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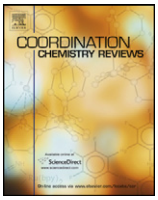

Review

# Oxovanadium complexes in catalytic oxidations

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ABSTRACT

This contribution is an overview on recent advances (since 2000) on the application of oxovanadium complexes as catalysts or mediators for oxidations by molecular oxygen, peroxidative oxygenations (both including epoxidations), halogenations and carboxylations of aliphatic and aromatic hydrocarbons, and/or olefins, toward the syntheses of a variety of organic compounds, such as alcohols, ketones, epoxides, aldehydes, organohalides and orcarboxylic acids. Some of these systems operate in liquid media, whereas others involve VO-catalysts immobilized on solid supports.

## 1. Introduction

The coordination chemistry of vanadium is experiencing a frank development with significance in important fields of biological, medicinal, material and synthetic chemistries [1–6]. Of particular synthetic interest is the use of vanadium complexes in oxidation catalysis, namely directed toward organic synthesis. In fact, this

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metal displays easily interconvertible different oxidation states, readily accessible high oxidation states, a variety of coordination numbers, a high affinity for oxygen and can behave as a Lewis acid, characteristics that can help its application in redox and Lewis acid catalyzed or promoted reactions.

Hence, it is not surprising that catalytic applications of vanadium compounds have appeared in a few reviews [7–12] usually focusing on selected fields concerning, *e.g.*, oxygenations with peroxides [10,11] or enantioselective syntheses of sulfoxides [8,9,12], a topic that thus will not be covered by the present work which also attempts to avoid considerable overlap with those of other contributions to this special issue.

The present review concerns significant advances of the last decade (2001–2010) on the use of oxovanadium complexes (and, in some cases, of non-oxo but closely related vanadium compounds) in oxidation reactions of organic compounds, as catalysts or promoters. We comment on the extended (and improper, in our opinion) use in the field, of the word "catalyst" to cases where the V-compounds are simply promoters or stoichiometric reagents is noteworthy to mention. We have also included in our review examples of such cases, but attempted to distinguish them (by denoting them as "promoters") from the real catalysts which should, in principle, display a turnover number (TON, moles of products per mol of V-complex) greater than unity. TON values are thus often indicated in this work, disclosing the catalytic nature of the V-complexes and allowing one to assess, at a first approximation, their efficiencies. Nevertheless, the reader interested on an effective catalytic system is advised to carefully check the original publications on this matter before selecting a catalyst.

The review mainly concerns homogeneous catalytic systems, but supported catalysts are also included in view of their advantageous easy separation. As substrates, it deals with not only well established unsaturated organic compounds (mainly alkenes and aromatics) but also saturated hydrocarbons (alkanes). The former can undergo well documented oxidations to a variety of oxygenates (*e.g.*, epoxides, alcohols, ketones, aldehydes, carboxylic acids), but the application of the latter compounds (alkanes) in organic synthesis remains essentially unexplored due to their high inertness, in spite of constituting huge potential carbon stocks on earth [10,13–21]. Their conversion into added value functionalized products, under mild conditions, is still a serious challenge, but vanadium complexes have already been successfully applied as catalysts or catalyst precursors for relevant alkane oxidation reactions, namely peroxidative oxygenations (to give alcohols and ketones), halogenations (to form organohalides) and carboxylations (to produce carboxylic acids).

Carboxylations are not typical oxidation reactions since they also involve C–C bond formation. However, they provide an alternative route to carboxylic acids (that can also be formed by simple oxidations), and can use common catalysts. Hence, they are mentionated, although rather shortly, also on account of their synthetic interest. All these types of alkane reaction, which have greatly attracted our interest in recent years, are promising toward the eventual exploration of alkanes as unconventional starting materials for synthesis and are briefly reviewed herein when catalyzed by oxovanadium (or closely related) compounds.

## 2. Oxidations by molecular oxygen

The use of molecular oxygen as an oxidant is particularly attractive from environmental and economic perspectives. It is the best (the "greenest" one) environmentally friendly oxidant, essential to aerobic life and is cheap. It can be used with either liquid or supported systems. This section concerns the cases where $O_2$ is applied as the oxidant in oxovanadium systems, without the assistance of any added peroxide reagent.

### 2.1. In liquid systems

Vanadium(IV) complexes bearing the deprotonated forms of 3-hydroxypicolinic acid $[(\mathrm{H_2hpic}) = \mathrm{N\overline{C(COOH)C(OH)CHCHC}H}]$ as ligands, $[VO(Hhpic)_2]$ and the cyclic tetramer $[(VO)_4(hpic)_4]$, exhibit catalytic ability for the oxidation, by $O_2$, at 120 °C, of a variety of primary and secondary benzyl alcohols in acetonitrile or protic solvents, such as, ethanol and water, affording the corresponding aldehydes and ketones (Scheme 1), with yields up to 97%, TONs up to 2500 and with high selectivities [22].

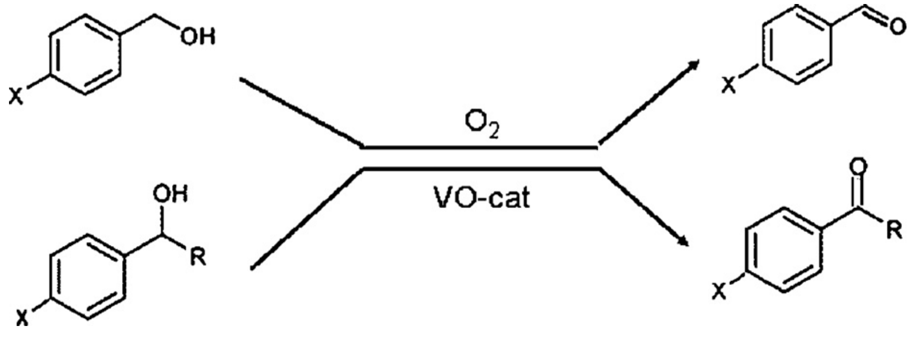
The aerobic oxidation of isopropanol to acetone in aqueous acid solutions is catalyzed by peroxovanadates, the reaction proceeding via inner-sphere oxidation of the alcohol coordinated to the metal and the mechanism involves radical intermediates [23].

The vanadium complexes $[VO(acac)_2]$ (acac = acetylacetonate) (**1A**) and $[VO(OiPr)_3]$ (**2A**) (O*i*Pr = isopropoxy) act as co-catalysts in the aerobic oxidation of some alcohols (cyclohexanol and 2-pentanol) to the corresponding ketones catalyzed by *N*-hydroxyphthalimide as a radical-producing agent, with or without the addition of a simple salt (*e.g.* LiCl) or base (*e.g.* pyridine), under 1 atm of $O_2$, at 50–75 °C, in acetonitrile [24] (Fig. 1).

