Solid Materials as Sources for Synthetically Useful Singlet Oxygen

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Abstract: Solid materials can generate $^1O_2$ ($^1\Delta_g$) either by irradiation of an immobilized dye in the presence of oxygen, or by catalytic decomposition of H_2O_2. The methods for obtaining such solid catalysts are described, and the usefulness of the obtained materials in preparative $^1O_2$ oxygenations ("ene" hydroperoxidation, [2+2]- and [4+2]-cycloaddition) is discussed, particularly with respect to substrate scope, solvent scope, reusability and productivity of the catalyst, regioselectivity and chemoselectivity of the oxidation.

Keywords: heterogeneous catalysis; hydrogen peroxide; photo-oxidation; singlet oxygen

1 Introduction

Apart from the most abundant, triplet form of dioxygen, two excited singlet states are known.[1–4] Of these, $^1\Delta_g$ has the lowest energy; this $^1\Delta_g$ state is 94.2 kJ · mol^{-1} above the ground state. Singlet oxygen is an electrophilic reagent; hence it preferentially reacts with electron-rich molecules such as highly substituted alkenes or sulfides. Several reactions of $^1O_2$ with alkenes are well-known; they all proceed through two-electron oxidation processes, rather than *via* free radical intermediates. In the Schenck or "ene" reaction with olefins containing an allylic hydrogen atom, an unsaturated hydroperoxide is formed, in which the double bind is shifted in comparison with the starting product. Other reaction modes with alkenes are the [2+2]-cycloadditions; with dienes, a [4+2]-cycloaddition can be observed, leading to endoperoxides. Because of this specific reactivity and chemoselectivity, $^1O_2$ is a valuable reagent.

However, singlet oxygen has a very short lifetime. For instance, in water, its lifetime τ_Δ amounts to only 4 µs.[2] Therefore $^1O_2$ has to be generated *in situ*. From a practical viewpoint, it is much more advantageous if the actual source of $^1O_2$ is a solid. Generally, two types of processes can be distinguished. First, a photosensitizing molecule may be used to capture light energy, which is then transferred to ground state oxygen. Open and patent literature contains a wealth of useful information on the immobilization of sensitizers on solid materials. On the other hand, singlet oxygen may be generated in the dark, for instance starting from peroxides such as H_2O_2. Over the last few years, several solid catalysts have emerged for the transformation of H_2O_2 into singlet dioxygen.

2 Immobilized Dyes as Solid Sources of $^1O_2$

When exposed to an appropriate light source and O_2, immobilized photosensitizers can generate $^1O_2$, and numerous applications have been proposed for these materials, e.g., in biochemical studies, or in studies on waste water purification. However, the present review is restricted to proven synthetic applications of solid sources of singlet oxygen. In the same line, studies of self-sensitized degradation of dye molecules, adsorbed on solid supports, are not discussed.[5]

The advantages of using a dye, dispersed on a solid carrier, are manifold:

(1) oligomerization of the dye can be prevented, resulting in less self-quenching and enhanced quantum yields for singlet oxygen formation,

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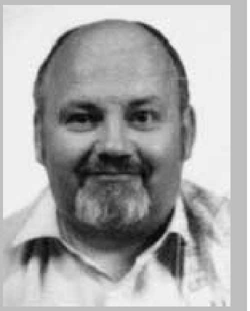


Pierre Jacobs (1943) is the Head of the Department of Interphase Chemistry at the Katholieke Universiteit Leuven. Since his Ph. D. work on infrared characterization of acid sites in zeolites, he has deployed a broad range of activities in solid state chemistry, supramolecular chemistry, and heterogeneous catalysis. He is a former president of the International Zeolite Association, and is a working member of the Royal Academy of Sciences of Belgium. He is the recipient of numerous awards, including the P. H. Emmett award and the Donald Breck award of the International Zeolite Association.

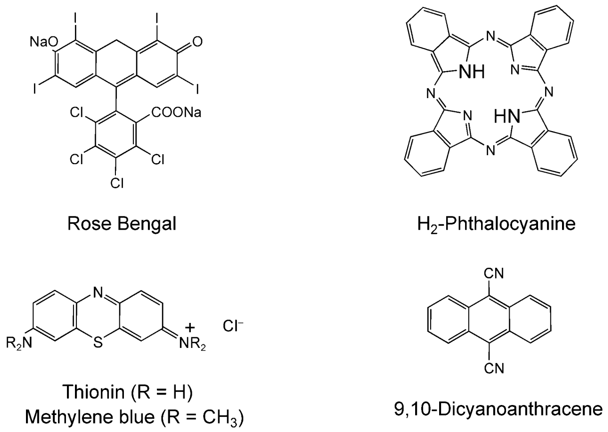
Paul Alsters (1965) received his Ph. D. at the University of Utrecht (The Netherlands) in 1992. He did his Ph. D. work on C-O coupling reactions of organopalladium compounds under the guidance of Prof. G. van Koten. He did postdoctoral work on asymmetric titanium-mediated nucleophilic additions to aldehydes in the laboratory of R. O. Duthaler at Ciba-Geigy in Basel (Switzerland). He joined DSM in 1993, where he is currently working as a senior scientist within the DSM Pharma Chemicals "Advanced Synthesis, Catalysis, and Development" research laboratory in Geleen (The Netherlands).

(2) the photostability of the dye is increased, because bimolecular degradation mechanisms are suppressed,

(3) a wider variation of reaction media may be used,

(4) the dye is easily removed from the reaction medium, resulting in a purer product and a possible re-use of the dye.

However, in comparison with a homogeneous, dissolved dye, an immobilized version might also present disadvantages. In particular, if a solid support is used, part of the $^1O_2$ may be lost through interaction with the support. Such quenching of $^1O_2$ is well documented for SiO_2 and related materials; interaction of $^1O_2$ with OH and CH oscillators results in electronic-to-vibronic energy transfer.[6–8] The quenching can be diminished by modifying the SiO_2 through trimethylsilylation. Moreover, the loading of the support with the dye should not be too high, in order to avoid self-quenching. In the following paragraphs, the immobilized dyes are grouped per type of dye. The structures of some important dyes are given in Figure 1.



Rose Bengal

H_2-Phthalocyanine

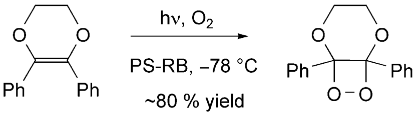
Thionin (R = H)
Methylene blue (R = CH_3)

9,10-Dicyanoanthracene

Figure 1.

