).<sup>79</sup> Gradual degradation of the MTO is obviously a concern if long lifetimes are sought, but there remains scope for further research to this end as for less demanding or less expensive syntheses. Novel procedures involve alkyloxorhenium(v) complexes. It appears that methyl mono-oxo rhenium(v) complexes, with two picolinate chelating ligands  $[(CH_3)Re(O)(pic)_2]$  (or analogues) can be synthesized from rhenium or perrhenic acid.<sup>81</sup> When reacted with excess 10 or 30%  $H_2O_2$  in a two-phase system, it forms peroxy species responsible for the high catalytic activity.<sup>81</sup> Associations of the onium salts of "PW<sub>4</sub>" and "PW<sub>2</sub>" were found to be as active and selective as the two-phase systems: " $[(CH_3)Re(O)_3]$  or  $[(CH_3)ReO(pic)_2]/H_2O_2-H_2O/CH_2-Cl_2$  or toluene/proton sponge" for olefin epoxidation (cyclooctene, oct-1-ene, (*R*)-(+)-limonene,  $\alpha$ -pinene, (-)- $\beta$ -citronellene,  $\Delta$ -3-carene, etc.<sup>81,82</sup>

**4.3.3. Organic or inorganic polymer-supported catalysts for epoxidation.** TS-1 (see Box 2) is one of the most valuable heterogeneous catalysts with no homogeneous analogue, distinct from immobilized complexes on polymeric supports, although there is enormous scope in this field.

Electrostatic immobilization and covalent linking of the species on modified silica materials have been proposed. Table 4 presents promising results with "PW<sub>2</sub>" species.

It has also been possible to attach "XW<sub>2</sub>" species, X = P, As, S, Si, etc.), particularly  $[HPO_4\{W_2O_2(\mu-O_2)_2(O_2)_2\}]^{2-}$  complexes, covalently to solid supports, *e.g.* silica-based materials whether isolated titanium(IV) sites are present<sup>83</sup> or not.<sup>70</sup> An approach is the grafting of phosphate species on Ti centres of TS-1,<sup>83</sup> Ti-MCM41, Ti-SBA, etc.; these phosphate groups can anchor tungsten oxoperoxo moieties. The resulting supported catalysts, with 30%  $H_2O_2$ , are capable of converting limonene at RT mainly to 1,2-epoxides. This is a clear demonstration that tungsten is the active species, since limonene is too large to reach the titanium(IV) sites in the TS-1 micropores, and the Ti centres of the external surface cannot activate  $H_2O_2$  at RT. As for fully organic supports, polybenzimidazole/phosphoramidate systems are remarkable in eliminating metal leaching, one of the challenging problems for supported catalysts.<sup>84,85</sup>

**4.3.4. Why graft or insert d<sup>0</sup> metal species? Another interest of oxoperoxo species for the preparation of mesostructured materials.** TS-1 is a unique material, even if titanium is leached out under certain conditions.<sup>87</sup> The titanium centres must be

isolated, and many groups are looking for alternatives with  $d^0$  transition metal species and larger pore apertures than silicalite or zeolites. The synthesis of several oxoperoxo-heterosiloxanes involving the various functionalities of the silica surface,<sup>88,89</sup> such as  $[R_2SiO_2\{M_2O_2(\mu-O_2)_2(O_2)_2\}]^{2-}$ ,  $[R_3SiO\{MO(O_2)_2\}]^-$ , where  $M = Mo, W$  (Fig. 5) and more recently of  $[(Ph_3SiO)_2VO(O_2)]$ ,  $[(Ph_3SiO)_2VO_2]^-$ ,  $[(Ph_2SiO_2VO_2)_2]^{2-}$ , etc.,<sup>16,17</sup> and the recent discovery of mesoporous materials<sup>90-93</sup> have opened up new possibilities in many fields such as material chemistry, adsorption processes and especially catalysis. These results have led to an original approach for incorporating transition metal species, first into a mesostructured silica matrix, by means of low-nuclearity peroxidic species in acidic medium. This methodology was developed for  $MoO_x$ -containing MCM-41<sup>94</sup> and has been successfully extended to  $WO_x$ -MCM-41<sup>95-97</sup> and  $MoO_x$ -SBA-15.<sup>98</sup> Several physicochemical techniques show that high incorporation levels (Si/M molar ratio of the order of 35/1) can be obtained, with a nearly homogeneous distribution of the dopants in the calcined materials. In contrast, without oxoperoxo metal precursors (polyoxo route), there is generation of polyoxometalates, which lead to phase segregation of the calcined materials and formation of  $MO_3$  clusters. The very dispersive structure of the  $MO_x$ /siliceous MCM-41 promotes the generation of highly active oxidation catalysts, but initially leaching of the redox-active species into the solution is observed. To control these systems better, thermal treatments can decisively modify the resistance to attrition and to leaching in the presence of the nucleophilic reagent (*t*-BuOOH with  $MoO_x$ /siliceous MCM-41 and  $H_2O_2$  with  $WO_x$ /siliceous MCM-41). Work is in progress to control these systems better, to optimize their preparations and catalysis tests; comparisons of these mesoporous materials with amorphous silica or alumina with supported M catalysts ( $M = Mo, W$  or  $Re$ ) have to be considered. Among the factors studied (support, metal environment, nature of oxidant, etc.) all have significant influence on both the results of the reaction and the stability of the catalysts.