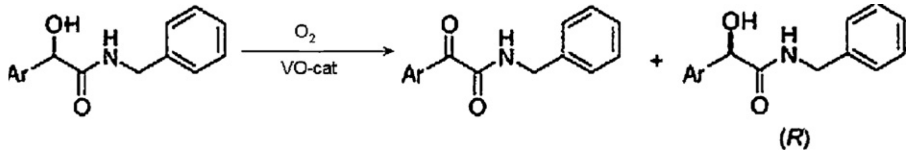
Various oxovanadium(V) complexes with chiral ligands derived from *N*-salicylidene-L-α-amino acids and methoxide (one with two oxovanadium centers) (**3A**) are highly enantioselective catalysts for asymmetric oxidation of α-hydroxy-esters and/or-amides (*e.g.*, Scheme 2) with a diverse array of α-, *O*-, and *N*-substituents [25].

Enantioselective synthesis is possible for both aromatic and aliphatic secondary alcohols, including those containing olefins and alkynes [26]. A ligand with an *O,N,O*-coordination type can lead to a significant enhancement in stereoselectivity, in comparison with tetradentate salen-related [see (**1B**)] ligands [26] (Fig. 2).

The best stereoselective systems involve the combination of L-*tert*-leucine (**2B**) and 3,5-di-*t*-butyl-, 3,5-diphenyl-, or 3,4-dibromo-salicylaldehyde. The reactions were carried out with



**Scheme 1.** Oxidation of primary and secondary benzyl alcohols by dioxygen catalyzed by oxovanadium complexes.



**Scheme 2.** Enantioselective oxidation of α-hydroxy-amides by dioxygen catalyzed by oxovanadium complexes.

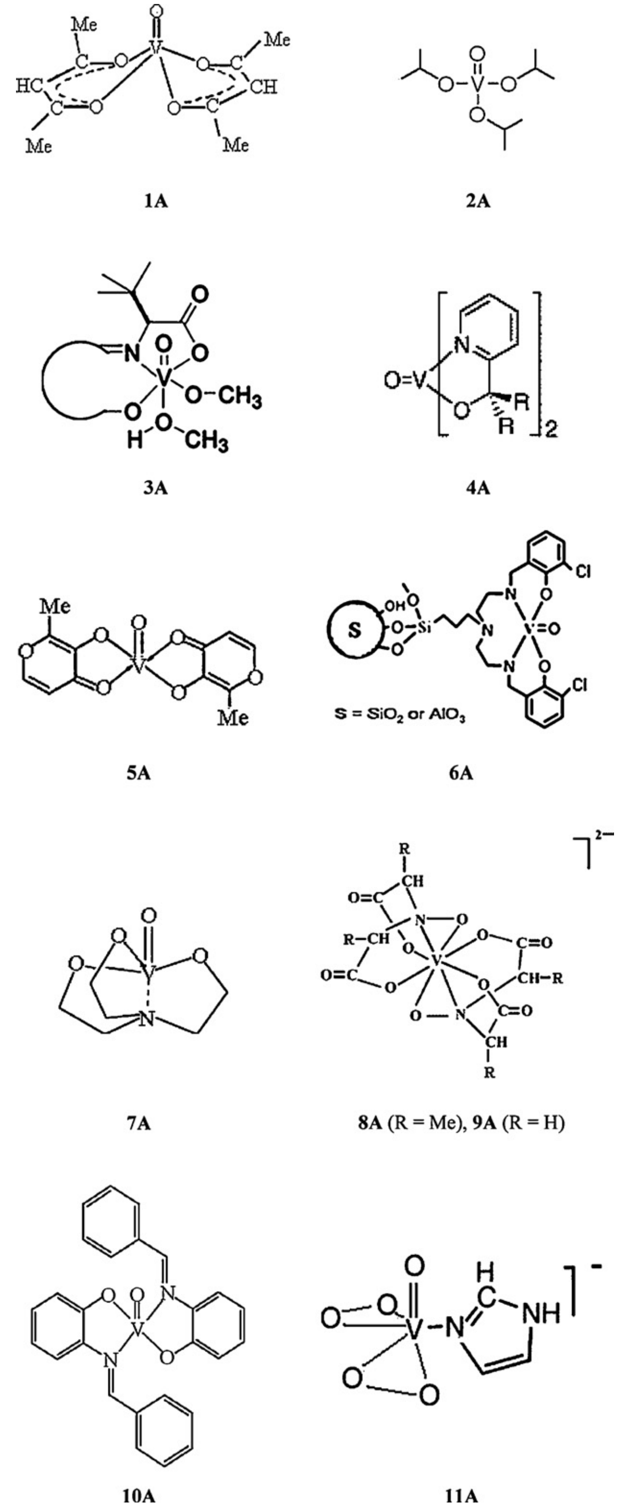


**Fig. 1.** Some vanadium complexes (catalysts or catalyst precursors) mentioned in the text.

vanadyl catalysts (3–5 mol%) in dioxygen saturated toluene at room temperature, and the optimal kinetic resolution was obtained with high selectivity factors, allowing recovery of the enantiopure reagent (ee > 99%) in high yields (45–48%) [25]. Structural studies of a vanadyl complex–substrate adduct show several particularities, such as, the substitution of the alkoxide ligand of the complex by a similar group of the substrate, the coordination of amide carbonyl group *anti* to the VO bond and specificities for each enantiomer in chelation [25].

Tridentate Schiff base oxovanadium(V) complexes with ligands derived from salicylaldehydes (see reagent in Scheme 15) and *tert*-leucinol (**3B**) or *tert*-leucine are catalysts for the asymmetric oxidation of α-hydroxy esters [27]. The catalyst acts not only in homogenous solution but also as supported, in both semi-soluble and insoluble forms. All the cases present similar activities in the oxidation of ethyl mandelate (**1C**), but the mesoporous silica supported catalyst is more selective than the other supported ones [27] (Fig. 3).

The aerobic oxidation of 1,2,3,4-tetrahydronaphthalene to the corresponding hydroperoxide, alcohol and ketone, in the pure liquid state and in its solutions in chlorobenzene at 70 °C, is catalyzed by $[VO(acac)_2]$(**1A**) [28].