2.1 Immobilized Rose Bengal

Much of the early work on immobilized sensitizers has focused on Rose Bengal, a dye which is used as such in water or polar solvents. One of the seminal contributions to this field was that of Schaap and his coworkers.[9–11] They explored many materials as supports for Rose Bengal (RB), including polyamides, polymethacrylate, bromomethylated glass, or even cotton, but the best results were obtained with cross-linked, chloromethylated polystyrene. Rose Bengal is covalently attached to this polymer by a simple nucleophilic substitution in refluxing DMF. The photocatalyst is advantageously used in solvents such as $CHCl_3$ or C_6H_6, which to some extent swell its polymeric structure. Demonstrated reactions include 1,4-additions, as with 1,3-cyclohexadiene, Schenck ene reactions, e.g., with 1,2-dimethylcyclohexene, or 1,2-additions, e.g., with 3,4-dihydro-2*H*-pyran.[9–13] Even unstable dioxetanes were readily prepared with PS-immobilized RB at low temperature, as in the oxygenation of 1,2-diaryl-*p*-dioxenes,[14] Eq. (1).



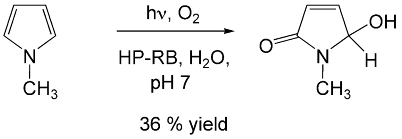
(1)

In a reaction with terpenes such as α- or β-pinene, hydroperoxides were produced in yields up to 40%, but bleaching of the dye necessitated addition of new loads of the PS-immobilized RB.[15] However, RB on polystyrene is clearly a more stable sensitizer than RB in cellulose acetate.[16] While leaching of RB from the latter matrix by the solvent is negligible, photobleaching is very fast, as was demonstrated in the $^1O_2$-mediated oxidation of butyl sulfide to the sulfoxide.

The PS-immobilized RB is a much more efficient sensitizer than solid RB, suspended in the same solvent, e.g., CH_2Cl_2, which clearly proves that the scope of useful solvents is considerably expanded.[11] PS-RB was also used in a "three-phase" experiment, in which $^1O_2$, generated on the solid sensitizer, is trapped by an olefin bound to another polymer.[17] Such experiments clearly demonstrate the diffusion of $^1O_2$ through various media.

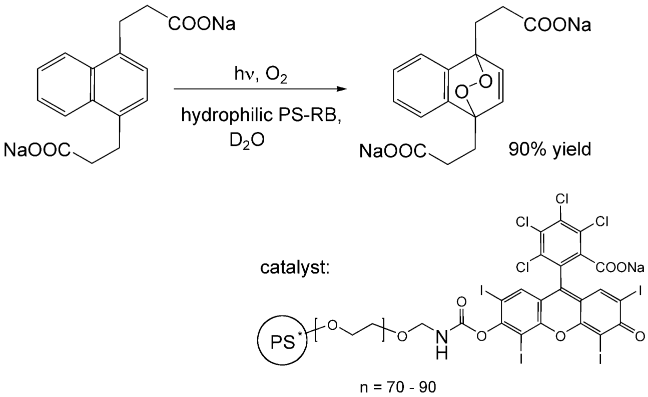
The performance of the insoluble polymer can be further improved by treatment of the polymer with tertiary amines or phosphines, either before or after reaction of the polymer with RB.[18] If the chloromethylated polymer is first quaternized with ammonium or phosphonium groups, anion exchange sites are created, which will retain the anionic dye RB. Alternatively, the residual $–CH_2Cl$ groups in the polymer may be quaternized after covalent binding of RB. In either case, the improved performance of the polymer for reactions in, e.g., CH_2Cl_2 was ascribed to an improved swelling and openness of the structure.

Since PS poorly swells in polar solvents such as water, more hydrophilic polymers have been prepared by copolymerization of chloromethylstyrene with the mono- and bis-methacrylate esters of ethylene glycol.[19] After functionalization with RB, the hydrophilic polymer (HP) is a suitable sensitizer for reactions in water or in methanol. A typical reaction is the oxidation of *N*-methylpyrrole, Eq. (2).



(2)

Compared with the quantum yield of RB in methanol (0.76), the RB-HP displays an acceptable quantum yield of 0.48. However, this RB-HP is not commercially available, and its synthesis is rather complex. Therefore, it was proposed to couple RB to an alternative, commercial support, *viz.* a polyethylene glycol modified polystyrene with functional amino groups.[20] This wettable resin is normally used for peptide synthesis. Using conventional carbodiimide chemistry, the RB was linked *via* amide groups to this resin. As a test reaction, the water-soluble disodium (3,3′-naphthalene-1,4-diyl)-dipropionate was photo-oxygenated to its endoperoxide in 90% yield, Eq. (3).

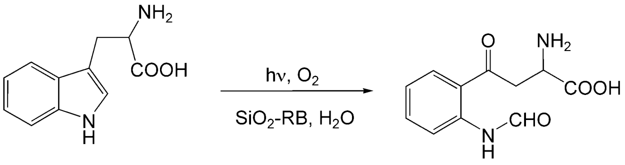


(3)

Alternatively, RB has been attached to water-soluble polymer chains, for instance, sulfonated polystyrene. An advantage of such sensitizers is that the quantum yield is virtually identical to that of dissolved RB as such, while the ionic polymer backbone maintains the dye in the monomeric state. The dye-loaded polymer can be recovered by a dialysis procedure.[21,22] Another useful, water-soluble polymer which allows RB anchoring is poly(*N*-isopropylacrylamide-*co*-vinylbenzyl chloride) (PNIPAM-VBC).[23] This polymer is thermoresponsive: due to its low critical solubility temperature, it precipitates by gentle heating of the aqueous reaction mixture above 35 °C. The RB/PNIPAM-VBC catalyst was applied in the photo-oxidation of phenol to benzoquinone.

Reports on anchoring of RB to inorganic supports are scarce. RB can be simply adsorbed on SiO_2 from methanol solution;[24] in order to avoid dye bleeding, the supported dye can only be used in a solvent which does not dissolve the RB, such as cyclohexane or $CHCl_3$. In a similar approach, glass beads were coated with a film of RB embedded in a polytitanate.[25] The polytitanate is formed by exposure of Ti alkoxides to heat; it is proposed that the RB is withheld on the titanate by coordination of an alcohol group of RB to a Ti atom. This titanate-based material has been used in the photo-oxidation of mercaptans to disulfides.

Chloropropylated SiO_2 can be functionalized with RB through covalent bonding.[26] This material can be successfully used either in organic solvent mixtures, e.g., CH_2Cl_2, or even in water. For instance, tryptophan was oxidized to *N*-formylkynurenine in water, Eq. (4).



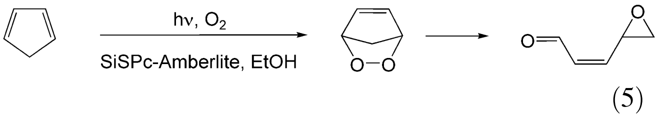
(4)

Finally, a solid phase-transfer catalyst was designed by immobilizing onium salts, e.g., pyridinium compounds on SiO_2.[27] After association with RB, the solid catalyzed the oxygenation of a series of olefins under irradiation in chloroform. This clearly illustrates the expansion of solvent scope as one of the advantages of dye immobilization.

