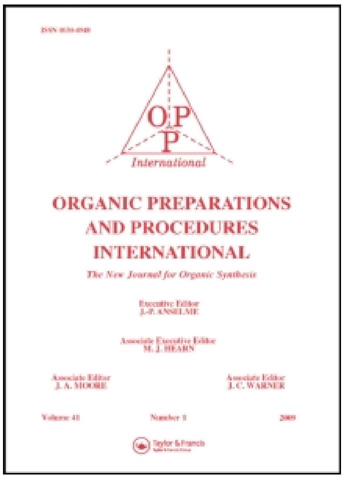

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INTRODUCTION

Oxidation is one of the most widespread processes in organic synthesis. Industrial chemists are especially interested in conducting oxidations in a simple way which avoids expensive reagents and solvents, and tedious work-up wherever possible. Therefore phase-transfer catalysis (PTC) has much appeal as a technique with great potential in industry. This simple and inexpensive method finds special attention for many applications, including oxidations and autoxidations.

In a typical PTC oxidation, the compound to be oxidized and the reagent (*e.g.*, sodium hypochlorite) are located in different phases, namely in a non-polar organic solvent and water. The catalyst is a quaternary ammonium salt, Q^+X^-, which transfers the OCl^- anion to the organic layer in form of a poorly solvated ion pair, Q^+OCl^-. A rapid reaction occurs in the organic phase, and the catalyst cation returns with the spent anion (Cl^-) to the interphase for an exchange of Cl^- for OCl^-. We shall see that the standard PTC scheme has to be modified somewhat to accomodate the title reagents. Furthermore, the joint application of transition metal compounds and phase-transfer agents combines the merits of the two methods and creates novel synthetic possibilities.

The goal of this review is to update information on the two title oxidants under PTC. Previous overviews of the subject can be found in the well-known monographs on phase-transfer catalysis.[1-4] The present compilation gathers scattered reports in a systematic fashion. The PTC chemistry of the related superoxide radical anion (from KO_2) is not included in this treatise.

I. HYDROGEN PEROXIDE

a) Extraction of Hydrogen Peroxide by R_4NX into Organic Media

If transition metal compounds and other co-factors are absent, there are two conceivable ways to extract the "oxidative power" from aqueous H_2O_2 into non-polar organic media, which do not dissolve H_2O_2 by themselves readily.

i) PTC Extraction of the Anion (HO_2^-) by Exchange for X^- in the Catalyst QX

It is well known that competitive transportation of OH^- ions from aqueous into organic media is very difficult; the hydrogen peroxide anion behaves similarly. Since H_2O_2 is a stronger acid (pK_a 11.6) than water (pK_a 15.7), the anion HO_2^- must be strongly hydrogen bonded to water and it is difficult therefore to extract it into a non-polar environment. This expectation is born out by experiment.

Firstly, it is not unexpected that hydrophilic catalysts are of little use. A catalyst partitioned predominantly into the aqueous phase cannot be of significant help. Both the anion and cation of the catalyst influence its organophilicity, and the more lipophilic the catalyst, the greater its extraction capability: 0.1 m solutions of Hex_4NBr, Aliquat 336, NBu_4Br, and NBu_4Cl extract 0.99, 0.88, 0.68, and 0.30 equivalents of H_2O_2 per equivalent of catalyst from 35% H_2O_2, respectively, into dichloromethane. Addition of a little sulfuric acid results in no change in H_2O_2 extraction characteristics, but addition of 1.25 mmol of sodium hydroxide reduces the extractable oxidizing equivalents by half.[5] Thus, extraction of the HO_2^- anion is possible but the concentration of "oxygen equivalents" will be higher under neutral or acidic conditions.

ii) PTC Extraction of Molecular H_2O_2 by Hydrogen Bonding to the Catalyst Anion X^-

Equilibration of 35% H_2O_2 and dichloromethane gives only negligible titrimetric oxygen equivalents in the organic phase, but as discussed above, the presence of Hex_4NBr, for instance, brings about an entirely different situation. It has been demonstrated repeatedly[1-4] that aqueous/organic equilibration of salts QX occurs with the transfer of a number of molecules of water (2-6 H_2O oftentimes, depending on the nature of the salt, the concentrations, the solvent and the temperature), which are hydrogen bonded to the QX salt anion. The same type of interaction is possible with H_2O_2. Indeed, crystalline complexes of the stochiometry ($R_4NX \cdots H_2O_2$) are known.[6] Here is a more detailed listing of the H_2O_2 extracting ability of various QX salts between 35% H_2O_2 and dichloromethane (equivalents of H_2O_2 transferred per equivalent of QX): $PhCH_2NEt_3Cl$ 0.013; Bu_4NHSO_4 0.1; $(Bu_4N)_2SO_4$ 0.09; Bu_4NCl 0.3; Bu_4NBr 0.68; Bu_4N-ß-naphthalenesulfonate 0.92; Aliquat 336 0.88; Hex_4NBr 0.99; Hep_4NBr 1.0; Oct_4NBr 1.0. It can be seen that the more organophilic quaternary salts are the more efficient hydrogen peroxide transfering agents indeed.[5]

b) Reactions with PTC-H_2O_2 and Base

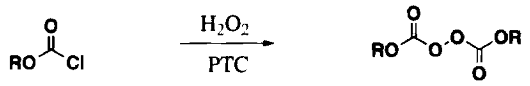
Numerous reactions can be performed advantageously by simple addition of a PT catalyst in previously reported procedures. Thus, a PTC variant of the basic hydrogen peroxide hydrolysis of nitriles to amides proceeds at room temperature in the presence of Bu_4NHSO_4 with a large rate acceleration (Eq. 1).[7]

$$\text{R–CN} \xrightarrow[\text{PTC, OH}^-]{H_2O_2} \text{R–CONH}_2 \qquad (1)$$

The phase-transfer catalyzed reactions of trialkylboranes, generated *in situ via* hydroboration of alkenes, with chloroform and aqueous sodium hydroxide, followed by treatment with hydrogen peroxide, provide an economic and convenient method for the synthesis of trialkylmethanols (Eq. 2).[8]

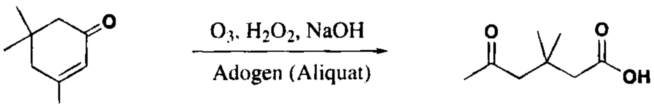
$$R_3B \xrightarrow[\text{PTC}]{\text{CHX}_3,\ \text{OH}^-} \left[R_3B\text{-}\overset{\ominus}{C}X_3\right] \longrightarrow R_3C\text{-}B(OH)_2 \xrightarrow[\text{PTC}]{H_2O_2} R_3COH \qquad (2)$$

Perfluoropropene oxide[9] can be prepared similarly in 87% yield by oxidation of $CF_2{=}CFCF_3$ with H_2O_2 in an aqueous alkaline medium in the presence of a phase-transfer catalyst selected from quaternary ammonium or phosphonium salts or from lipophilic complexing agents for cations, such as certain crown ethers. Peroxydicarbonates are produced by reaction of a chloroformate in an inert organic solvent with H_2O_2 in presence of aqueous NaOH and a phase-transfer catalyst (Eq. 3).[10]



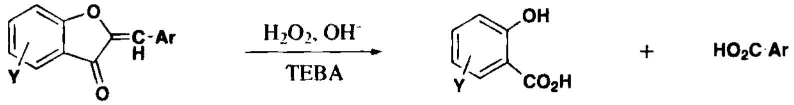
(3)

High yield oxidative cleavage of α,β-unsaturated ketones can be effected by a two-step "one-pot" procedure of ozonization and convenient work-up utilizing aqueous hydroperoxide anion as the oxidant in conjunction with a phase transfer catalyst. This is exemplified for isophorone (Eq. 4),[11]



(4)

but has been accomplished with many compounds. Thus, aurones and chalcones[12] are oxidized directly to the corresponding benzoic acids (Eqs. 5 and 6).