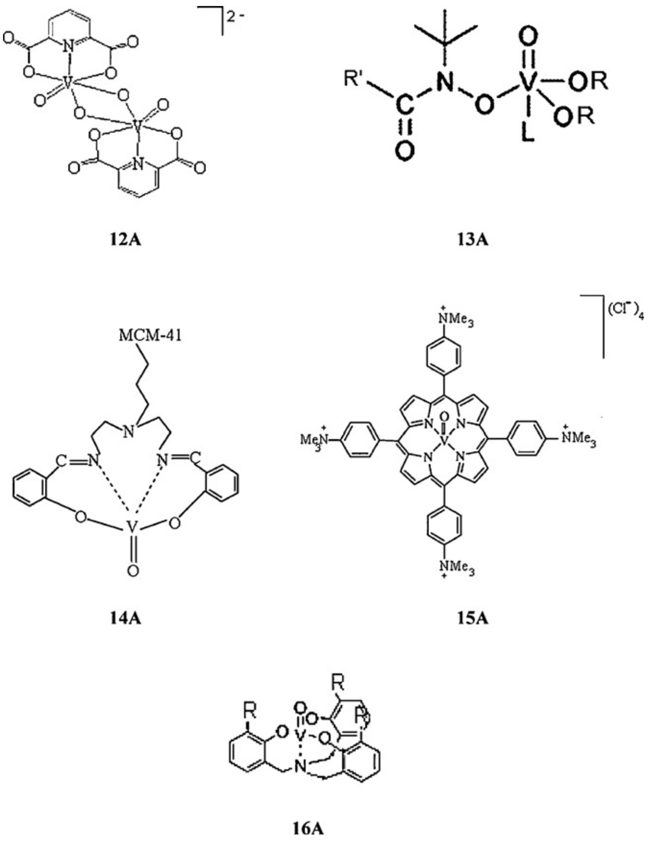
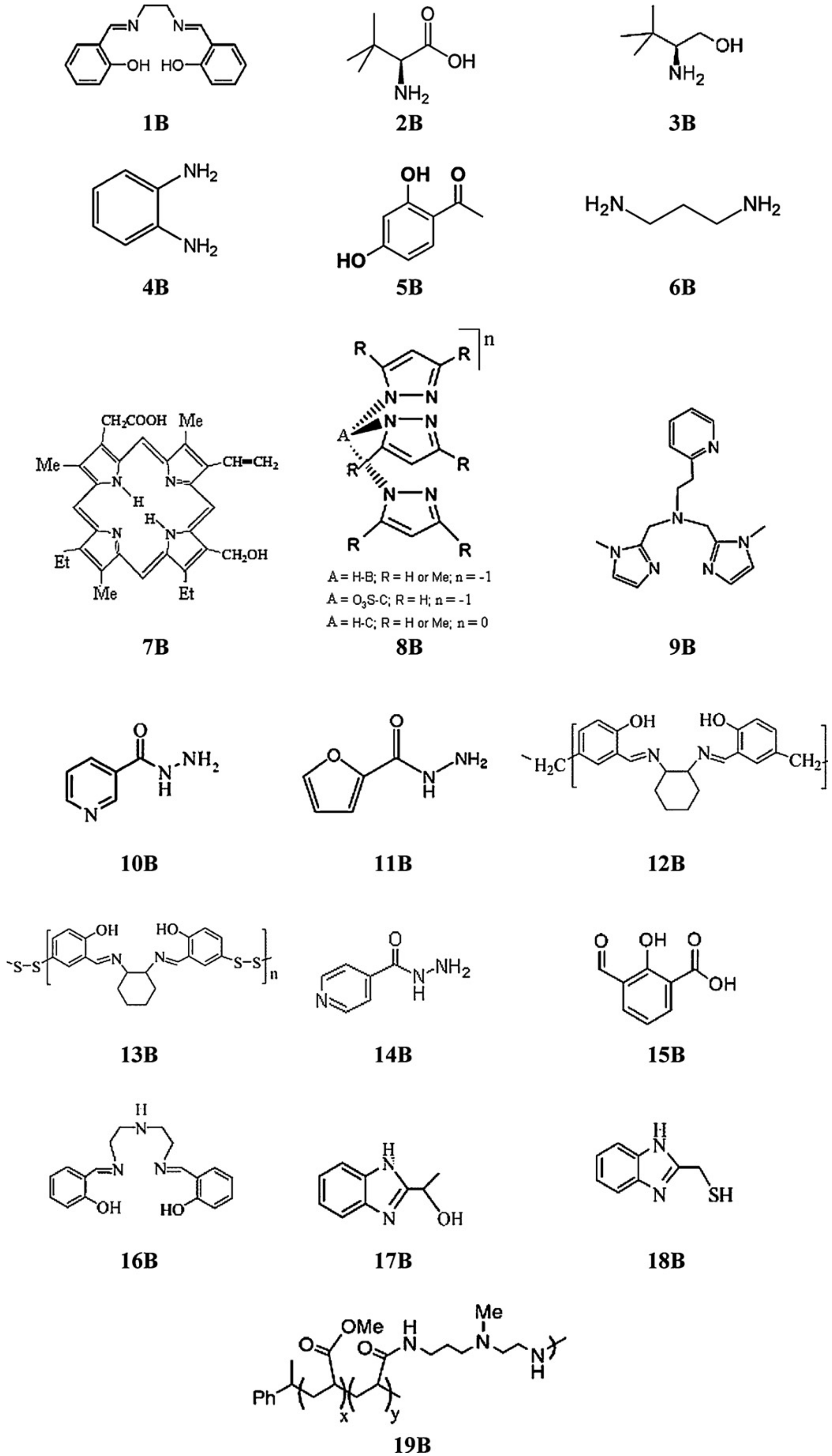


**Fig. 1.** (*Continued*).



A = H-B; R = H or Me; n = -1
A = $O_3S$-C; R = H; n = -1
A = H-C; R = H or Me; n = 0

**Fig. 2.** Some ligands or ligand precursors mentioned in the text.

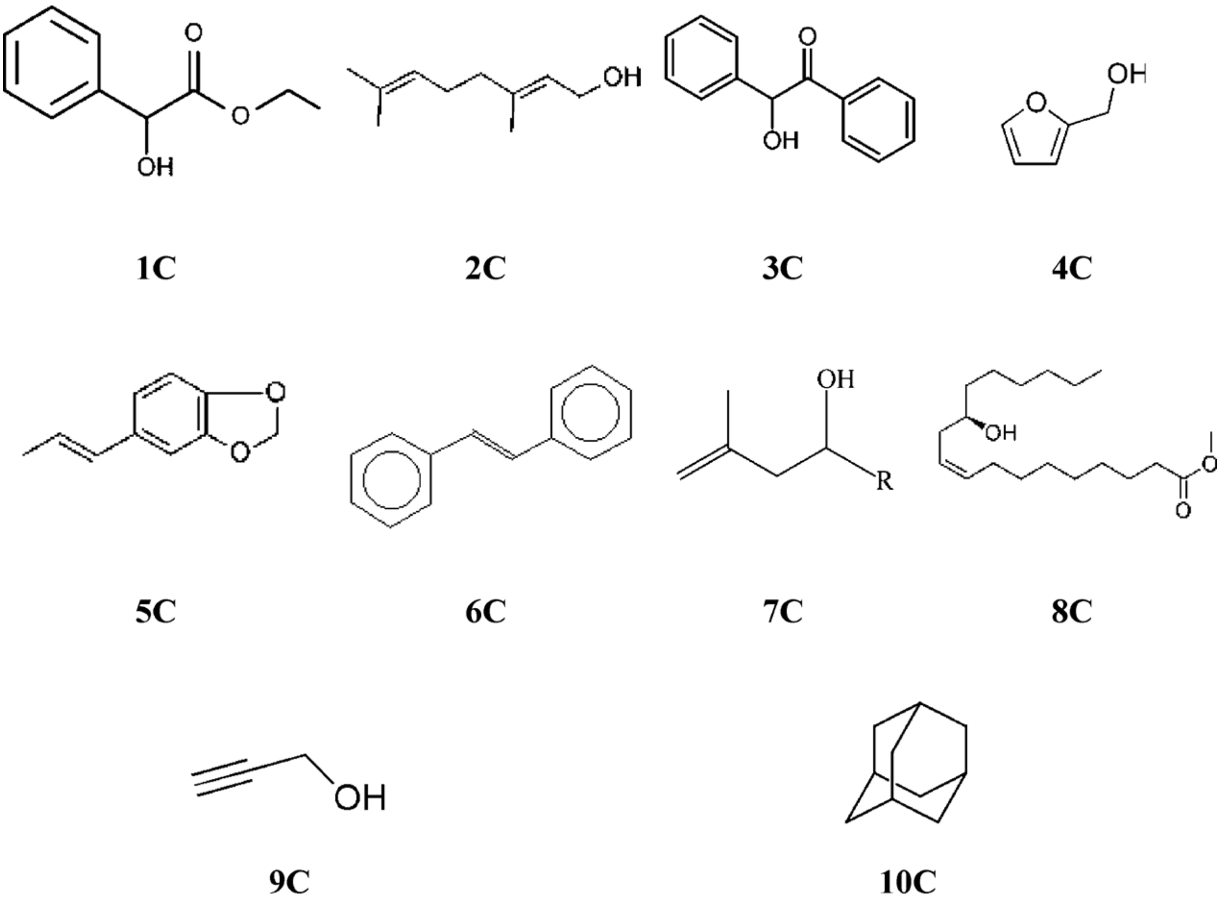
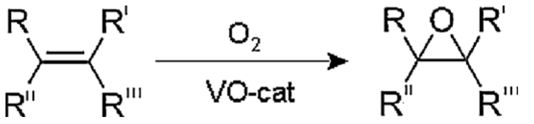