**4.3.5. Oxidative desulfurization, ODS.** ODS could be an important alternative to hydrodesulfurization, HDS, or a useful complementary process for deep desulfurization. The greatest advantages of ODS are the low reaction temperature and pressure in the conversion of sterically hindered dibenzothiophenes which are resistant to HDS. Phosphotungstic/ $H_2O_2$  systems with  $[PO_4\{WO_2(\mu-O_2)_2(O_2)_2\}]^{3-}$  and  $[HPO_4\{WO_2(\mu-O_2)_2(O_2)_2\}]^{2-}$  are significantly more active than the phosphomolybdic or vanadic counterparts,<sup>62</sup> and less expensive than rhenium-based systems.

#### 4.4. Selective oxidations in fine chemistry: bio-inspired catalysis systems

The importance of stereoselective reactions is emphasized in several review articles. Selective hydroxylations of alkanes and aromatic compounds or the epoxidation of alkenes catalysed by two large families of iron-based enzymes have given rise to much work in the last thirty years. Whether they concern the P-450 cytochromes or methane monooxygenases (MMO), these systems activate dioxygen *in situ* by the formation of iron peroxide complexes (Fig. 7). These then react selectively with the substrates, *via* iron species having a high degree of oxidation,  $Fe(V)/Fe(IV)$ , without forming long-lived alkyl radicals likely to propagate autoxidation reactions.<sup>99,100</sup> The structure and the reactivity of the P-450 cytochromes have been understood with the help of different metalloporphyrins, and in the case of MMO, by the synthesis of binuclear complexes of iron bridged by carboxylate ligands (Fig. 7). Biomimetic systems generally work in the presence of oxygen donors, like hydroperoxides, and more rarely with dioxygen and electron and proton sources. Iron complexes, if they have not been stabilized, lead to the

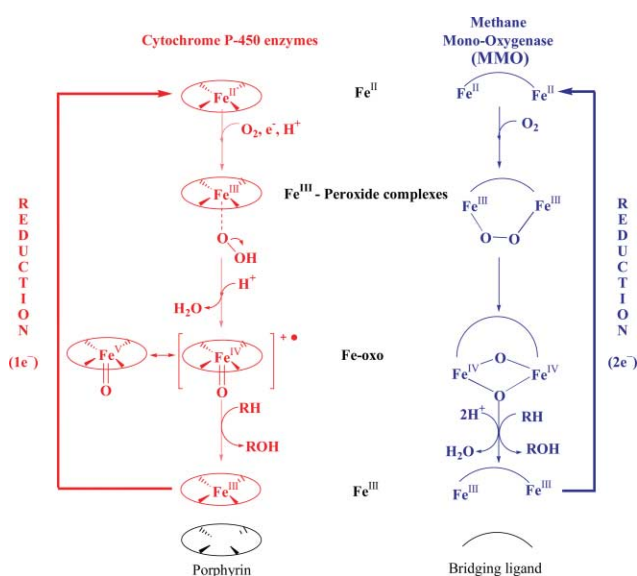
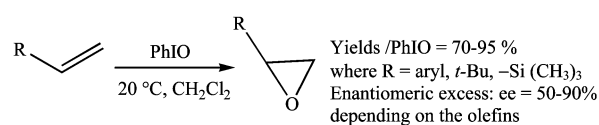


Fig. 7 Hydroxylation of alkanes: analogy between the mechanisms proposed for reactions catalysed by enzymes involving Cytochrome P-450 and MMO.

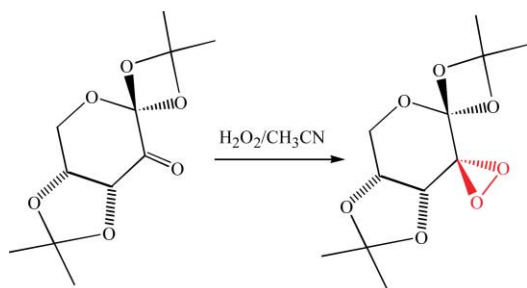
formation of alkoxy radicals which are rather unselective. Different model epoxidation systems using iodosylbenzene, PhIO (Table 1) have been developed. The enantioselective conversion of certain olefinic substrates, performed with good turnover numbers, features among recent results.<sup>101</sup> It remains, however, that such an oxidant, if it is not recyclable, is ecologically less interesting than dioxygen, hydrogen peroxide or alkyl hydroperoxide.