2.2 Porphyrins and Phthalocyanines

Photosensitizing phthalocyanines and porphyrins are easily obtained with a variety of coordinated metals (Zn, Al, Ga, Ge, Si, ...) and peripheral functional groups (– COOH, $-NH_2$, $-SO_3^-$, ...). The latter functional groups often indicate the best immobilization strategy.

For instance, an $Si(OH)_2$-tetrasulfophthalocyanine (Si-SPc) was anionically exchanged on IRA-400 anion exchanging resin beads.[28,29] Using this catalyst in ethanol, and with a substrate:phthalocyanine ratio of 8000 to 1, cyclopentadiene is fully converted to mainly 4,5-epoxy-2-pentenal, Eq. (5).

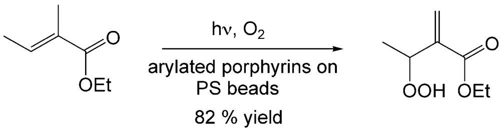


(5)

The high photostability of this class of sensitizers is also apparent from the oxidation of citronellol in methanol to a mixture of secondary and tertiary hydroperoxides. With the heterogenized Si-SPc, 9 successive oxygenation cycles are possible without any decrease of the reaction rate. In a comparative test, RB on IRA-400 already loses 50% of its activity after 5 runs. The immobilized phthalocyanines are also considerably more resistant to photodegradation than the Pc in solution.

The anion exchanging resin, with its quaternary ammonium groups, is also suitable for the aqueous photo-oxidation of phenol, which proceeds best at high pH values. In these conditions, phenol occurs in its anionic form, which is enriched in the inner voids of the resin.[28] An analogous material was prepared by successive reaction of chloromethylated polystyrene with tetracarboxy-AlPc and pyridine.[30] The material contains covalently bound phthalocyanines dispersed in between quaternary pyridinium groups.

Even simple adsorption may be sufficient for retention of the porphyrin sensitizer in the polymer support.[31] Thus, neutral *meso*-arylated porphyrins are loaded on EtOAc-swollen PS beads by impregnation; next photo-oxygenation substrates such as β-pinene or ethyl tiglate are impregnated from EtOAc as well. After evaporation of the solvent, the loose solid is irradiated with visible light, and after reaction, the products are unloaded from the beads by EtOH extraction. Thus, the photo-oxygenation proceeds in the absence of a solvent! The singlet oxygen lifetime is then only determined by quenching on the polymer; the lifetime τ_Δ of 19 μs resembles that in toluene solution. The yields are excellent (80–99%) even for poorly reactive substrates, see Eq. (6).



(6)

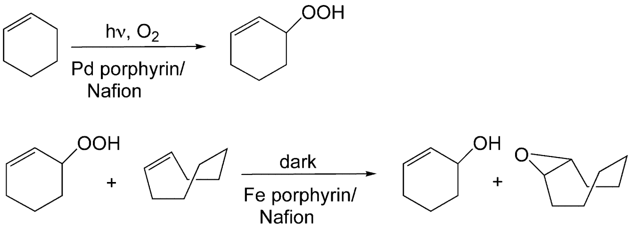
However, the final product yield per g of polymer remains as low as 1 g per g, and the sequential loading/unloading of the substrate and products is a cumbersome procedure.

Apolar dyes such as ZnPc, or Zn- or H_2-tetraphenylporphyrin, are easily incorporated in hydrophobic polydimethylsiloxane (PDMS).[32] This elastomeric material, which is easily shaped in the form of membranes, is light transparent and highly oxidatively stable. If the PDMS-entrapped phthalocyanines are used in ethanol, olefinic substrates are preferentially adsorbed in the PDMS, and this leads to fair oxygenation rates. Moreover, ethanol is not capable of leaching the sensitizers out of the PDMS structure.

Alternatively, Si–H groups in the polysiloxane prepolymer may be used to covalently anchor a 4-allyloxyphenyl-type porphyrin. Typically, in the oxygenation of 1-methyl-1-cyclohexene, 40000 moles of hydroperoxide are formed over 12 h, corresponding to 13 g product per g of porphyrin-containing PDMS polymer.

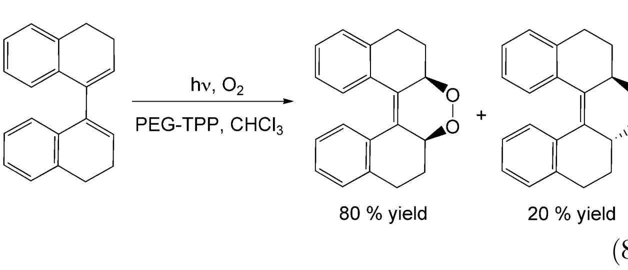
Covalent anchoring of phthalocyanine photocatalysts can also be achieved by forming covalent bonds with functionalized polystyrene,[33] with poly(methylmethacrylate),[34] or with a functionalized SiO_2, e.g., containing $-(CH_2)_3Cl$ or $-(CH_2)_3NH_2$ groups[35]. Such systems have been used for the photo-oxidation of 2-mercaptoethanol in aqueous base to the disulfide. Again, the immobilized complex displays higher photostability than the homogeneous counterpart.

In some cases, it has been found advantageous to immobilize two different macrocyclic compounds within the same polymer host. For instance, when a mixture of tetrasulfonated phthalocyanine and tetraphenylporphyrin is exchanged together on an Amberlite, the spectrum of the irradiating light is used more effectively.[29] In another example, Pd(II) *meso*-tetrakis(*N*-methyl-4-pyridyl)porphyrin and Fe(III) *meso*-tetrakis(2,6-dichlorophenyl)porphyrin were exchanged together on a Nafion membrane.[36] The Pd-porphyrin mediates the $^1O_2$ oxygenation of cyclohexene to the allylic hydroperoxide, with over 90% selectivity; the Fe-porphyrin uses this hydroperoxide as an oxidant in the epoxidation of cyclohexene or cyclooctene, Eq. (7).



(7)

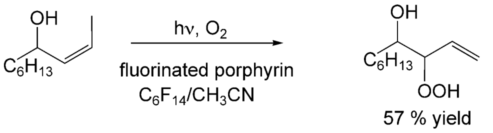
Immobilization of porphyrin sensitizers on a solid competes with other approaches, such as covalent anchoring to soluble polymers or perfluoroalkylation of the catalyst. For example, a non-metallated *meso*-tetrakis(hydroxyphenyl)porphyrin was covalently coupled to polyethylene glycol.[37] The photo-oxidation of a series of olefins and dienes was performed in CH_2Cl_2, Eq. (8).