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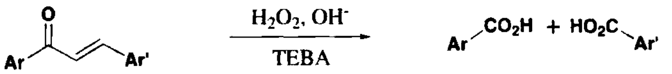
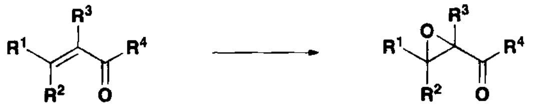


(6)

Although the epoxidation of α,β-unsaturated ketones with basic hydrogen peroxide has been known for a long time, the yield of epoxide can be nearly doubled when the reaction is carried out in a biphasic system (CH_2Cl_2-H_2O) in the presence of phase-transfer catalysts (Eq. 7).[13] The 2,3-epoxy derivative of citral for instance, is obtained in 70-77% yield (benzene, TEBA, 50% NaOH, 30% H_2O_2).[14]



(7)

The base-catalyzed hydrogen peroxide or *tert*-butylhydroperoxide mediated epoxidation of electron-poor olefins is subject to catalytic asymmetric induction. Very many types of catalysts have been tested, mostly chiral onium salts and crown ethers.[15-21] Whereas most enantiomeric excesses were low to negligible in early reports, some old and more recent developments stand out. Thus, for instance, chalcone was epoxidized in NaOH/H_2O_2/toluene with the very unusual catalyst poly-(S)-alanine and other modified polypeptides as catalysts leading to up to 97% e.e.[22]. Naphthoquinone was transformed to its epoxide with *tert*-butyl-peroxide/NaOH/toluene using benzylquinidinium chloride as catalyst giving 78% e.e.[23] Very recently, cinchona alkaloid derived catalysts were also shown to yield up to 92% e.e. from certain unsaturated ketones with H_2O_2 and LiOH as a base.[24] These PTC epoxidations can also be performed with sodium hypochlorite as oxidant. By the use of the same N-anthracenylmethyl-O-benzyl cinchona alkaloid derivatives as catalysts, epoxides of opposing configurations may be obtained with NaOCl and with H_2O_2/NaOH, although in differing enantioselectivities.[25]

Inverse PTC (extraction from the organic to the aqueous layer) has also been tested for epoxidations. Thus, various cyclodextrins were used together with H_2O_2 for the epoxidation of cinnamaldehyde and chalcone. In these cases, the organic substrate forms an inclusion complex with the cyclodextrin, and consequently optical induction might be expected. The results were somewhat disappointing in that high conversions corresponded to very low enantiomeric excesses (< 8%).[26]

It has also been found that quaternary ammonium salts can act as "multifunctional catalysts" in oxidative brominations[27] of aromatic hydrocarbons in the presence of hydrogen peroxide. Hydrohalic acids and hydrogen peroxide yield free halogens, which then can halogenate aromatic compounds. The R_4NX seems to function both as a Lewis acid and as a PT catalyst (*Scheme 1*).

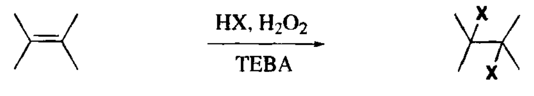
$$2HX + H_2O_2 \longrightarrow X_2 + 2H_2O$$

$$R_4NX + X_2 \longrightarrow NR_4X_3$$

$$\text{Ar—H} \xrightarrow[\text{Bu}_4\text{NBr}]{\text{HBr, H}_2\text{O}_2} \text{Ar—Br}$$

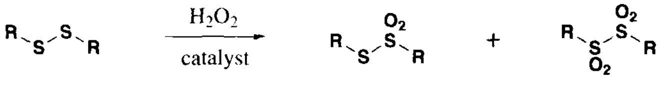
Scheme 1

In another application (Eq. 8), an ice-cooled alkene solution in CCl_4 is treated with concentrated hydrohalic acid and a little TEBA, and 30% H_2O_2 is added dropwise, whereby X_2 is liberated and consumed at once.[28] No side-products from allylic halogenation are observed, and the method has the additional advantages of a facile dosage of chlorine and fewer environmental problems.

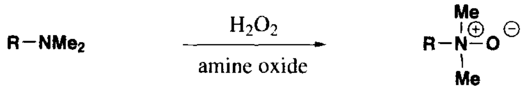


(8)

Disulfides are oxidized to thiosulfonate esters and disulfones in the presence of catalysts cetyltrimethylammonium bromide or benzyltrimethylammonium chloride (Eq. 9).[29] Relative yields depend on concentrations and conditions.


(9)

Although used rarely as such, amine oxides can also function as PT catalysts. In particular, they are able to extract H_2O_2 into organic media. A peculiar synthesis of amine oxides is catalyzed therefore by 1-10 mol % of the desired amine oxide itself (which one wants to produce in bulk). The reaction is performed in an amine/H_2O_2 emulsion for 4-8 h at 40-60° and gives 85-95% yields (Eq. 10).[30] It seems reasonable that this type of reaction might be extended to phosphine oxides.


(10)

$$R{-}NMe_2 \xrightarrow[\text{amine oxide}]{H_2O_2} R{-}\overset{\overset{\large Me}{|\oplus}}{\underset{\underset{\large Me}{|}}{N}}{-}O^{\ominus} \qquad (10)$$

Triphase catalysis is applied in the conversion of benzyl chloride into benzaldehyde. The onium salt catalyst anchored on a capsule membrane transfers H_2O_2 (which again is hydrogen bonded to the X^- of the catalyst) to the organic phase (Eq. 11). Reaction kinetics were interpreted *via* a Langmuir-Hinshelwood adsorption model.[31] The capsule membrane is a porous nylon capsule to which the catalyst has been grafted.

$$Ph{-}CH_2Cl \xrightarrow[\text{triphase catalyst}]{H_2O_2} Ph{-}CHO \qquad (11)$$

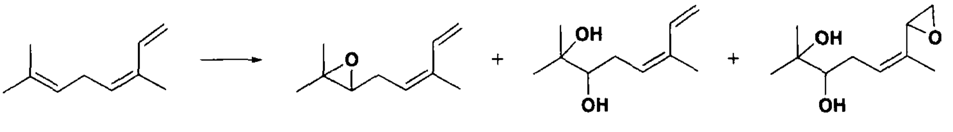
c) Reactions with PTC-H_2O_2-Heavy Metal Compounds

The PTC reactions considered earlier are straight-forward mechanistically; the catalyst assists in the transfer of an oxidizing species (hydrogen peroxide or its anion) resulting in an acceleration of the reaction. The situation becomes more complex under certain conditions to be covered now. In these cases, the transition metal compound is the real oxidant, and the lower valence state formed in the course of the conversion has to be reoxidized by H_2O_2. in principle, there are numerous ways of interplay between the many species present in the system; thus, mechanistic scrutiny as well as optimization may not be easy to perform and some of these oxidation methods are not well understood yet. Typically, a metal salt MX_n might be extracted from water by the action of a PT catalyst QX in form of an anionic complex salt $[Q_m(MX_{n+m})]$. A redox reaction furnishes another salt with lower oxidation number, which is sometimes reoxidized by the extracted H_2O_2/HO_2^-. Alternatively, the lower valent metal compound may decompose and/or return to the aqueous phase for reoxidation. Similarly, metal cations or metal oxides may be extracted by complexing agents to give neutral, cationic or anionic species. These species might or might not be stable in different oxidation states and under the reaction conditions; therefore, they may or may not return to the aqueous phase before reoxidation. The situation may be even more complex if several metal compounds are present. Clearly the role of the PT catalyst may be "multifunctional" in such cases. A detailed discussion of the very divergent proposed mechanisms is beyond the scope of this review.