Very recently it was reported that hydrogen peroxide can be used in the presence of iron(II) salts and nitrogen-containing chelating ligands to epoxidize, for example, dec-1-ene<sup>102</sup> (yield 85%), or to selectively dihydroxylate oct-2-ene (yield 38%, ee 82%).<sup>103</sup> The second procedure has the advantage of avoiding the use of osmium salts and employs an oxidant,  $H_2O_2$ , which is more advantageous at the industrial level than those used in the original method. It may be a potential replacement of the Sharpless osmium-based method. Another alternative, a half-way solution, consists in using dioxygen and a two-phase system to regenerate osmium salts at a high oxidation level. The transposition to catalysis by supported complex is interesting if the active species is not leached out,<sup>104,105</sup> given the toxicity of osmium derivatives (see section 4.2).

Sometimes for iron complexes in oxidation catalysis with different oxidants, complete mass balances are lacking. Since the systems studied lead to the formation of peracids, to the oxidation of ligands and to solvent/substrate reactions, the literature data must be examined more critically. This was the case with "aldehyde (coreducer)/dioxygen/solvent/alkene" systems for catalytic epoxidation at room temperature: sophisticated complexes were synthesized, but soluble mononuclear inorganic complexes as well as inorganic oxides are also very efficient precursors or catalysts.<sup>77,106</sup>

Catalysts for oxidation reactions are not necessarily inorganic. Quite resistant organic compounds, sometimes water-soluble, can also be used (cat./substrate  $\approx 0.20$ ); these have the advantage of not contaminating the reaction products with traces of metals.<sup>107</sup> Thus, chiral ketones derived from natural products efficiently catalyse enantioselective epoxidations *via* the formation of dioxirane *in situ* (ee  $\geq 90\%$ ).



The replacement of customary terminal oxidants: oxone® (2KHSO<sub>5</sub>·KHSO<sub>4</sub>·K<sub>2</sub>SO<sub>4</sub>) or PhIO (see Table 1) by hydrogen peroxide has given a new impetus to catalysis with porphyrins.<sup>108</sup> Another important class of oxidation reactions, that of alcohols, calls for transition metals and for catalytic amounts (cat./substrate ≈ 0.03–0.05) of nitroxyl radicals in the presence of dioxygen. In this case, primary alcohols are oxidized more easily than secondary. The transformation of alcohols into carbonyl derivatives is performed traditionally in the presence of stoichiometric reactants, some of which are highly polluting (chromium salts). Its conversion to a catalytic process, more environmentally friendly and above all selective, motivates many studies. The preferential oxidation of secondary alcohols by hydrogen peroxide in the presence of Na<sub>2</sub>WO<sub>4</sub> constitutes a significant advance in this direction, all the more in that this reaction is characterized by a high chemoselectivity.<sup>26</sup> The controlled oxidation of ketones is also an essential tool for the valorization of these compounds in fine chemistry in the form of esters or lactones. The transformation of the original Baeyer–Villiger reaction, a relatively dirty procedure, into a catalytic system using hydrogen peroxide or even dioxygen is effective in the case of cyclic ketones.<sup>109</sup> Results are, however, less satisfactory with aliphatic compounds; another challenge is to equal the performances of microorganisms in the asymmetric version of the reaction.

## Conclusion

Homogeneous catalysis oriented towards controlled, selective oxidations can be very efficient: it is at the origin of procedures involving complex radical reactions and also of heterolytic routes. The systems which have been developed in industry, with productions reaching millions of tons, have no counterpart in heterogeneous catalysis. Improvements are still actively sought; those which we have presented often come from a synergy between industry, fundamental research and chemical engineering. Progress results from the treatment of by-products (N<sub>2</sub>O, NO<sub>x</sub>, etc.), or the recycling of co-products (*tert*-butanol, 2-phenyl-2-propanol, etc.). Innovations based on dioxygen or hydrogen peroxide as oxidants are at the centre of many research programmes, for a more environmentally friendly chemistry, with atom economy. It is conceivable that in the future, an integrated process will involve the manufacture and use of hydrogen peroxide for the selective oxidation of key intermediates and low-level destruction of organic pollutants. Inorganic catalysts or precursors, without any oxidizable ligand, easy to prepare and to apply, are a trump card for homogeneous, two- or even three-phase systems. We can learn a lot from more sophisticated systems which may lead to a better understanding of the living world. It remains that the modifications of organic ligands aimed at reinforcing their resistance to “oxidative degradation” can have effects on the reactivity of the active centre (shift from a heterolytic process to another, homolytic). To the best of our knowledge, industrial preparations with this sort of complex are uncommon. A good equilibrium and synergies remain to be found between experts on supports and materials and those on inorganic molecular chemistry, in order to develop transpositions to heterogeneous chemistry. Such collaborations of

experimentalists can only be fruitful if based on a broad knowledge of the different fields of chemistry allowing a good analysis of the “State of the Art”. This implies a better adaptation of teaching and a critical analysis of the literature data, so easily acquired by the networks to which we have access.

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