(8)

After completion of the reaction, diethyl ether is added, and the high molecular weight porphyrin quantitatively precipitates from the reaction solution. With the recycled photocatalyst, at least 6 consecutive cycles are possible.

Alternatively, a tetrakis(heptafluoropropyl)porphyrin can be employed, in order to perform reactions in fluorous biphasic media.[38] As such, the perfluorinated porphyrin is already much more stable to visible light irradiation than tetraphenylporphyrin. When such a sensitizer is used in a perfluorohexane/acetonitrile biphasic system, the sensitizer is mainly located in the fluorous layer, which protects it from degradation, and which facilitates recuperation of the photocatalyst at the end of the reaction. Moreover, $^1O_2$ has a long lifetime (100 ms) in perfluorinated solvents. The stability of the dye under the reaction conditions allows long reaction times, and hence, even poorly reactive substrates, such as *Z*-4-OH-2-decene can be converted in reasonable yields, Eq. (9).



(9)

2.3 Other Anchored Metal Complexes

While procedures for the intrazeolite assembly of $[Ru(bpy)_3]^{2+}$ have been reported, Fox and Pettit exchanged preformed $[Ru(bpy)_3]^{2+}$ on a NaY zeolite.[39] In such conditions, it is certain that all the complexes are present at the outer surface of the zeolite crystals. Hence it is not surprising that the chemoselectivity in the "ene" reaction of 1-methyl-1-cyclohexene, using $[Ru(bpy)_3]^{2+}$-NaY as the sensitizer, is virtually the same as with dissolved sensitizers. In work with the same $[Ru(bpy)_3]^{2+}$ exchanged on a Dowex cation exchange resin,[40] it was observed that an increasing water content of the hydrophilic resin decreases the photo-oxygenation yields of hydrophobic substrates such as 2,3-dimethyl-2-butene. The water seems to form a layer on the surface, from which the olefin is excluded. Since $^1O_2$, after its formation at the surface, first must diffuse throughout the water layer before it can react with the olefin, this negatively affects the hydroperoxide yield. Enhanced physical quenching of $^1O_2$ is also observed upon irradiation of $Ru(bpac)_2^{2+}$, bound to a Sephadex-linked carboxylated bipyridine (bpac = 4,4′-dicarboxy-2,2′-bipyridine).[41] This is ascribed to the numerous OH groups in the Sephadex polymer (see Figure 2).

Coordinative interactions have as well been used to anchor a the complex $[Ru(bpy)_2]^{2+}$ to partially quaternized poly(1-vinylimidazole).[42] The material can be quaternized with hexyl or hexadecyl groups (see Fig-

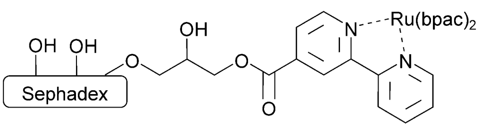


Figure 2.

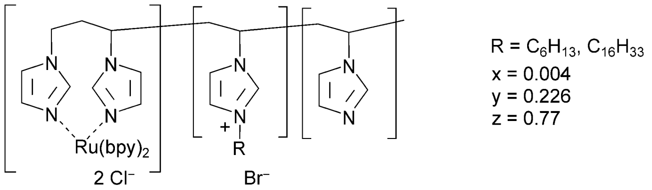
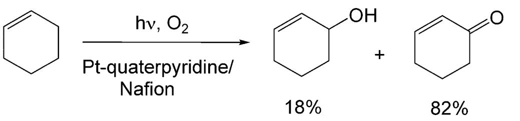


Figure 3.

ure 3). Particularly when a reaction is performed at low substrate concentration with the hexadecyl-containing material, the hydrophobic substrate, e.g., cyclopentadiene, can be enriched close to the $^1O_2$ generating Ru centers, resulting in higher reaction rates at low substrate concentrations. However, the long-term stability of these sensitizers is limited; after repeated use, gradual decoordination of one of the imidazole residues is observed, and the efficiency of photo-oxygenation decreases.

A recent example of an immobilized metal complex sensitizer is Pt(II)-quaterpyridine, which can be incorporated in a Nafion membrane from an aqueous solution (quaterpyridine = 2,2′:6′,2″:6″,2‴-quaterpyridine).[43] Obviously, the Nafion matrix itself is highly oxidation-resistant and stable in most solvents. While the Pt-quaterpyridine in solution is susceptible towards photochemical decomposition, the membrane-immobilized complex is stable when irradiated over long periods. Full conversion of several unsaturated compounds is possible in a few h, with substrate to Pt ratios between 1400 and 14000. In the oxygenation of cyclohexene, allylic alcohols and ketones are the products, which seems to indicate that the Pt decomposes the formed hydroperoxides, Eq. (10).



(10)

Finally, the hexanuclear cluster Mo_6Cl_{12} has been anchored on poly(vinylpyridine).[44] The material is a useful sensitizer for $^1O_2$ oxygenations of olefins in acetonitrile, with hydroperoxide selectivities identical to those of solution reactions.

2.4 Thionin and Methylene Blue

These structurally strongly related cationic dyes are discussed together since many analogous singlet oxygenations have been reported with either thionin or methylene blue, exchanged in very low concentrations in zeolites.[4,45–58] In order to obtain effective photosensitization, e.g., with thionin, it is important that the dye is in a monomeric state in the zeolite. This can be controlled by the dye loading and by the hydration degree of the zeolite.[45]

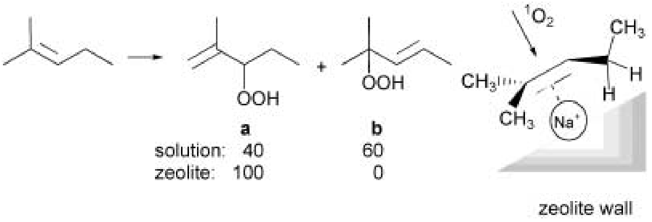
Product yields are low: typically, only 10–30 mg of olefin is converted per g of zeolite, and the adsorbed products must be extracted from the zeolite in a separate step with a well-selected solvent mixture, possibly in the presence of PPh_3 as a reducing agent.[46] Only recently have experiments on a somewhat larger scale been performed, e.g., even when starting from 500 mg 2-methyl-2-heptene, the reaction still requires a 10-fold weight excess of zeolite with respect to olefin.[54]

An additional complication is that the products, and in particular hydroperoxides, may be strongly adsorbed on the cation-exchanged zeolites, and may even undergo secondary reactions. Therefore, it is important to evaluate chemoselectivities at low olefin conversions or short irradiation times, and to ensure that the mass balance of the reaction is as complete as possible.[4,50,51]