Early work showed that molybdates and wolframates (tungstates) are especially inexpensive and useful carriers of oxidizing power in form of their peroxo compounds generated *in situ*. Such applications are described in this section among examples of the use of other metals. Subsequently, however, it turned out that PTC reactions with Mo and W containing heteropolyanions with phosphoric acid are often far more efficient in rates and yields. These results are discussed in Section Id.

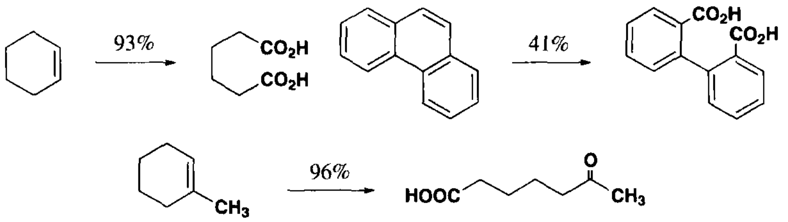
It is known that Mo(VI) and W(VI) peroxo species are formed from H_2MoO_4 and H_2WO_4 with aqueous H_2O_2. Depending on the pH, anions of these species might be PT extracted by QX into the organic phase. Alternatively, neutral peroxo compounds might be formed which complex ligands such as amine oxides or phosphoramides. These complexes $MoO(O_2)_2L{\cdot}H_2O$ are sparingly soluble in water, but can lose the coordinated H_2O easily whereas the ligand is bound more tightly. The dehydrated forms, $MoO(O_2)_2{\cdot}L$ or $WO(O_2)_2{\cdot}L$ are soluble in many organic solvents and can act as oxidants directly.

The use of a heavy-metal derived catalyst in conjunction with a phase-transfer catalyst for PTC oxidations of several typical olefins with H_2O_2 has been described in patents and journal articles. Many of these conversions are of industrial interest although selectivities are often relatively low. Thus, the H_2O_2 oxidation of cyclohexene may yield mixtures of cyclohexene oxide, 1,2-cyclohexanediol, 1-hydroxy-2-cyclohexene and cyclohexenone. Osmium tetroxide, MoO_3, and H_2WO_4 favor the two first mentioned products whereas various cocatalysts containing Se, V, Cr, Ti, Ce, Ni, Mn, Co, Pt, Fe, Pb or Pd compounds give more of the products of allylic oxidation.[32,33] Thus, (Z)-ß-ocimene yields a mixture of the shown products (*Scheme 2*) with H_2O_2 / Na_2WO_4 / $PhCH_2NOct_3Cl$.[34]



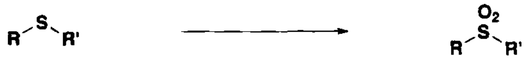
Scheme 2

A 1998 report describes a very efficient cleavage of olefins to ketones and carboxylic acids by 30% hydrogen peroxide/sodium wolframate/methyltrioctylammonium hydrogensulfate at 75-90° in ca. 8 hours.[35] As no aggressive oxidants are involved, this economical method may be of special industrial interest as an example of so-called "green chemistry" (*Scheme 3*).



Scheme 3

Oxidation of sulfides with hydrogen peroxide to sulfones is carried out in water/dichloromethane with Na_2WO_4 / Bu_4NCl (Eq. 12).[36,37] Bortolini *et al.*[38] developed a procedure which also allows the PTC oxidation of organic sulfides to sulfones and of alkenes to epoxides (Eq. 13) by employing dilute hydrogen peroxide, Mo(VI) and W(VI) catalysts, and neutral lipophilic monodentate ligands as extracting agent. These are 4-substituted pyridine N-oxides or phosphoric acid amides including HMPTA. By adjustment of the pH, neutral peroxy species are obtained for extraction. The yields and selectivities observed are generally rather high. Similar alkene epoxidations have been performed by Trost *et al.* using $(NH_4)_2MoO_4$ / H_2O_2 / NBu_4Cl in THF or DMF;[39] a similar approach is described in ref.[40] Under these conditions, alcohols (including allyl alcohols) are not oxidized, the only exception being secondary allyl alcohols which are converted into α,β-unsaturated ketones.



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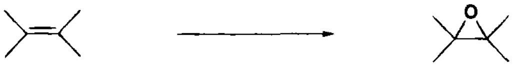
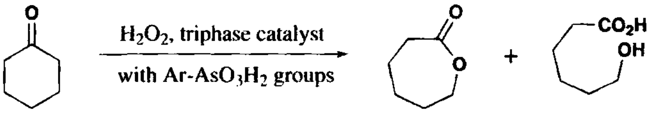


(13)

In a triphase catalytic process, this epoxidation is performed in dioxane / 90% H_2O_2 with polystyrene-ancored phenylarsonic acid.[41,42] This catalyst system is also effective for Bayer-Villiger oxidations giving lactones and ω-hydroxycarboxylic acids. (Eq. 14)[43]

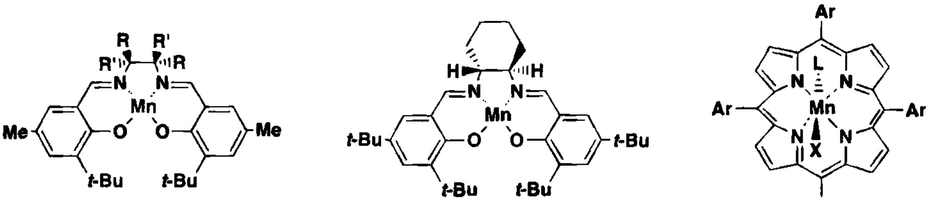


(14)

Finally, a selective epoxidation of allyl methacrylate and similar compounds is possible with 20% H_2O_2/Na_2WO_4 /PT catalyst under rigorous pH control.[44] The epoxidation occurs almost exclusively at the allylic position.

The previously mentioned polystyrene supported phenylarsonic acid tri-phase catalysts can be easily separated from the reaction mixture and recycled. In the case of water insoluble substrates, the hydrolysis of the oxidation products can be prevented. The choice of solvent, however, is critical in these triphase reactions. The solvent should at least provide a limited miscibility of aqueous hydrogen peroxide with the substrate or the products; furthermore, the solvent must interact with the catalyst beads to improve diffusion of the reagents and the products in and out of the polymer.

Quite a different approach towards epoxides was realized with hydrogen peroxide and chiral or achiral (salen)Mn(III)complexes. (1-3, *Scheme 4*). These must be used together with a nitrogen



1 R = R' = H
2 R = Ph, R' = H

3

4 L = ligand

Scheme 4

heterocycle (*e.g.* N-methylimidazole) as an axial ligand. With 1,2-dihydronaphthalene and catalysts (S,S)-**2** and (R,R)-**3**, chemical yields of 50-60% and enantioselectivities up to about 60% e.e. were obtained (Eq. 15).[45]

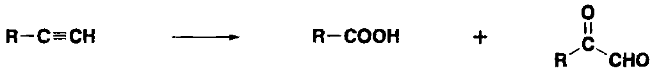
(15)

(optically active)

Still another effective system for H_2O_2 alkene epoxidation utilizes manganese(III)tetraaryl-porphyrin chloride (**4**, *Scheme 4*) as an active species (aryl = phenyl, 2,6-dichlorophenyl, or mesityl). The reaction mixtures must contain nitrogen heterocycles (1-alkylimidazoles or 4-alkylpyridines) as axial ligands (L); small amounts of benzoic acid act as accelerator. At 0° to 25°, conversions performed with CH_2Cl_2 or CH_2Cl_2 / CH_3CN as the organic phase at pH 4.5-5.0 exhibit high epoxide conversions up to 100%.[46,47] Here the complex itself acts both as phase-transfer and oxidation catalyst.