**Fig. 3.** Some substrates mentioned in the text.



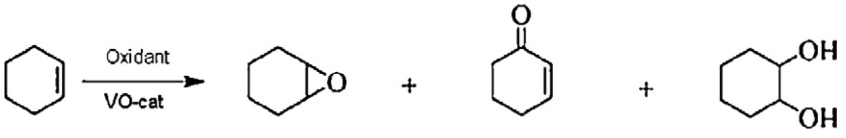
**Scheme 3.** Epoxidation of olefinic compounds by dioxygen catalyzed by oxovanadium complexes.

*2.1.1. Epoxidations*

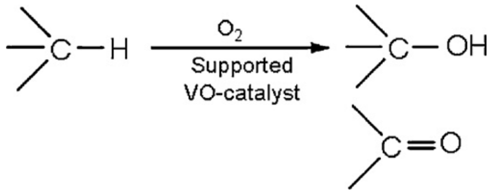
The epoxidation of olefinic compounds is an important synthetic reaction for both commodity and fine chemicals. A number of oxidizing agents has been used, namely molecular oxygen, peroxides, peracids and its salts, and vanadium Schiff base complexes have been applied as common catalysts in the case of aerobic alkene epoxidation (Scheme 3).

Oxovanadium(IV) complexes with tetradentate unsymmetrical Schiff base ligands [resulting from condensation of 2′,4′-dihydroxyacetophenone (**5B**), 2′-hydroxyacetophenone or salicylaldehyde (see reagent in Scheme 15) and 1,2-diaminoethane or 1,3-diaminopropane (**6B**)] have been applied as catalysts for epoxidation of cyclohexene in freshly distilled acetonitrile or dimethylformamide (DMF) at 78–81 °C under $O_2$ (1 atm, constantly reloaded) [29]. The catalytic activity increases with the $V^V/V^{IV}$ reduction potential and the selectivity is ligand dependent [29]. The vanadyl complexes bearing unsymmetrical diimino tetradentate Schiff bases {derived from 1,2-phenylenediamine (**4B**) and 1,3-naphthalene diamine [30]} and salen (**1B**) [*N*,*N*′-ethylenebis (salicylideneimine)] ligands have also been used as catalysts for the selective aerobic oxidation of cyclohexene (Scheme 4) to afford a mixture of 1,2-epoxycyclohexane, 2-cyclohexene-1-ol and 2-cyclohexene-1-one [31]. These systems are moderately selective catalysts for olefin epoxidation, and the catalytic activity is enhanced by decreasing the number of electron-donor substituents at the ligands.

The complexes used in [29] and under comparable conditions, but at lower temperature (75–78 °C) and reaction time (12 instead of 24 h), catalyze the epoxidation of cyclooctene to yield the epoxide (1,2-epoxycyclooctane) usually as the main product (maximum selectivity of 49%, overall yield of 23–59%), although the alcohol and the ketone are also formed in considerable amounts [32]. The most active complex has a total TON of 492. As above, that catalytic activity increases with a decrease in the number of electron-donating



**Scheme 4.** Cyclohexene oxidation, catalyzed by oxovanadium complexes, to 1,2-epoxycyclohexane, cyclohex-2-enone and cyclohexane-1,2-diol.



**Scheme 5.** Alkane oxidation by dioxygen catalyzed by oxovanadium complexes.

groups. At a higher catalyst concentration and a shorter reaction time, a lower yield but a higher epoxide selectivity was observed [32].

Vanadium(IV) complexes with $N_2O_2$-donor ligands [resulting from salicylaldehyde (see reagent in Scheme 15), 2′-hydroxyacetophenone or 2′,4′-dihydroxyacetophenone (**5B**) and 1,2-diaminopropane] are able to catalyze the selective epoxidation of cyclooctene under similar conditions of [32] or in mixed acetonitrile/DMF (3:2 ratio) [33]. As for the above catalysts, the epoxide is usually the major product (maximum 60% selectivity) and the activity is hampered by electron releasing substituents [33].

Vanadium(IV) complexes with bis(aryl)-2-pyridylmethanol ligands (**4A**) catalyze the oxidation of 1-octene at 100 °C with *ca.* 30% epoxide selectivity [34]. In general, these complexes are more efficient than $[VO(acac)_2]$ (**1A**) under the same conditions [34].

Vanadyl porphyrin [see ligand (**7B**)] complexes synthesized from petroleum metal porphyrines catalyze the epoxidation of olefins (38–75% yields), in DMF with a small amount of glacial acetic acid that acts as a protonating agent, facilitating the formation of the electrophilic oxygen responsible for the epoxidation [35]. The optimum temperature range is 60–70 °C and the autoclave has a steady dioxygen supply (3 atm) [35].

The aerobic oxidation of cyclohexene (Scheme 4) to the corresponding hydroperoxide, epoxide and alcohol in the pure liquid state and in their solutions in chlorobenzene at 70 °C is dependent of the concentration of the catalyst, $[VO(acac)_2]$ (**1A**) [28].

$[VO(acac)_2]$ (**1A**) acts as a redox mediator for the electrosynthesis of epoxides from olefinic compounds (especially acids) [36]. The overall process occurs in several steps, including the cathodic reduction of molecular oxygen to hydrogen peroxide that promotes the oxidation of the vanadyl complex [36].