Zeolite effects on the selectivity of the "ene" hydroperoxidation are especially strong for structures containing small, hard cations such as Li^+ or Na^+.[46,47] These are capable of strongly adsorbing olefins, or strongly polarizing the perepoxide intermediate of the hydroperoxidation.[46,52,53] When, in contrast, a Cs^+-zeolite is used, the selectivities are much less changed in comparison with the behavior of singlet dioxygen in solution. Additionally, Cs^+-exchanged zeolites are richer in electrons than the Na^+ or Li^+ counterparts, and as a result, bleaching of a dye such as thionin by electron transfer occurs more readily in a Cs^+ zeolite.[49,50]

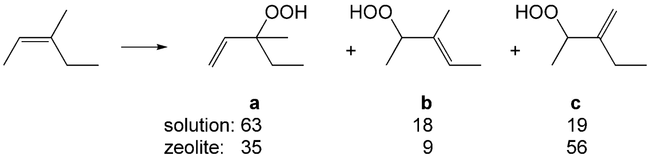
Zeolites exchanged with divalent cations such as Ca^{2+} or Mg^{2+} are not suitable as host materials since cation hydrolysis leads to Brönsted acidity in the material.[49,50] This acidity may not only result in protonation of the dye, but also in other complications, such as rearrangement of alkenes before the photo-oxygenation, and decomposition of the hydroperoxide products.

The mechanistic insight in this intrazeolite selective singlet oxygenation has considerably evolved during the past years. One original line of thought, proposed by Ramamurthy, states that the complexation of the alkene by the cation on the zeolite wall determines which allylic H atoms are available for abstraction by singlet oxygen.[46] Thus, the cations would control the substrate conformation and the singlet oxygen approach geometry. An example is the photo-oxygenation of 2-methyl-2-pentene, which in a zeolite gives only one product, while a mixture is obtained in solution. This result can be rationalized by assuming that an Na^+ ion binds to the π-cloud of the olefin. As a result, the allylic CH_3 group is directed away from the surface, with the allylic H atoms pointing towards the surface. Consequently, the allylic H atoms cannot be abstracted by $^1O_2$, and **a** is exclusively formed, Eq. (11).



(11)

While this model is successful with a series of substrates, an important amendment to this concept was made by Clennan et al., based on the absence of a "*cis*" effect for singlet oxygenations in zeolites.[4,52,53] In solution, the "*cis*" effect implies that hydrogen atoms are preferentially abstracted from the sterically most crowded side of the olefin. For instance, with *cis*-3-methyl-2-pentene, **a** and **b** constitute 81% of the products in CH_3CN. In a zeolite, this fraction decreases to 44%, and **c** becomes the dominant product, Eq. (12).



(12)

In the zeolite, it is proposed that the incipient perepoxide intermediate is stabilized by the cation. Clearly, this interaction is easier *via* the less crowded side of the olefin, and this explains the unusually high selectivity for **c** (see Figure 4).

A similar reaction at the sterically less hindered side of the olefin was observed for zeolite-adsorbed β,β-dimethylstyrene. In a reaction with zeolite-exchanged thionin, the "ene" hydroperoxide **a** is formed in 90% yield, while in solution, this compound represents only 20% of the conversion; in solution, other reaction pathways, such as [2 + 2] and [4 + 2] reactions are more favored, leading to, amongst others, products **b** and **c**,[57] Eq. (13).

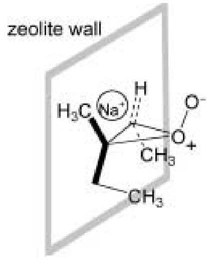
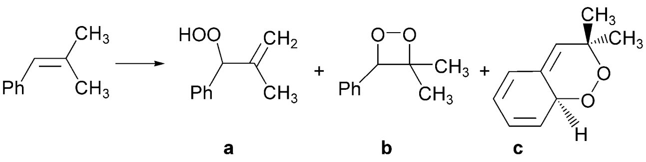
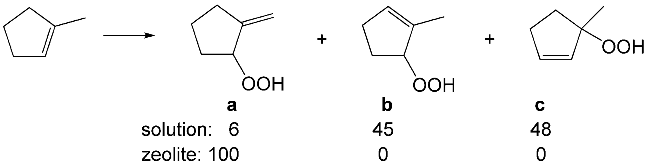


Figure 4.



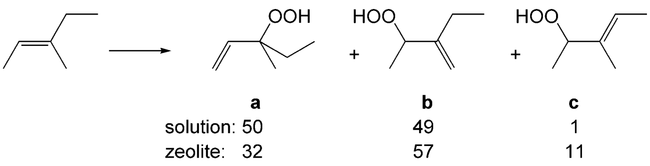
(13)

In the oxidation of cyclic alkenes such as 1-methyl-1-cyclopentene, similar effects lead to a very high selectivity for the product **a** with an exocyclic double bond. Obviously, coordination of the peroxide intermediate by the cation is almost impossible over the ring, and this disfavors products **b** and **c**, Eq. (14).



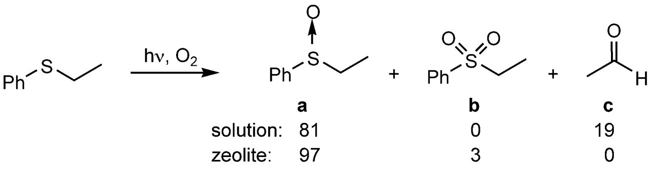
(14)

Finally, singlet oxygenations in a zeolite are more influenced by Markovnikov-type directing effects than the analogous reactions in solution. This effect was ascribed to polarization of the perepoxide by the coordinated cation, and consequently, an increased charge in the carbon skeleton of the perepoxide in the transition state. Such a partial charge is better stabilized at the more substituted C atom; in the reaction of *trans*-3-methyl-2-pentene, this explains the preference for **b** over **a**,[53] Eq. (15).



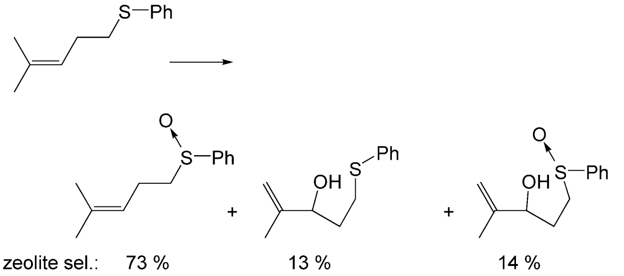
(15)

Such examples clearly illustrate the ability of zeolites to drastically influence the regioselectivities of singlet oxygen oxygenations of olefins. However, particularly the yields based on zeolite host will have to be improved for these reactions to become synthetically interesting. The same holds for the dye-zeolite-catalyzed oxygenation of sulfides to sulfoxides. In the zeolite, the oxygenation proceeds faster and with changed selectivities, which is again ascribed to complexation between the cation and the persulfoxide intermediate.[59] Particularly sulfur-carbon bond cleavage *via* the Pummerer reaction is suppressed in the zeolite in comparison with the reaction in solution, as illustrated for ethyl phenyl sulfide, Eq. (16).