A very recent addition to the arsenal of H_2O_2 alkene epoxidation catalysts, introduced by Sharpless, is $MeReO_3$ in the presence of pyridines (3-cyano, 4-*tert*-butyl, 4-methoxy). Again dichloromethane is the organic phase, and the resultant complex acts both as oxidant and transfer agent. Di-, tri- and tetrasubstituted alkenes require 4-substituted pyridines. The pyridines enhance rates and protect the epoxides formed against ring opening, if used in the proper concentrations.[48,49] Other authors utilized the same rhenium compound together with the ligand 2,2'-bipyridine N,N'-dioxide for similar epoxidations.[50]

Terminal alkynes (R = alkyl or aryl) have been oxidized to carboxylic acids with one carbon less and to α-ketoaldehydes. (Eq. 16) The catalytic system involves dilute hydrogen peroxide, Na_2MO_4 salts [M = Mo(VI), W(VI)] and $Hg(OAc)_2$. In the absence of the mercuric salt, no oxidation takes place. Changes in the pH of the aqueous phase and the nature of the phase transfer agent (either cationic or neutral) as well as the metal (Mo or W) may lead to carboxylic acids or α-keto aldehydes more or less selectively. Na_2WO_4 at pH 0.9 gives mainly the acid (up to 90% yield) using Aliquat 336 or hexaethylphosphoramide catalysts, whereas Na_2MO_4 / Aliquat / pH 1.1-4.6 favor formation of the ketoaldehydes.[51]



$$R{-}C{\equiv}CH \longrightarrow R{-}COOH + R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CHO \qquad (16)$$

Alcohol to ketone (or aldehyde) and aldehyde to acid oxidations (Eq. 17) were possible with Trost's system mentioned earlier [$(NH_4)_2MoO_4$ / H_2O_2 / NBu_4Cl in THF] in the presence of potassium carbonate.[39,52] Control of the pH may suppress olefin epoxidation in favor of alcohol oxidation. Secondary alcohols are cleanly oxidized in the presence of primary alcohols. Sterically more hindered

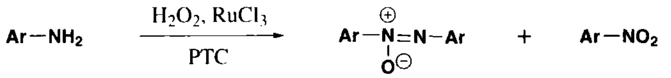
(17)

alcohols are reacted more rapidly than less hindered ones. The latter rate preference permits selective conversion of the 17-hydroxy group of several steroids into a keto function in the presence of a 3-hydroxy group. The chemoselective oxidation of aldehydes to carboxylic acids is another use of this inexpensive oxidation system. Likewise, oxidation of alcohol to ketone can be accomplished with hydrogen peroxide/Na_2WO_4 (pH 1.4) in H_2O / CH_2Cl_2 at 75° using Aliquat 336 or CTAB as PT agents.[53,54]

In the applications mentioned so far, only Mo and W compounds were used along with H_2O_2 and a PT catalyst. A more complex system described in a patent allows the oxidative cleavage of 1-octene to give heptanoic acid and heptanal in poor selectivity (37:23) (Eq. 18).[55] The solvent is *tert*-butanol, didecyldimethylammonium bromide is the PT catalyst, and MoO_3, $RuCl_3$, and a little acetic acid are present.

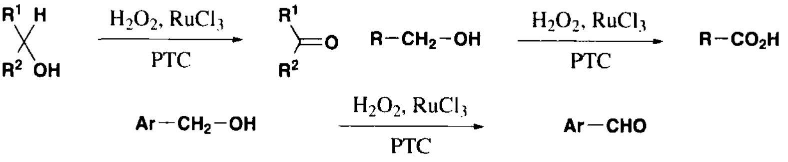
$$R{-}CH{=}CH_2 \longrightarrow R{-}COOH + R{-}CHO \qquad (18)$$

Sasson and co-workers pioneered the application of $RuCl_3$ / H_2O_2 / PT catalysts. They found that the quaternary ammonium compound QX might have a triple fold role in these cases: (a) Extraction of H_2O_2, (b) extraction of $RuCl_3$ (presumably in the form of a complex salt NR_4RuCl_4), and (c) stabilization of the ruthenium salt against reduction. In these conversions, didecyldimethylammonium bromide was the most effective PT catalyst, although others performed well also.[56,57] Thus, the $RuCl_3/H_2O_2$ oxidation of aniline at 90° in 1,2-dichloroethane yields azoxybenzene in the absence of PT catalyst or with NR_4Cl (Eq.19).[56] When R_4NBr is the catalyst, mixtures of azoxybenzene and nitrobenzene are formed and larger more lipophilic quats give relatively more nitrobenzene. Other influences on product ratio are exerted by the concentration of $RuCl_3$ and H_2O_2 in the mixture. The transition metal compounds $PdCl_2$ and $RhCl_3$ lead only to azoxybenzene, and $CoCl_2$ shows a tendency to produce nitrobenzene in addition.



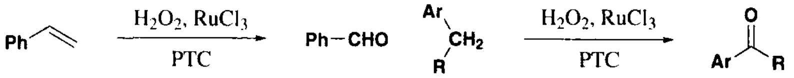
$$Ar{-}NH_2 \xrightarrow[PTC]{H_2O_2,\ RuCl_3} Ar{-}\overset{\oplus}{N}{=}N{-}Ar + Ar{-}NO_2 \qquad (19)$$

The reactions of (*Scheme 5*) were realized at a 625:1 substrate to $RuCl_3$ ratio with the following selectivities: Alcohols to carboxylic acids (60-70 %) or to ketones (100 %), benzylic alcohol to benzaldehyde (95-100%). Other metal salts ($PdCl_2$, $RhCl_3$, $MnCl_2$, $CoCl_2$) showed poor conversions and selectivities.[57] A kinetic and mechanistic investigation of this secondary alcohol to ketone oxidation indicated that the classical extraction and interphase mechanisms of PTC seemed not to be valid here. Vesicles formed from the PT agent in the organic phase were proposed as the catalytic reaction sites.[5]



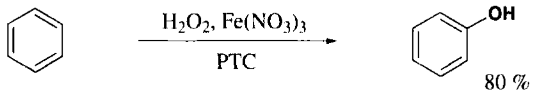
Scheme 5

The first conversion shown in Eq. 20 is also possible at pH 4-5. Only a small portion of the benzaldehyde is oxidized to benzoic acid. Replacing $RuCl_3$ by $PdCl_2$ results in the formation of acetophenone as major product.[59] Finally, the $RuCl_3$ / H_2O_2 / PTC combination permits the side-chain oxidation of alkyl benzenes to give ketones, although with relatively low selectivities (Eq. 20).[60]



(20)

A rare example of an aromatic hydroxylation by H_2O_2 / $Fe(NO_3)_3$ / cetyltrimethylammonium bromide was reported by Russian authors (Eq. 21).[6]



(21)

d) Reactions with PTC-H_2O_2-Heteropolyanions

It should be clear from the results detailed in Section Ic that the low cost of Mo(VI) and W(VI) makes them industrially most interesting species for hydrogen peroxide / phase-transfer oxidations. It has been mentioned already that rates, conversions, and selectivities could be improved, sometimes considerably, by using heteropolyanions formed from wolframate or molybdate with phosphoric acid or silicic acid. Accordingly, very many researchers have focussed their interest on such reactions. It is obvious that there are still more variables present here that influence processes, for instance relative proportions of wolframate and phosphate, addition of other metals for doping, optimal pH and catalyst to minimize unproductive decomposition of hydrogen peroxide. Some authors prefer to prepare a specific "catalyst salt" beforehand, for instance a pyridinium salt $(C_{16}H_{33}\text{-}NC_5H_5)_3(PW_{12}O_{40})$, which is then introduced into the reaction vessel. Other workers add the catalytic ingredients - sodium wolframate, phosphoric acid, and PT catalyst - directly to the mixture, so that the heteropoly acid anion is formed *in situ*. All of the reactions are chemically simple, but technically interesting processes, most of which have been dealt with in section Ic. Therefore information and references are given here in a tabular form (*Table 1*).