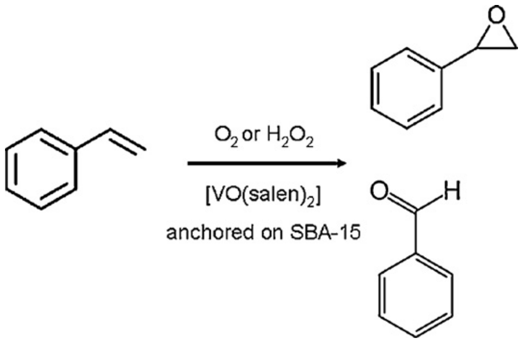
### 2.2. *In supported systems*

The immobilization of a catalyst or a catalyst precursor complex on a support is a common and suitable procedure for combining the advantages of homogeneous and heterogeneous catalyzes, and several types of support have been used for oxovanadium catalysts.

#### 2.2.1. *Alkanes*

Alkanes can be oxidized with molecular oxygen to alcohols and ketones as the main oxygenates, by using a supported oxovanadium complex as a catalyst (Scheme 5). However, one should note that, in several examples of supported metal catalysts, alkyl hydroperoxides are the direct oxidation products which during the reaction can convert to more stable ketones and alcohols as secondary products [37–40].

Hence, an oxovanadium compound bearing the Schiff base ligand 1,2-bis(salicylideneimino) phenylene, anchored on silica gel, catalyzes the oxidation of *n*-octane [41], *n*-heptane [42], *n*-hexane and *n*-pentane [43]. The reactions typically are performed at 150–200 °C under $O_2$. The oxidation of *n*-octane leads mainly to 2,3-butanedione (51%), together with octenes (11%), octanones (7%), octanols (6%) and octanoic acid (3%) [41]. The oxidation of *n*-heptane also forms a mixture of many derivatives [42]. The main product of *n*-pentane oxidation is mesaconic acid, $COOH(CH_3)C{=}CHCOOH$, (selectivity up to 92%), while *n*-hexane leads to 1-hexanol (the major product, up to 52%), 2-methyl-2,4-pentanediol, 1,6-hexanediol, ketones and acids [43]. All these reactions have low conversions.



**Scheme 6.** Styrene oxidation, catalyzed by $[VO(salen)_2]$ anchored on SBA-15, to epoxide and benzaldehyde.

The carbamated silica gel supported bis(maltolato)-oxovanadium(IV or V) complexes (the IUPAC name to the ligand is 3-hydroxy-2-methyl-4H-pyran-4-one), *e.g.* (**5A**), are catalysts for the oxidation with $O_2$ of cyclopentane and cyclooctane [44]. The corresponding ketones, cyclopentanone and cyclooctanone, are the main products (up to 10% and 25% yields, respectively) of the cycloalkane oxidations, but cyclopentanol and cyclooctanol are also detected in smaller amounts [44]. The oxidation of cyclohexane under similar conditions forms two major products, cyclohexanol and cyclohexanone in a smaller amount, with a good selectivity [45], and the oxidation of linear alkanes, *n*-pentane and *n*-hexane, under comparable conditions, yields the corresponding ketones and alcohols (84% selectivity to 2-pentanone and 2-pentanol from *n*-pentane; 58% selectivity to 2-hexanone, 1-hexanol and acetic acid from *n*-hexane) [46]. Typically there actions were performed at $pO_2$ *ca.* 10–15 atm and 150–175 °C.

Oxovanadium(IV) complexes with ligands derived from condensation of bis(aminopropyl)amine (DPTA) or 2,2-diaminoethylamine (DETA) and salicylaldehyde (see reagent in Scheme 15) or 5-chlorosalicylaldehyde, covalently supported on $SiO_2$ or $Al_2O_3$ by *n*-propyltrimethoxysilyl, catalyze the oxidation with $O_2$ of cyclohexane to cyclohexanol and cyclohexanone, *e.g.*, with yields up to 38% and 74% selectivity toward cyclohexanol, for complex (**6A**) with the ligand resulting from reaction of DPTA with 5-chlorosalicylaldehyde, at $p(O_2) = 10$ atm, 150 °C and 12 h reaction time [47].

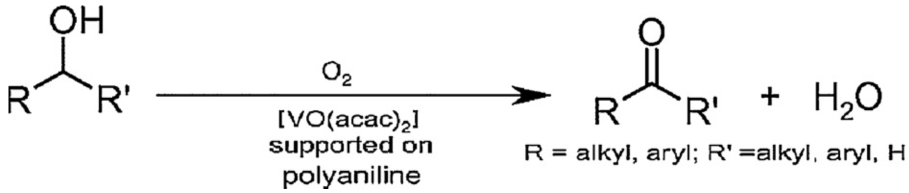
In the above oxidations, the presence of radical traps reduces considerably the yields, suggesting the involvement of a radical mechanism. In contrast, the reactions are promoted by pyrazine-2-carboxylic acid (PCA) and related co-catalysts.

#### 2.2.2. *Styrene*

The application of supported oxovanadium catalysts to alkene oxidations using molecular oxygen as oxidant is still an under developed field of research. $[VO(salen)_2]$ with salen (**1B**) anchored on mesoporous silica matrix (SBA-15) catalyzes styrene oxidation in acetonitrile, with a high selectivity to the corresponding epoxide, using air as oxidant [48] (Scheme 6). A better selectivity toward benzaldehyde is obtained when $H_2O_2$ is the oxidizing agent (Scheme 6). The catalyst could be recycled many times [48].

#### 2.2.3. *Alcohols*

$[VO(acac)_2]$ (**1A**) supported on polyaniline catalyzes the aerobic oxidation of alcohols to aldehydes and ketones, in acetonitrile, toluene or *p*-xylene as a solvent, typically at 80 °C [49] (Scheme 7). The oxidation of benzyl alcohol gives benzaldehyde (68%, 91% or



**Scheme 7.** Oxidation of alcohols catalyzed by $[VO(acac)_2]$ (**1A**) supported in polyaniline.

45% yields, respectively) at that temperature, whereas at *ca.* 100 °C in toluene it achieves 98% yield. No further oxidation of the aldehyde to benzoic acid was detected, whereas the oxidation of benzyl alcohol using free $[VO(acac)_2]$ (**1A**) was less selective and provided a 1:1:2.5 mixture of benzoic acid, benzyl benzoate and benzaldehyde (90% over all yield) in toluene at *ca.* 100 °C. The alcohols with both electron releasing and electron withdrawing groups in the aromatic ring, *i.e.*, 4-methoxy-, 4-nitro-, 4-hydroxy- and 3,4,5-trimethoxy-benzyl alcohols, were oxidized to the corresponding aldehydes in high yields. The same occurs in the case of allylic alcohols, and geraniol (2,6-dimethyl-*trans*-2,6-octadien-8-ol) (**2C**). The saturated alcohol heptan-1-ol was less reactive, while secondary alcohols, diphenylmethanol, benzoin (**3C**) and cyclohexanol provided the corresponding ketones in quantitative yields. Likewise, furfurol (**4C**) and pyridine-2-methanol could be oxidized to the respective aldehydes in high yields. No oxidation was observed at a phenolic OH, the *N*-atom of pyridine-2-methanol and the carbon–carbon double bond of the allylic alcohols. The supported catalyst can be recycled with preservation of the activity [49].