(16)

The sulfide oxidation is accelerated to such an extent by the zeolite matrix, that in unsaturated sulfides, it is preferred over the "ene" reaction, while the opposite phenomenon is observed in solution, Eq. (17).[60,61]

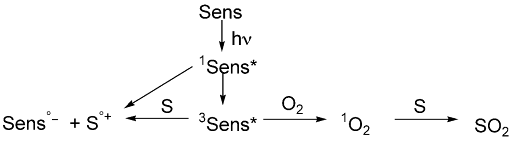


(17)

Methylene blue has also been exchanged or adsorbed on other solids, such as clays or SiO_2, and the materials were used in various reactions such as oxidation of olefins, sulfides or tryptophan.[62–65] In all these cases, it can be assumed that the reaction is performed by $^1O_2$ diffusing freely in the solution.

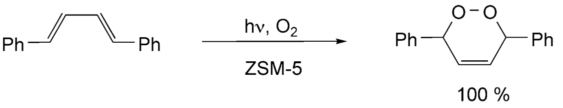
2.5 Polyaromatic Sensitizers

In an irradiated reaction mixture of a sensitizer (Sens), oxygen and an olefin substrate (S) such as *trans,trans*-1,4-diphenylbutadiene, several reactions compete: the olefin may react with $^1O_2$ generated by photosensitization to form an oxygenated product (SO_2), but it might also directly react with the dye by electron transfer to the excited triplet or singlet state, Eq. (18).[66]



(18)

By physically separating the dye from the olefin, the electron transfer can be selectively switched off. Thus, when the diene is adsorbed in the pores of a 10-membered ring zeolite such as ZSM-5, or in solid Nafion, and the dye is present in the surrounding solution, the adsorbed olefin can only react with $^1O_2$ which is formed in solution and then diffuses inside the matrix.[67] For example, 9,10-dicyanoanthracene, dissolved in isooctane, is size-excluded from the ZSM-5 channels and produces $^1O_2$ which reacts with *trans,trans*-1,4-diphenylbutadiene to form an endoperoxide, Eq. (19). The product is not extracted by the isooctane during reaction, and must be washed out in a separate work-up procedure, e.g., with dichloromethane. Obviously, yields based on catalyst weight are quite low, Eq. (19).



(19)

If on the other hand, the sensitizer and the substrate are in close proximity, e.g., when they are simultaneously adsorbed inside a Nafion membrane, only products resulting from electron transfer are formed, for instance, in the reaction between 9,10-dicyanoanthracene and *trans,trans*-1,4-diphenylbutadiene.[68]

In a more conventional approach, a functionalized dicyanoanthracene has been anchored on silica.[69] Despite a limited amount of leaking sensitizer, the material was successfully used in the oxidation of dibutyl or diphenyl sulfide to mainly the sulfoxides. However, convincing evidence was presented showing that not $^1O_2$ but rather O_2^- is the oxygen active species.

2.6 Fullerene-Based Materials

Buckminsterfullerene (C_{60}) is a relatively new sensitizer with a considerable photostability. However, C_{60} only has a limited solubility in many solvents, and its recuperation from solutions may be troublesome. Such problems may be resolved by appropriately dispersing the C_{60} on supports. C_{60} is easily functionalized for covalent grafting to inorganic or organic supports.

High loadings of C_{60} were obtained with a Sephadex material containing primary amine functional groups; refluxing with C_{60} in toluene results in direct addition of the $-NH_2$ group to C_{60}.[70] In water, the C_{60}-functionalized insoluble hydrophilic polymer forms a swollen gel. Coupling of C_{60} through amine addition was also performed with aminomethylpolystyrene beads.[71] The resulting C_{60}/PS was rendered more hydrophilic by reaction of the anchored fullerenes with polyallylamine, but it is unclear to what extent these multiple aminations affect the photosensitization by the fullerene.

More practical applications were achieved with amine-functionalized siloxane polymers of the Deloxan type.[72] Starting with a cyclopropanation of C_{60}, a carboxylate-functionalized fullerene was obtained,

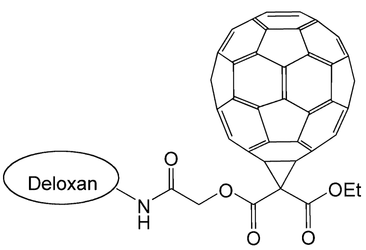


Figure 5.

which was coupled to aminated Deloxan *via* carbodiimide chemistry (Figure 5). A clear advantage is that the cyclopropanation hardly disturbs the π-system of the fullerene, thus preserving its photosensitizing properties. The material was applied in the oxygenation of sulfides to sulfoxides, which proceeds with the best selectivity in a polar solvent such as methanol. Recycling the polymer leads to gradually decreasing yields, either because of dye bleaching, or because of loss of the C_{60} from the polymer matrix.

Finally, fullerenes can also be adsorbed in zeolites or related molecular sieves. It has been demonstrated that the triplet excited state of C_{60}, entrapped in an LiY zeolite, has a lifetime of several minutes.[73] Vacuum heating at 500 °C of a physical mixture of C_{60} and the mesoporous sieve FSM-16 yields a composite material which was used for photo-oxidation of cyclohexene in benzene.[74] Even if considerable amounts of the allylic hydroperoxide were formed, there was no clear proof for the involvement of $^1O_2$ in the reactions. EPR measurements provided evidence that some radical species were involved in the reactions as well, as was also indicated by the observed degradation of the C_{60} sensitizer.

3 Dark Singlet Oxygen Reactions using Solids

A screening of the periodic system by Aubry revealed that there are several classes of inorganic compounds that, in contact with H_2O_2, are potential sources of $^1O_2$.[75] The stoichiometry of this process is shown in Eq. (20).

$$2\,H_2O_2 \longrightarrow 2\,H_2O + {}^1O_2 \qquad (20)$$

Hence, a $^1O_2$ generation yield of 100% corresponds to 1 mole of $^1O_2$ per 2 moles of H_2O_2. With four elements, truly solid sources of $^1O_2$ have been devised, *viz.* Mo, W, Ca and La. Mostly, the reaction is performed in alkaline conditions.