Some unconventional experiments and special observations warrant separate mention. Thus, the influence of ligands around peroxo niobium complexes[101] towards the efficiency of the niobium(V) catalyzed oxidation of benzyl alcohol to benzaldehyde by hydrogen peroxide has been analyzed; the use of ligands such as heteropolyphenylphosphonic acid and 2,2'-bipyridyl associated

Table 1. Oxidations with H_2O_2 / Phase Transfer Catalyst / Heteropolyanions

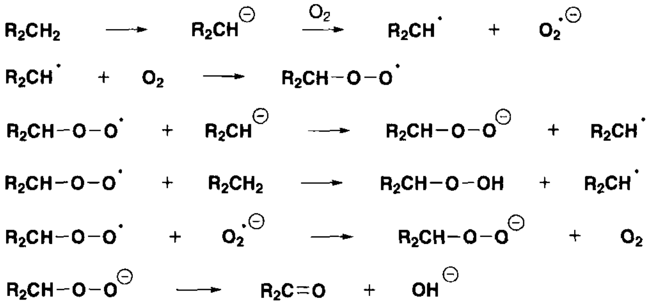
Reaction	Heteropolyanion	PT catalyst	Remarks	Ref.
alkane → ketone, alcohol	$SiRu(H_2O)W_{11}O_{39}^{5-}$	$NHex_4X$	t-BuOOH oxidant, low selectivity	62
polycyclic aromatics → dicarboxyclic acids				63
(subst.)alkene → epoxide, acrylic ester → glycidyl ester unsat.polymer → epoxide	$PW_4O_{16}^{3-}$, $PMo_{12}O_{40}^{3-}$, $WO_4^{2-} + H_3PO_4$, or $SiRu(H_2O)W_{11}O_{39}^{5-}$ or other heteropolyanions	$NMe_2(C_{18}H_{37})_2Cl$, $C_{16}H_{33}$-NC_5H_5Cl, cetylpyridiniumCl, Aliquat 336, $NHex_4X$, various others	varying selectivities and yields, sometimes strong pH influence, occasionally HOO*t*-Bu oxidant	37, 64-84
cycloalkene → dialdehyde	$PMo_{10}W_2O_{40}^{3-}$ trioctylbutylammiumX		solv.$ClCH_2CH_2Cl$	174
alkene → ketone, aldehyde, or acid	$SiRu(H_2O)W_{11}O_{39}^{5-}$	$NHex_4X$	t-BuOOH oxidant, low selectivity	56, 75,76
alkene → diol	$PW_4O_{16}^{3-}$	Aliquat 336 or $NMe_2(C_{18}H_{37})_2Cl$	fair yields, pH 1-2	31, 77, 85-87
alkene → diol or acid, aldehyde	$PW_{11}O_{39}^{7-}$, $PNiW_{11}O_{39}^{5-}$, $SiW_{11}O_{39}^{8-}$, $PFeW_{11}O_{39}^{4-}$,	NBu_4X	low selectivity	63
	or $WO_4^{2-} + H_3PO_4$ 1:2	cetyl-NMe_3Br		79
vinyl ether → α-hydroxy-acetal	peroxowolframate	cetylpyridinium X	solv.$MeOH/CH_2Cl_2$	88
alcohol → ketone	$PW_{12}O_{40}^{3-}$ WO_4^{2-}, MoO_4^{2-}, acid	Cetyl-NMe_3Br, Aliquat 336,others	high selectivity, yields; *t*-BuOOH poss.oxidant	48, 55, 89-91
vic-diol → α-hydroxy-ketone	WO_4^{2-}, $PW_{12}O_{40}^{3-}$	cetylpyridinium Cl	high yields	92
oxidative cleavage of vic-diols and alkenes	$PW_{12}O_{40}^{3-}$		fair yields in BuOH	75
α, ω-diol → lactone	$PW_{12}O_{40}^{3-}$, WO_4^{2-}, MoO_4^{2-}	various types	high yields	93-95
$RCH{=}C{=}CH_2$ + Nu- → RCHNu-CO-CH_3	$PW_{12}O_{40}^{3-}$, $PW_4O_{20}^{3-}$	cetylpyridinium X	good yields	96
allylic alcohol → glycidol	$PMo_{12}O_{40}^{3-}$		high selectivities solvent $CHCl_3$	70, 80
alkyne → carboxylic acids	$P(Mo,W)_{12}O_{40}^{3-}$, $PW_4O_{20}^{3-}$	cetylpyridinium X	high yields	82, 97
$NR_3 \rightarrow ONR_3$	$(P,As)(Mo,W)_4O_{20}^{3-}$			98
RCH_2NH_2 → oxime+nitrone	$PW_4O_{16}^{3-}$	cetylpyridinium X		99
$ArNH_2 \rightarrow ArNO + ArNO_2$	$PW_4O_{24}^{3-}$	cetylpyridinium X	best solvents $HCCl_3$, t-BuOH	100

with peroxoniobate gave efficient systems. Furthermore, phenols and their ethers are hydroxylated by H_2O_2 in the presence of an amorphous or microcrystaline zirconium phosphate (A) catalyst[102] in a solvent containing an aliphatic carboxylic acid. Amorphous (A) was digested by refluxing H_3PO_4 for 72 h and dried at 100° to give the microcrystaline Zr phosphate catalyst. The kinetics of H_2O_2 decomposition by $Na_2HPW_{12}O_{40}$ under PTC have been studied in detail.[103]

II. OXYGEN/AIR

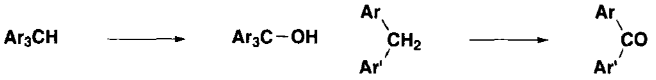
a) Autoxidations with O_2/Base/PTC

Concentrated aqueous or powdered sodium hydroxide and a phase-transfer catalyst permit the generation of high concentrations of carbanions from C-H acids which have a pK_a of up to about 23.[1-4] Less acidic compounds are deprotonated less efficiently, but H/D exchange experiments indicate that low equilibrium concentrations of carbanions must be formed from variously substituted benzyl compounds and methyl group carrying aromatics. Furthermore, the presence of a *vic*-diol as co-catalyst brings about a rate acceleration of deprotonation of C-H acids of a pK_a up to about 27 by NaOH/PTC.[104,105] The carbanion so formed can be trapped by molecular triplet oxygen, and a radical chain reaction will occur that is often formulated as follows for attack at CH_2 groups (*Scheme 6*):



Scheme 6

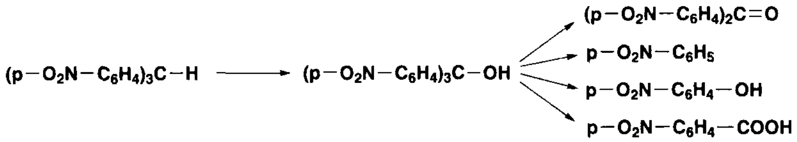
Tertiary CH groups may be transformed into a hydroperoxide or into an alcohol similarly. A number of investigators have used this PTC method with air or oxygen at 1 atm pressure and room temperature (or slightly above). High yield test transformations included fluorene to fluorenone (87%),[106-109] diarylmethanes to benzophenones (up to 98%),[107,110-114] triarylmethanes to triarylcarbinols (62%) (Eq. 22).[110,112,113] Recently even fullerene could be polyhydroxylated to give $C_{60}(OH)_{24\text{-}26}$ with aqueous sodium hydroxide and Bu_4NOH,[116] although the mechanism must be of a different type.