## 3. Peroxidative oxygenations

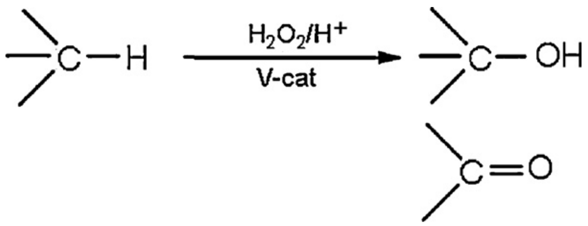
Several oxovanadium(IV or V) complexes with *N*,*O*- or *O*,*O*-bonded ligands have been used as catalysts for the peroxidative oxygenation (*i.e.*, with a peroxide) of organic molecules, for instance hydrocarbons (including aromatics) to give the corresponding alcohols and ketones, epoxides, aldehydes and, in some cases, other types of product, such as carboxylic acids. It is noteworthy to mention that dioxygen can be the main oxidizing and oxygenation agent, while the peroxide reagent can display another role such as the source of hydroxyl radical which is an H-abstractor. Examples with liquid systems and with supported catalysts will be discussed below. The use of microwave and ionic liquids has also been reported [50].

### 3.1. In liquid systems

### 3.1.1. In acetonitrile solvent

Acetonitrile is a convenient solvent for the peroxidative oxidation of hydrocarbons in liquid systems due to its resistance to oxidation and capacity to solubilize the reagents and organic products.

*3.1.1.1. Alkanes.* The peroxidative oxygenation of alkanes to the corresponding alcohols and ketones (Scheme 8) is usually carried out in acetonitrile and acidic medium, with aqueous $H_2O_2$ as the oxidizing agent. Shul'pin and co-workers have developed highly efficient vanadium catalytic systems that have been reviewed [10,19,20] and herein we stress the following points. The addition of nitric [51], sulfuric or oxalic [52] acids often has a promoting effect, which is also observed with other additives, such as pyrazine-2-carboxylic acid (PCA) and related heterocyclic acids [20,53]. The promoting role of PCA proceeds by assisting proton-transfer steps ("robot's arm mechanism") which are involved in the formation of hydroxyl radical ($HO^\bullet$) from $H_2O_2$ [19,20,53].



**Scheme 8.** Peroxidative oxidation of alkanes catalyzed by vanadium complexes.

However, recent theoretical (DFT) and experimental studies [54,55] indicate that a water-assisted mechanism of proton transfer steps is more effective than the "robot's arm mechanism". In the new proposed mechanism (Scheme 9) the rate limiting is the H-transfer from ligated $H_2O_2$ to an hydroxo-ligand (step promoted by $H_2O$ via a transition state with a 6-membered metallacycle, **1** – Fig. 4) and not the unimolecular elimination of $HOO^\bullet$ radicals, the role of the co-catalyst PCA being that of a stabilizer of the transition state species involved in the rate-limiting step [54,55]. It was then shown [54,55] that water plays a relevant role as a $H^+$-transfer promoter, apart from being a solvent.

The oxovanadium(V) complex with triethanolaminate ligand [VO(tea)] (**7A**) or vanadate ($VO_3^-$), in acetonitrile and in the presence of PCA, efficiently catalyze (TOF = 220 $h^{-1}$), at 40–50 °C, the oxidation of cyclohexane, with aqueous $H_2O_2$, to cyclohexyl hydroperoxide (CyOOH) from which cyclohexanol and cyclohexanone are derived [54,55]. The formation of CyOOH is believed to involve $HO^\bullet$ (from $H_2O_2$) which acts as a $H^\bullet$-abstractor from the alkane to give $Cy^\bullet$ that, upon oxidation with $O_2$, forms $CyOO^\bullet$ [53–55].

Alternatively, peroxyacetic acid can be used as an oxidizing agent in the above oxidation, at 60 °C, catalyzed by vanadium(V) and vanadium(IV) complexes (without strongly bond bulky ligands), and promoted by acetic acid [56].

[VO(tea)] (**7A**) also acts as a catalyst, at 20 °C, for the peroxidative oxidation of cyclohexane to the corresponding alcohol and ketone, in acidic medium, with $H_2O_2$, with a total yield of 11% and TON 53 [57–59]. The same reaction is also catalyzed, under the same conditions, by the related non-oxovanadium(IV) complexes $[V(HIDPA)_2]^{2-}$ (**8A**) (HIDPA = *N*-hydroxyimino-(2,2′)-dipropionic

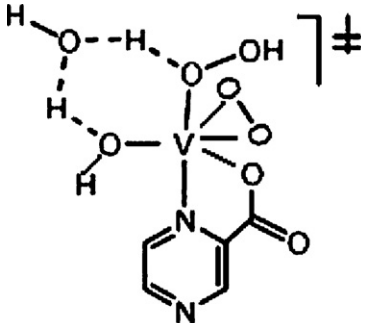
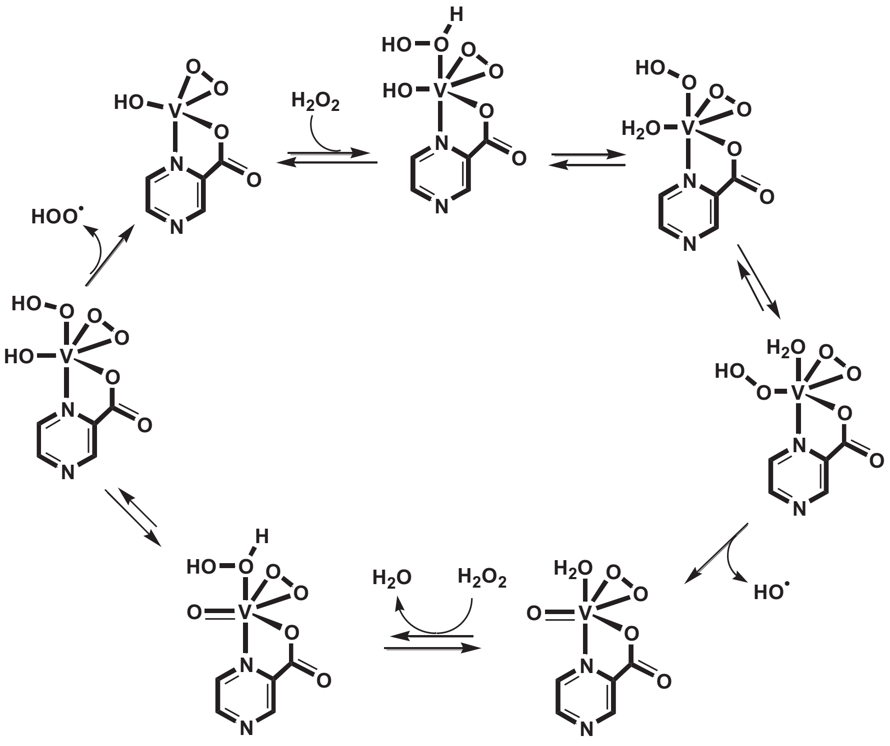


**Fig. 4.** Transition state in the water-promoted $H^+$-transfer from ligated $H_2O_2$ to a hydroxo ligand in the peroxidative oxidation of alkanes [54].