In view of the cost of Mo and La, recuperation and reuse of these metals seem mandatory. Another challenge is to limit the amount of expensive H_2O_2 needed for the peroxidation. When substrates with a moderate or poor chemical reactivity are oxidized in a solvent with non-negligible quenching properties (as expressed in a high β-value), only a fraction of the generated $^1O_2$ is used for oxygenation.[76] Moreover, as more H_2O_2 is added and consumed, the reaction mixture becomes enriched in water, which increases the chances for solvent-quenching of $^1O_2$. As for the photosensitized reactions, solvent compatibility is an important issue: the solvent should dissolve both H_2O_2 and possibly apolar substrates. Finally, side reactions catalyzed by the employed metals must be avoided.

3.1 Molybdenum and Tungsten

In the presence of H_2O_2 and base, molybdate is transformed into several anionic monomeric peroxo species, Eq. (21).[77–80]

$$MoO_4^{2-} \underset{H_2O}{\overset{H_2O_2}{\rightleftharpoons}} Mo(O_2)O_3^{2-} \underset{H_2O}{\overset{H_2O_2}{\rightleftharpoons}} Mo(O_2)_2O_2^{2-} \underset{H_2O}{\overset{H_2O_2}{\rightleftharpoons}} Mo(O_2)_3O^{2-} \underset{H_2O}{\overset{H_2O_2}{\rightleftharpoons}} Mo(O_2)_4^{2-} \qquad (21)$$

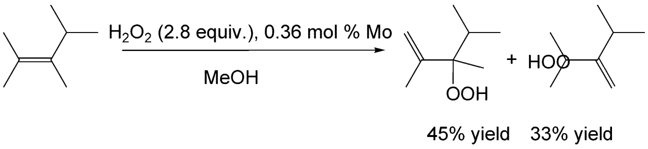
Of these, especially the triperoxoMo species releases $^1O_2$ at a high rate; the tetraperoxo species $Mo(O_2)_4^{2-}$ is less reactive. This implies that the reaction rate decreases at high $[H_2O_2]$; hence efficient reaction requires that the peroxide is gradually added over time. In homogeneous solution, the $^1O_2$ release rate is maximal at pH 10.

In order to separate the Mo from the solution after reaction, several options have been described. For instance, if Na_2Mo_4 reacts in MeOH with H_2O_2, the Mo dissolves to form soluble peroxo species; at the end of the reaction, a large part of the molybdate salt precipitates out of the solution again.[81] However, if the reaction mixture contains too much water, the molybdate stays dissolved, and this technique is no longer feasible. Therefore, heterogenization of the Mo seems a more reliable option, especially if one desires to work with truly catalytic amounts of Mo, i.e., with a high amount of H_2O_2 per Mo.

Since all the Mo intermediates are anionic, exchange on a resin,[82] or on an inorganic material seems an obvious option. The use of layered double hydroxides (LDHs) has been explored in detail.[83–86] These inorganic layered materials have a high exchange capacity (up to 3 mequiv. · g^{-1}), which is determined by the degree of isomorphous substitution of Mg^{2+} by Al^{3+} in the lattice. Moreover, the higher the Mg/Al ratio, the higher is the basicity of the LDH surface. When molybdate-exchanged LDH (Mo-LDH) is dispersed in a solvent and exposed to H_2O_2, peroxomolybdates are formed at the surface and $^1O_2$ is released into solution. In contrast with the homogeneous molybdate catalyst, addition of NaOH or a similar base is not required with the Mo-LDH catalyst, since the LDH surface locally provides the optimal basicity for $^1O_2$ generation at a high rate.[83]

With the homogeneous Mo system, the theoretical yield of 100% based on H_2O_2 has been achieved. With an optimal heterogeneous Mo-LDH system, the $^1O_2$ yield maximally amounts to 75%. The lower yield is probably due to quenching of $^1O_2$ on the hydrophilic LDH support. The best catalysts contain a small amount of exchanged molybdate, which is located at the outer surface of the LDH crystallites. $^1O_2$ then diffuses away from the surface, and performs "ene" hydroperoxidations with chemoselectivities that are indistinguishable from those of photosensitized reactions.

The solvent scope of the heterogeneous Mo-LDH is clearly broader than that of homogeneous molybdate. The latter prefers water or methanol, while the former is useful in a larger solvent range, including dioxane and DMF.[86] Just like homogeneous molybdate, Mo-LDH is a fast generator of $^1O_2$: in an optimal H_2O_2 concentration, 25 moles of $^1O_2$ can be generated per mole of Mo per h. Due to these high rates, the use of Mo in truly catalytic amounts becomes possible, e.g., with 0.36 mol % of Mo, Eq. (22).[84]



(22)

Moreover, the complete retention of the Mo by the LDH, and the reusability of the catalyst have been established.[86]

Singlet oxygen can also be generated by peroxotungstates, either in solution, or exchanged on an LDH.[84,87] However, epoxidation by peroxoW is a potential side reaction, making this system less useful than Mo. On the other hand, a tungstate-exchanged LDH efficiently catalyzes the oxidation of Br^- to "Br^+" species, e.g., OBr^-. Unless these reactive Br^+ species are trapped by a suitable olefin or by an aromatic compound, singlet oxygen can be formed, as in Eq. (23a and b). The synthetic use of this reaction has yet to be exploited.[88]

$$Br^- + H_2O_2 \longrightarrow BrO^- + H_2O \qquad (23a)$$

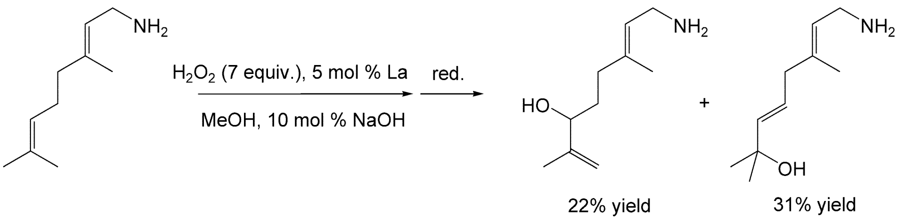
$$BrO^- + H_2O_2 \longrightarrow {}^1O_2 + Br^- + H_2O \qquad (23b)$$

3.2 Lanthanum

Lanthanum is able to decompose H_2O_2 into $^1O_2$, but the success of the peroxidation strongly depends on the procedure.[89] Starting from a suspension of insoluble La compounds such as La_2O_3 or $La(OH)_3$ in water at pH 9, hardly any $^1O_2$ is formed upon addition of H_2O_2. Clearly, the peroxide has insufficient access to the La atoms inside the (hydr)oxide particles. In contrast, when a solution of a soluble La salt is mixed with H_2O_2 and brought at pH 9, $^1O_2$ formation starts. In such conditions, a precipitate is formed, containing mainly $La(OH)_3$, but the gel is sufficiently highly dispersed to allow access of the H_2O_2 to a large number of La centers. The gel functions as a heterogeneous catalyst, although re-use of the material still needs to be demonstrated.