$$Ar_3CH \longrightarrow Ar_3C{-}OH \qquad Ar(Ar')CH_2 \longrightarrow Ar(Ar')CO \tag{22}$$

Solvent/base/catalyst combinations can be varied widely and were optimized only occasionally. Typical systems are: benzene/aqueous KOH/18-crown-6,[115] THF/solid KOH/cryptand[2.2.2],[106] DMF/solid KO*t*Bu/PEG,[102] chlorobenzene or toluene/50% NaOH/Aliquat 336 or Bu_4NHSO_4,[111] DME/KOH/18-crown-6,[112] benzene/KOtBu/PEG 6000.[110]

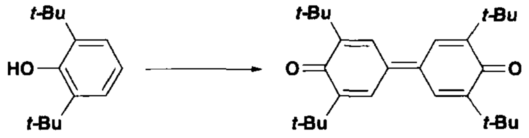
Depending on reaction conditions and substituents on the starting materials, further oxidative or base-induced reactions can occur to a greater or lesser extent. Thus, tris-(p-nitrophenyl)methane may give all of the following products (*Scheme 7*).[113]



Scheme 7

Similarly, special forcing conditions can transform diphenylmethane not only into benzophenone but also into benzoic acid and triphenylcarbinol and a little phenol.[110,112,113] The basic PTC autoxidations can be extended to various related substrates, such as xanthene to xanthone, acridane to acridone, 9,10-dihydroanthracene to anthracene, 1,4,4a,5,8,8a,9a,10a-octahydroanthraquinone to anthraquinone[109] and dihydroquinacridone to quinacridone.[117] _

These conditions were also shown to be useful for oxidation of 2 6-di-*tert*-butylphenol to the respective diphenoquinone (Eq. 23).[118] In an industrial application, colored pitch specks in the pulp of tropical woods were bleached oxidatively with O_2 / NaOH / NR_4X.[11]

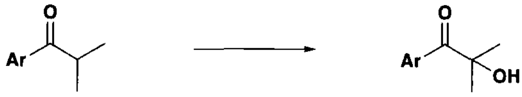


(23)

Many research groups concentrated on the oxidation of methyl groups in aromatic and heteroaromatic compounds (Eq. 24) using principally the same methodology as above, although the conditions were sometimes more severe (5-6 atm. pressure of O_2 or air, higher temperature, longer reaction time); 20% yields of *m*- or *p*- halobenzoic acids were obtained after 5 hours at 60° with KOH-DME-crown. Whereas *p*-fluorotoluene was not oxidized, the *m*-isomer was.[113] *o*-Xylene gave 92% of a mixture of *o*-toluic and phthalic acid after 20 hours at 100°;[110] the picolines[107,113,120] and methylpyrazine[121] were oxidized similarly. β-Methylnaphthalene gave 80% of β-naphthoic acid (96 h, 20°), but the process was sluggish for α-methylnaphthalene.[113] When p-nitrotoluene was oxidized with KOH and various PEG catalysts in toluene, only 1,2-*bis*-(*p*-nitrophenyl)ethane and 1,2-*bis*-(*p*-nitrophenyl)ethene were obtained.[122] The selectivity changed towards partial formation of *p*-nitrobenzoic acid if ultrasonication was applied under the same PTC conditions.[122]

$$\mathrm{Ar{-}CH_3} \longrightarrow \mathrm{Ar{-}COOH} \qquad \mathrm{Hetaryl{-}CH_3} \longrightarrow \mathrm{Hetaryl{-}COOH} \qquad (24)$$

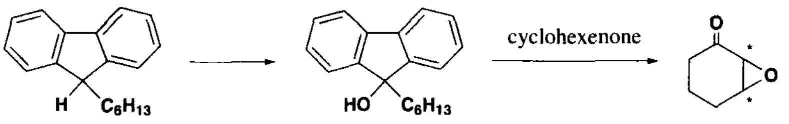
α,α-disubstituted aryl and vinyl ketones can be hydroxylated with O_2, NaOH, Aliquat 336 or TEBA in CCl_4 or benzene (Eq. 25, 26).[123-125]



(25)

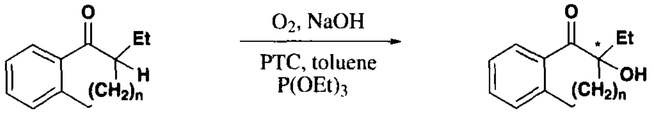
(26)

In a more elaborate application of this reaction, 9-hexylfluorene was converted into its hydroperoxide (TEBA, aq. NaOH, pyridine/toluene, up to 93%). Without isolation of the product, α,β-unsaturated ketones were added thereafter, and 57-85% yields of the epoxy ketones were obtained after stirring overnight (Eq. 27).[126,127] If the achiral PT catalyst TEBA was replaced by chinchonine derived chiral catalysts, the epoxide end-product was formed in optical yields of 9-54 %.[126,127]



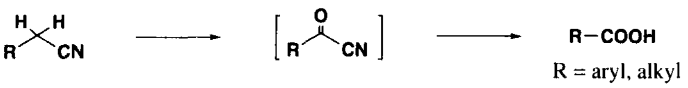
(27)

An enantioselective hydroxylation reaction championed by Shioiri and coworkers[128] (Eq.28) iscuted in the presence of triethyl phosphite to reduce the intermediate hydroperoxide *in situ*. Cinchoninium derived PT catalysts are the most enantioselective ones, giving up to 74% e.e. Subsequently, many other chiral catalysts (crown ethers[129], various onium salts[130-132]) were tested in this conversion. None compared to the quinine or cinchonine derivatives; very low e.e.s were recorded when 18-crown-6 or Bu_4NBr were combined with a chiral *vic*-diol cocatalyst.[105] It is important to remember in this context that certain *vic*-diols accelerate deprotonations (see above).



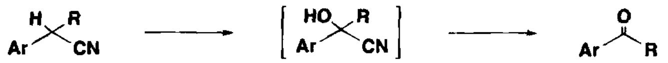
(28)

Quite a different chemistry unfolds when base/O_2 /PTC is applied to nitriles. Cyano compounds are transformed into carboxylic acids with one carbon less by aeration of THF solutions containing potassium *tert*-butoxide and 18-crown-6. Acyl cyanides are the primary reaction products that are hydrolyzed immediately. The best yields (about 90%) are obtained with long chain aliphatic compounds without α-branching (Eq. 29).[133]



(29)

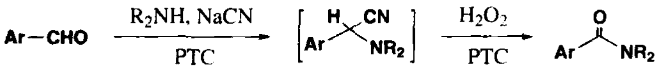
Secondary nitriles bearing a sufficiently acidic α-hydrogen atom (aromatic or heteroaromatic benzylic) are decyanated oxidatively to ketones, oftentimes in excellent yields (Eq. 30).[134-138]



(30)