**Scheme 9.** Mechanism of peroxidative oxidation of alkanes catalyzed by a vanadium complex.

acid) and $[V(HIDA)_2]^{2-}$ (**9A**) (HIDA = *N*-hydroxyiminodiacetic acid), both close models of the natural complex Amavadin (present in *Amanita muscaria* fungi, and still with an unknown biological function), with total yields up to 10% and TON up to 50 [57–59].

The dioxovanadium(V) complexes $[VO_2(3,5\text{-}Me_2Hpz)_3][BF_4]$ (pz = pyrazolyl), $[VO_2\{SO_3C(pz)_3\}]$, $[VO_2\{HB(3,5\text{-}Me_2pz)_3\}]$ and $[VO_2\{HC(pz)_3\}][BF_4]$, bearing pyrazole or scorpionate ligands (**8B**), also reveal catalytic activity for cyclohexane and cyclopentane peroxidative oxidations with yields up to 24% and TONs up to 117 [51]. The sulfonate derivative is water soluble, a feature that is favorable to the establishment of a green catalytic system [51].

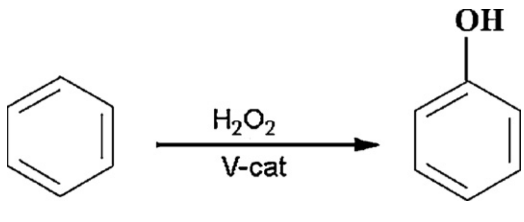
$[VO(acac)(BMIMAPY)][ClO_4]$ [BMIMAPY = bis(1-methylimidazol-2-yl)methyl)(2-(pyridyl-2-yl)ethyl)amine (**9B**) (a imidazole-rich tripodal ligand)] catalyzes cyclohexane oxidation, under an inert atmosphere at room temperature, with $H_2O_2$ or TBHP as the oxidant [60]. The use of TBHP leads to a low overall conversion, but $H_2O_2$ is more efficient resulting into a cyclohexane over all conversion of 47% to cyclohexanol, cyclohexanone and cyclohexylhydroperoxide [60].

Oxovanadium(V) complexes with salicylhydroximate ligands and the related $[V(O)(Cl)(PBHA)_2]$ ($PBHA^-$ = *N*-phenyl benzohydroxamate) catalyze the peroxidative oxidation of aliphatic hydrocarbons (cyclohexane, *n*-hexane and *n*-heptane) to their corresponding alcohols and ketones, using $H_2O_2$ as terminal oxidant, at 60–85 °C [61,62].

*3.1.1.2. Aromatic compounds.* The compounds $[K(H_2O)][V^VO_2(\text{sal-nah})]$ and $[K(H_2O)][V^VO_2(\text{sal-fah})]$ [sal = salicylaldehyde (see reagent in Scheme 15), nah = nicotinic acid hydrazide (**10B**), fah = 2-furoic acid hydrazide (**11B**)] catalyze the oxidation of benzene to phenol (Scheme 10) and of phenol to catechol and *p*-hydroquinone at 80 °C and with $H_2O_2$ as oxidant (the maximum conversion is 34% after 15 h of reaction) [63]. The vanadium complex/PCA system catalyzes the benzene hydroxylation at 25 °C [64].

The methoxy-oxovanadium(V) complex with an aminebis(phenolate) ligand $[V^VO(L)(OMe)]$ promotes the oxidation, with $H_2O_2$, of toluene to benzoic acid, and of isomers of xylene to the corresponding hydroxy acids (TONs in the 134–188 range) [65]. The host–guest vanadium(V) complexes with 2,2′-dipyridine and cyclodextrin synthesized *in situ* catalyze the formation of benzoic acid and benzaldehyde, from toluene, with the same oxidant ($H_2O_2$) at 50 °C [66]. Lower amounts of cyclodextrin allow 100% of selectivity toward benzoic acid, but with a lower conversion. These systems are more efficient than the similar ones with iron. The supramolecular catalysts behave as "nanoreactors" with a hydrophobic cavity which favors the formation of entities with non-polar substrates, and these frameworks can increase the catalyst efficiency for this type of reaction [66].

A number of the above systems (Section 3.1.1.1) that catalyze alkanes peroxidative oxidations also catalyze related oxidations of aromatic compounds. Hence, the oxovanadium complexes [VO(tea)] (**7A**), $[VO(ada)(H_2O)]$ [ada = basic form of *N*-(2-acetamido)iminodiacetic acid], $[VO(Hheida)(H_2O)]$ [Hheida = dibasic form of *N*-(2-hydroxyethyl)iminodiacetic acid] and Amavadin related complexes (**8A**,**9A**) act as catalysts for the peroxidative oxygenation, with $H_2O_2$, of benzene and mesitylene (1,3,5-trimethylbenzene) [57–59,67] to phenol (Scheme 10) and 3,5-dimethylbenzaldehyde, respectively, in acidic (nitric acid)



**Scheme 10.** Peroxidative oxidation of benzene to phenol, catalyzed by vanadium complexes.

acetonitrile medium. The best conversion (40%) was obtained for the oxidation of mesitylene catalyzed by [VO(Hheida)($H_2O$)] [67]. An excessive increase of the $HNO_3$ or $H_2O_2$ amounts results in an inhibition effect [67].

[VO(acac)(BMIMAPY)][$ClO_4$] [BMIMAPY (**9B**)] catalyzes the oxidation of benzene, under argon at room temperature, with $H_2O_2$ or TBHP, the former oxidant being more effective (11% conversion of benzene to phenol with 100% selectivity) [60] (Scheme 10).

Oxovanadium(V) complexes with salicylhydroximate ligands and [V(O)(Cl)(PBHA)$_2$] exhibit good catalytic activities for the peroxidative oxidation, with $H_2O_2$, at 60–85 °C, of benzylic and aromatic compounds (including pyridine), to their corresponding hydroxylated and oxygenated products, *i.e.*, aldehydes, phenols, oxides, alcohols and ketones (overall yields usually higher than 96% and overall TONs up to 517) [61,62].

Three polymeric insoluble oxovanadium(IV) complexes, derived from Schiff bases resulting from 5,5′-methylenebis(salicylaldehyde) (**12B**) and 1,2-diaminoethene, 1,2-diaminopropane or 1,3-diaminopropane (**6B**), catalyze the hydroxylation, with $H_2O_2$, of phenol into a mixture of catechol and hydroquinone, in acetonitrile at 80 °C [68]. Under the optimized conditions, the selectivities toward the formation of catechol (main product) and hydroquinone are within the 90–98% and 2–10% ranges, respectively, and the overall conversion is 32–40% [68].