The yield of $^1O_2$, based on H_2O_2, is about 45% of the theoretical maximum, which means that only 0.45 mole of $^1O_2$ is formed per 2 moles of H_2O_2. It is possible that part of the $^1O_2$ is lost by quenching on the hydroxide gel. The pH range in which useful $^1O_2$ generation rates are observed is between 6.5 and 9.5, which is clearly a lower range than for the homogeneous Mo systems (pH 8.5–10.5). The rate increases with H_2O_2 concentration, which implies that there is no inhibition of the $^1O_2$ formation when a large peroxide excess is added at once.

Preparative reactions were performed with 3–10 mol % of La with respect to the olefin, and using a 7- to 30-fold excess of H_2O_2 in water or in methanol. In the "ene" hydroperoxidations catalyzed by the $La(OH)_3$ gel, the regioselectivities seem indistinguishable from those of standard $^1O_2$ reactions in a solvent, indicating again that the actual oxygenation is performed by freely diffusing $^1O_2$. However, as to chemoselectivity, an important advantage of the La system is that it has a low tendency to perform other oxygen transfer reactions, such as epoxidation of double bonds in allylic alcohols, or oxidation of the amine group in unsaturated amines. A beautiful illustration is the oxidation of geranylamine, Eq. (24). Since the La catalyst needs only a small amount of base, the reaction can be performed in



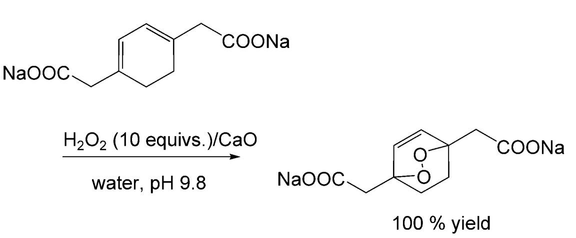
(24)

conditions in which the amine group is protonated by the excess H_2O_2. As a result, the peroxidation is directed to the terminal $(CH_3)_2C{=}C$ bond. Much lower selectivity is obtained in a reaction catalyzed by homogeneous Mo.

3.3 Calcium

It has been known for some time that in the presence of base and H_2O_2, Ca^{2+} promotes the formation of significant amounts of singlet oxygen. Two practical procedures have been proposed. First, Ca^{2+} may be used in aqueous reaction media in combination with H_2O_2.[90] Obviously, this precludes the successful transformation of apolar substrates. Alternatively, calcium peroxide diperoxohydrate has been identified as the true immediate precursor of $^1O_2$.[91,92] This compound is easily isolated, and can then be used as a $^1O_2$ source for reactions of organic compounds in organic solvents.

When the reaction is performed with aqueous H_2O_2 and $Ca(OH)_2$, the $^1O_2$ release rate is highest at pH 10.5.[89] The $^1O_2$ release rate monotonically increases with H_2O_2 concentration, indicating that a highly peroxidized species is the $^1O_2$ precursor. In order to avoid non-productive H_2O_2 decomposition, it is important to use a Ca source of very high purity. Obviously, the reaction is restricted to water-soluble substrates. With a substrate:Ca:H_2O_2 ratio of 1 : 2 : 10, complete conversion of a substituted cyclohexadiene is possible, Eq. (25).

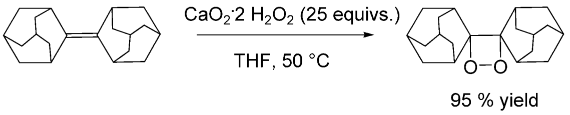


(25)

The reactions with isolated $CaO_2 \cdot 2\,H_2O_2$ are synthetically more useful.[92] This perhydrate decomposes at 50 °C according to Eq. (26).

$$CaO_2 \cdot 2\,H_2O_2 \longrightarrow CaO_2 + 2\,H_2O + {}^1O_2 \qquad (26)$$

Careful evaluation has shown that, in practice, only 0.25 – 0.5 mole of $^1O_2$ is formed per mole of Ca. $CaO_2 \cdot 2\,H_2O_2$ is easily synthesized and isolated; it can be stored for several weeks at – 80 °C prior to use. Several solvents are suitable to perform the reaction, but MeOH and tetrahydrofuran are preferred. In these solvents, the solid $CaO_2 \cdot 2\,H_2O_2$ is well dispersed, and this facilitates capture by the organic substrates of the released $^1O_2$. While reaction rates are optimal at 50 °C, care should be taken in order to avoid uncontrolled decomposition of the peroxidic reaction products. With highly reactive compounds, just the theoretical, 4-fold $CaO_2 \cdot 2\,H_2O_2$ excess with respect to the substrate is sufficient to obtain high substrate conversions (> 90%); higher amounts are needed for a less reactive compound such as adamantylideneadamantane, Eq. (27). In principle, it should be possible to recuperate the spent Ca material, *viz*. CaO_2, and to regenerate it to $CaO_2 \cdot 2\,H_2O_2$. However, this has not yet been demonstrated in practice.



(27)

4 Conclusion

For preparative reactions on a laboratory scale, dye-sensitized oxygenations continue to be a valuable method. The immobilization of the dye on a support greatly simplifies the product purification; at full substrate conversion, the solvent contains the reaction product as sole organic compound, and this contributes to the "green" character of such photo-oxidations. A clear disadvantage of many photosensitized reactions, is that they require chlorinated organic solvents, which constitute an environmental burden. The procedures for immobilization of classical dyes such as Rose Bengal are easy; from a practical viewpoint, simple immobilization procedures such as ion exchange or adsorption are preferred over the creation of covalent links *via* a complex sequence of reaction steps. Finally, the recent development of highly photostable dyes makes it possible to perform reactions with extremely high substrate over dye ratios. As for the dark reactions, influencing the product distributions of $^1O_2$-mediated oxygenations remains an important challenge. Even if encouraging results have been obtained by performing reactions with dyes in zeolites, the product yield per weight of zeolite clearly needs to be increased in order for these reactions to become synthetically relevant.

In comparison with these dye-sensitized reactions, the dark route, with catalyzed decomposition of H_2O_2, offers a number of clear advantages. The preparation of the catalysts is simple; no expensive lamps or dedicated photoreactors are required; the yields of $^1O_2$ based on H_2O_2 are high, especially for the Mo catalysts (up to 75%) and the product is not contaminated by the dye or its decomposition products. A disadvantage of the dark routes is the accumulation of $^1O_2$-quenching water in the reaction medium, particularly for poorly reactive substrates which require a large amount of $^1O_2$. However, on a larger scale, the dark route will probably eventually be preferred, certainly if further progress is made with respect to rates and the efficiencies based on H_2O_2 consumed.

Acknowledgements

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