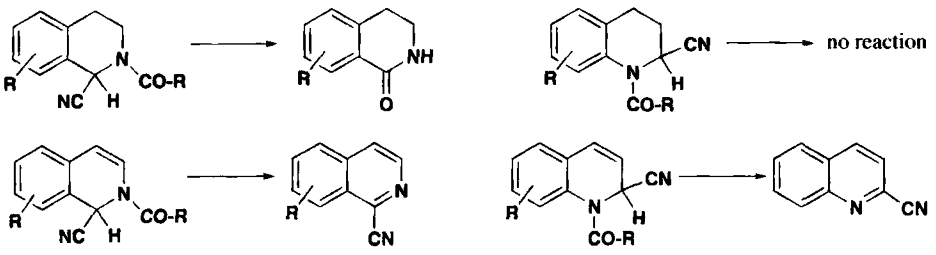
Typical reaction conditions are: bubbling oxygen through a vigorously stirred benzene solution with 50% NaOH and TEBA or NBu_4Br present;[137]sometimes DMSO is added.[136] The procedure is applied even in one step of the total synthesis of a highly active estrogen.[138]

Substituted N,N-dialkylbenzamides are formed from α-dialkylaminoacetonitriles (Eq. 31) quite analogously with 50 % NaOH/DMSO/TEBA by bubbling oxygen through for 4 hours.[139]



(31)

Rozwadowska and Brózda showed that similar oxidative decyanations occur with dihydroisoquinoline Reissert compounds[140,141] giving dihydroisocarbostyrils (*Scheme 8*). Not unexpectedly, dihydroquinoline Reissert compounds are inert towards oxidative attack. PTC/O_2/base reactions of both types of Reissert compounds themselves lead to aromatization in contrast.[140]



Scheme 8

It may also be mentioned, that the base/O_2/crown ether catalyzed oxidation of aniline to azobenzene was reported.[108]

b) Oxidations with O_2-PTC

There are some reports in which a different PTC process is initiated where no base or metal compound is involved; again hydroperoxides are the primary products or intermediates. Thus, a high temperature (120-140°) oxidation of *p*-xylene in chlorobenzene/water proceeds with lipophilic quaternary ammonium bromides alone, and the process has been investigated thoroughly. At low conversions *p*-toluic acid, *p*-tolualdehyde, and *p*-tolylmethanol can be found in addition to the hydroperoxide, the amount of the acid increasing with time. In this case, the extracted bromide is the source of bromine radicals which initiate the peroxidation in the interpretation of Harustiak *et al.*[142,143] Many reaction variables were well scrutinized by Csányi and Jáky in the autoxidation of tetralin, cyclohexene and cumene, again without the presence of base;[144] the presence of hydroperoxide (either added or formed *in situ*) is essential for these PTC catalyzed oxidations.[144] Rate accelerations are found also with certain non-ionic, anionic, and cationic surfactants. In these cases, the cation of the catalyst influences the rates, and the presence of water decreases the reaction rate. Interestingly, chloride as catalyst counter ion often (but not always) has a higher catalytic activity than bromide or iodide. Csányi and Jáky's mechanistic concept is at variance with that of Harustiac.[142,143] They feel that the catalyst interacts with the hydroperoxide intermediate facilitating its homolysis.[144] Indeed, the decomposition of 1-tetralin hydroperoxide to tetralone can be shown to be catalyzed by lipophilic R_4NX compounds, X = Cl or Br. The cation R_4N^+, however, has no influence in the last mentioned reaction.[145] It is obvious that this subfield needs further investigation for a better understanding of the ways reaction variables participate, but the reactions proceeding in the presence of heavy metal compounds (Sect. IIc) generally have more preparative interest.

c) Oxidation with O_2-Heavy Metal Compounds-PTC

Very divergent types of reactions have been performed by combinations of transition metal compounds, phase transfer agents, and air or oxygen.

i) Cobalt

Although the O_2 oxidation of aromatic hydrocarbons is possible in the presence of only water and an R_4NBr (see preceding section), the process is accelerated by the addition of catalytic amounts of $CoBr_2$ in the reaction mixture. Other metal bromides are less active. In this case, the role of the PT agent is considered to be the extraction of both Br^- and $CoBr_2$ into the organic medium where bromine radicals are generated for initiation of the radical chain process. Bu_4NBr seems to be the best catalyst, and the kinetics and the mechanism have been investigated in some detail. In addition to xylenes, toluene, ethylbenzene, cumene, *n*-nonane, and methylcyclohexane have also been studied as substrates.[142,146-150] The allylic oxidation of cyclohexene and 1-alkenes has also been investigated with a number of metal bromides at 120° in the presence of cetyltrimethylammonium bromide. $CoBr_2$ and $CoBr_3$ were the most active salts.[151]

A unique approach towards epoxidation in a so-called "fluorous biphasic system" was taken by Pozzi and co-workers.[152] They use cobalt tetraarylporphyrin acetate (aryl = 3,5-diperfluorooctylphenyl) as catalyst. This catalyst is soluble in perfluorohexane which is not miscible with acetonitrile, the second phase (which contains the alkene and some isobutyraldehyde). Aeration at 25° gives high conversion and epoxide selectivities for various alkenes. Isobutyraldehyde is transformed into the peroxy acid, the actual oxidant.

In another unusual method, tetralin was transformed into 1-tetralol and 1-tetralone with cobalt(II)-pyridine complexes bound to a polymer colloid in a water/tetralin mixture. The colloid was prepared from co-polymer latexes of styrene and acrylic (or methacrylic) acid cross-linked by divinylbenzene. The carboxylic acid groups were transformed into the cobalt salts, then treated with pyridine. With this catalyst, the oxidation was much faster than in conventional procedures.[153] Furthermore, certain block co-polymers carrying quaternary ammonium groups were combined with phthalocyanato cobalt(II)-tetrasulfonate. These functioned as catalysts in the oxidation of 1-dodecanethiol to give the disulfide. The catalytic activity was 40 times higher as compared with the polymer-free system.[154]

ii) Manganese

Catalytic air oxidation of *p*-xylene is also possible to some extent in the presence of a catalytic amount of permanganate and a PT catalyst $RNMe_3Cl$. At low conversion, *p*-toluic acid is the main product, terephthalic acid the minor one.[155]

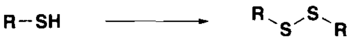
The oxidative coupling of sodium 4-nitro-2-methylbenzenesulfonate gives 4,4'-dinitrostilbene-2,2'-disulfonic acid in the presence of $Mn(OAc)_2$, when 30% methanolic NaOMe is the base. Liquid ammonia or alkylamines/water are used as solvents and PT catalysts, and O_2 is the oxidant.[156]

iii) Copper

The exclusive chlorination of 2-alkanones at position (3) is not easy to achieve normally. It was discovered that this reaction can be performed in high selectivity with a mixture of ethylammonium nitrate, copper(II) chloride, water, and the alkanone, using O_2 as the oxidant and cetyltrimethylammonium chloride as PT catalyst (Eq. 32). The side-product was the carboxylic acid with one atom less. Under optimal conditions 80% of the chloroketone and 15% of the carboxylic acid are obtained.[157]

(32)

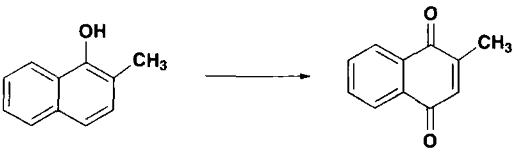
Disulfides are formed efficiently also when oxygen is bubbled through a mixture of thiol in xylene and 15% NaOH containing copper sulfate and TEBA (Eq. 33).[158]



(33)

iv) Heteropoly Acids

Whereas most heteropoly acid oxidation processes use H_2O_2 as the primary oxidant (see Section Ic, above), the conversion 2-methyl-1-naphthol to menadione was patented in the form of a biphasic PTC process with air in the presence of vanadomolybdophosphoric heteropoly acid (Eq. 34).[159]

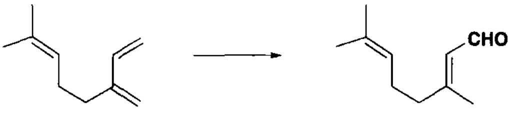


(34)

v) Palladium with Copper

The conversion 1-alkene to 2-alkanone is another rare reaction case. This oxidation with oxygen in water was described by Alper *et al.* in the presence of catalytic amounts of $CuCl_2$, $PdCl_2$, and a cyclodextrin (inverse PT catalyst) (Eq. 35).[160] The process can also be performed with onium salts instead of cyclodextrins and CTAB or dodecyltrimethylammonium chloride are the most suitable catalysts.[161] The reaction can be extended to internal olefins with PEG 400 as the PT agent; mixtures of ketones result then. Even in the oxidation of 1-decene, however, small amounts of other ketones (3-, 4-, 5-) are formed in addition to the main product, 2-decanone.[162] In a patent, the conversion myrcene to citral is carried out in butanol/H_2O with O_2 in the presence of all of the following four catalysts: cetyltrimethylammonium chloride, Li_2MoO_4, $CuCl_2$, and $PdCl_2(MeCN)_2$ (Eq. 36).[163]

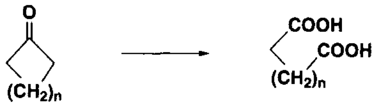
(35)



(36)

vi) Rhenium

Dirheniumdecacarbonyl is the heavy metal compound which allows the oxidative cleavage of cyclic ketones to dicarboxylic acids by air oxidation in the presence of powdered solid KOH in addition to solid K_2CO_3 with PEG 400 as PT agent in DME at room temperature. tris[2-(Methoxyethoxy)ethyl]amine (TDA-1) and TEBA are also useful PTCs for this purpose. Yields are in the 70-90% range (Eq. 37).[164]



(37)

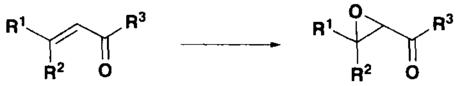
III. TAMED HYDROGEN PEROXIDE: PERBORATE, PERCARBONATE, AND *tert*-BUTYL HYDROPEROXIDE

Inexpensive sources of oxidizing power other than hydrogen peroxide itself are metal peroxides, solid or dissolved peroxy acids, peroxo salts, or easy to handle hydrogen peroxide complexes. Although these types of reagents have been utilized frequently under "normal" reaction conditions, phase-transfer catalysis applications have been described only rarely. It seems reasonable to expect that this field could benefit from PT, and it may be considered therefore an "undeveloped area".

It may be emphasized here, that *tert*-butyl hydrogen peroxide is an additional low-priced oxidant of industrial importance that is beginning to make an impact in the PTC literature. Manyfold uses of it instead of H_2O_2 have already been described in previous sections. Sasson and co-worker for instance, oxidized secondary alcohols to ketones with 70% *tert*-butyl hydrogen peroxide, 1 mol % of $CuCl_2$, 3 mol % Bu_4NBr at 25° in dichloromethane/water. No conversion was observed in the absence of either catalyst. In a clean but slow reaction, cyclooctane is transformed to cyclooctanone by the same system.[165]

Magnesium peroxide (MgO_2) as well as alkali metal peroxides can be considered as latent H_2O_2. In a PTC process, MgO_2 is utilized for the transformation of substituted aromatic acyl halides into magnesium peroxybenzoates, which are precursors of peroxybenzoic acids. The reactions are performed in ethyl acetate for 60 h at room temperature with Bu_4NOH as catalyst.[166] The preparation of peroxidicarbonates from chloroformates[10] has been mentioned already in Section Ib.

The conversion shown in Eq. 38 can be performed with aqueous alkaline perborate/CH_2Cl_2, using Hex_4NHSO_4 catalyst under mild conditions,[167] and has been optimized.[168] Commercial sodium perborate ($NaBO_3$ + H_2O_2) is sparingly soluble in water; in this aqueous solution, sodium perborate seems to exist in a strongly concentration- and pH-dependent equilibrium with boric acid and H_2O_2.[169] PTC extraction experiments (water, pH 10; dichloromethane) indicate that hydrophilic catalysts - up to Bu_4NX and beyond - do not extract any oxidizing equivalents. Lipophilic catalysts such as Hex_4NHSO_4 and Oct_4NHSO_4 extract 0.2 equivalent per catalyst equivalent.[167] The nature of the extracted species remains uncertain, but it is not H_2O_2. A mixture of neutralized boric acid or of sodium tetraborate and hydrogen peroxide is much less effective than perborate in the epoxidation of α,β-unsaturated ketones.[167]


(38)

Somewhat divergent observations were reported by Pande and Gupta,[170] who worked with borax, $Na_2B_4O_7$, 30% H_2O_2 and TEBA in benzene under weakly acidic conditions (pH 5.1). This system is useful for Bayer-Villiger oxidations (*cf.*, Eq. 14) of aliphatic and alicyclic ketones in 2-4 h at 80°. Aromatic ketones give lower conversions. The extraction of oxidizing equivalents into the benzene solution can be demonstrated even in the absence of the PT agent, but the transfer is about six times larger in its presence. However, since the yield of lactones is not increased to the same extent, the usefulness of the catalyst is only marginal in this case. The group of Muzart recommends the use of catalytic amounts of chromium(VI) oxide along with sodium perborate in the presence of Aliquat 336 as PT catalyst. Alcohols are oxidized to ketones or carboxylic acids[171](benzene/H_2O at 60-80°). The same type of oxidation is also performed with sodium percarbonate/Aliquat 336 in dichloroethane at 80°, when 0.1 equivalents of Cr(VI) are added in the form of pyridinium dichromate.[172] Benzylic hydrogens in indane (as a model compound) are also oxidized in the presence of sodium percarbonate/Aliquat 336/Cr(VI), 1-indanone being the major product and 1-indanol the minor one.[173] In this case, the most useful chromium species seems to be *bis*(tri-*n*-butyltin) chromate, $(Bu_3SnO)_2CrO_2$, in refluxing acetonitrile as the solvent; a small amount of *p*-toluenesulfonic acid must also be present.

IV. CONCLUSIONS AND OUTLOOK

The reader will have noticed that we used a very liberal definition of "phase-transfer catalyst" for this review. Most often, an onium salt, crown ether, or complexing agent is the PT catalyst. But we have also included cases where the active species was transferred to the aqueous phase in a cyclodextrin complex ("inverse PTC") and cases where a complexed metal derivative functioned both as oxidation and transfer catalyst.

In the area of PTC hydrogen peroxide oxidations without added transition metal compounds, a certain maturity has been achieved as far as common functional groups are concerned. This also seems to be true for oxidations with heteropolyanions / H_2O_2 / PT agent. There exists still a wide potential, however, for the development of applications in the presence of various other metal compounds. In this case, the oxidation of less activated hydrocarbons is the most urgent and economically rewarding task. Many further functional groups are potential candidates for phase-transfer hydrogen peroxide conversions. Actually, the number of possible combinations of substrate/solvent/metal derivative/oxidant/PT agent is so large, that it would be pure coincidence if optimal conditions as to conversion and selectivity as well as the costs would have been discovered already.

As to air/oxygen applications, it can be predicted that base-catalyzed autoxidations of CH_2 groups adjacent to activating functional groups wait discovery; however, an efficient functionalization of hydrocarbons would be a breakthrough. The investigation of additional transition metals in various oxidation and complexation states might be rewarding both from an industrial and a more academic standpoint.

tert-Butyl hydroperoxide and other "tamed" forms of H_2O_2 (perborate, percarbonate, metal peroxides, and others) may find attractive applications in the near future.

Many of the reactions reviewed here have been performed only on a laboratory scale up to now; their potential for industrial applications, however, must not be underestimated.

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