### 3.1.2. *In other solvents*

Under the above-mentioned conditions of [56] (Section 3.1.1.1), but using pure acetic acid as solvent, only cyclohexanone and cyclohexanol are formed (total TON = 50) by V-catalyzed oxidation of cyclohexane with peroxyacetic acid.

[VO(tea)] (**7A**) in the presence of PCA as a co-catalyst and $H_2O_2$ as oxidant, at 40–50 °C, exhibits an efficient catalytic activity for the oxidation not only of cyclohexane (Section 3.1.1.1) but also of isopropanol to acetone in the absence of any other solvent [54].

In ethanol, oxovanadium(V) complexes with tridentate Schiff-bases or 2,6-dihydroxymethyl-substituted piperidines catalyze, at 20 °C, the synthesis of a mixture of β-hydroxyl-substituted tetrahydrofurans from alkenols using TBHP as oxidant [69].

The oxovanadium(IV) [$VOL_2$] complex (**10A**), with the deprotonated form of the Schiff base *N*-(phenolyl)benzaldimine (HL), catalyzes the oxidation of several alcohols (including aromatic, cyclic and linear ones) to their corresponding aldehydes with a high selectivity but low TONs (*ca.* 12–20) using potassium peroxomonosulfate as oxidant, under biphasic reaction conditions [70]. The most efficient conversions (98%) occur in the system formed by dichloromethane/water and tetra-*n*-butylammonium bromide as phase transfer agent, under air at room temperature, for a short reaction time (typically 5 min) [70].

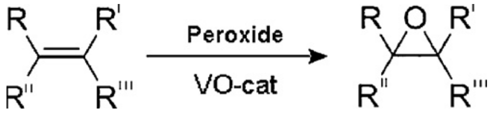
1-methoxy-4-(1-propenyl)benzene is oxidized to 4-methoxybenzaldehyde by oxovanadium(IV) complexes with aromatic carboxylate ligands, such as, phthalate, salicylate and benzoate, in acetone with $H_2O_2$ as oxidant, at 30 °C. The complex bearing the phthalate ligand achieves a quantitative conversion and a good selectivity (74%) [71].

### 3.1.3. *Epoxidations*

In this section we illustrate olefin epoxidation catalysis with oxovanadium complexes in liquid systems (Scheme 11), whereas examples with supported catalysts will be given later.

A theoretical DFT study of olefin epoxidations, using diperoxovanadate imidazole complexes (**11A**) as catalysts and $H_2O_2$ as oxidant, showed that the rate-determining step is the initial oxygen atom transfer from the catalyst to the substrate [72].

The V(IV)and V(V) complexes [VOL] and [$VO_2L$], respectively, with salicyladimine ligands derived from salicylaldehyde (see reagent in Scheme 15) and 1,3-diaminohydroxypropane, and the V(IV) complex [$VOL_2$], with the ligands resulting from condensation of 3-methoxysalicylaldehyde and 1,3-diaminohydroxypropane, catalyze the epoxidation of cyclohexene (Scheme 4), with TBHP as oxidant, in dichloroethane or the substrate as solvent [73]. [$VO_2L$] is more efficient than the V(IV) complexes, but the results are modest and 1,2-cyclohexenediol is also formed as by-product [73]. Complexes of tripeptide glutathione with several metals act as catalysts in the oxidation of the same substrate (cyclohexene) and with the same oxidant (TBHP) in toluene at 80 °C, leading to products of both epoxidation and hydroxylation [74]. The V(IV) and Mo(VI) complexes present higher activities in the cyclohexene epoxidation compared to the other tested metal complexes, namely of Cr(III), Mn(II), Cu(II), Fe(II), Co(II), Cd(II) and Th(IV) [74].

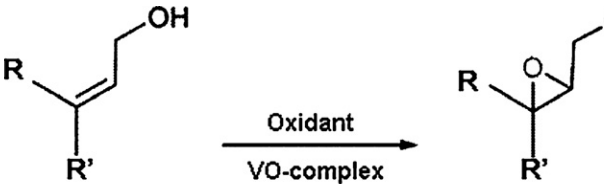


**Scheme 11.** Epoxidation of olefinic compounds with peroxide ($H_2O_2$ or TBHP) catalyzed by oxovanadium complexes.

The hexacoordinate oxovanadium(V) complex of 2-(2-butoxyethoxy)ethanolate [$VOCl_2(OCH_2CH_2OCH_2CH_2O^nBu)$] catalyzes the epoxidation of cyclooctene to the corresponding epoxide, with TBHP as oxidant in dichloromethane, with a conversion up to 68% [75]. The oxovanadium(IV) complexes with tetradentate Schiff base ligands derived from aromatic aldehydes and an aliphatic diamine (2,2′-dimethylpropandiamine) act as catalysts in oxidation of cyclooctene and styrene (overall reaction of Scheme 6), using the same oxidant [76]. The best results are in chloroform at 60 °C. The epoxidation of cyclooctene has a conversion and selectivity up to 100% and TONs up to 312, and for styrene the corresponding epoxide and benzaldehyde are formed with a conversion up to 74% and TONs up to 231 [76]. The di-μ-oxo-bis[oxovanadium(V)] compound [$(VOL)_2(\mu\text{-}O)_2$], with the tridentate Schiff base ligand derived from 1,2-propylenediamine and 2′-hydroxy-4′-methoxyacetophenone, catalyzes in chloroform at 61 °C and with TBHP, the selective epoxidation of cyclooctene to 1,2-epoxycyclooctane (100% selectivity and 312 TON) [77]. The dinuclear μ-bis(oxido)bis[oxovanadium(V)] dipicolinato complex (**12A**) (apyH)$_2$[$(VOL)_2(\mu\text{-}O)_2$]·2$H_2O$ (L = 2,6-dipicolinate; apyH = 2-aminopyridinium) exhibits a high catalytic activity for the same epoxidation reaction under similar conditions, with comparable results, and the catalyst is reusable without purification [78].

The vanadium(IV) complexes [$VO_2L$], formed from the reactions of salicylaldehyde (see reagent in Scheme 15) or its derivatives and chiral diamines (1R,2R-diaminocyclohexane, 1S,2S-diaminocyclohexane and 1S,2S-diphenylethylenediamine), act as catalysts for the oxidation of styrene (overall reaction of Scheme 6), cyclohexene and cumene to mixtures of oxygenates [79]. A typical reaction was carried out at 80 °C with $H_2O_2$ in acetonitrile. The oxidation of styrene gives benzaldehyde, 1-phenylethane-1,2-diol, benzoic acid and phenylacetaldehyde, with a conversion up to 69%. Cyclohexene is oxidized to (see also Scheme 4) 1,2-epoxycyclohexane, cyclohexane-1,2-diol, cyclohex-2-enol and cyclohex-2-enone, with a conversion up to 66%, whereas the cumene gives acetophenone, 2-phenylpropanal, 1,2-epoxy-2-phenylpropane, and 2-phenylpropan-2-ol, with a conversion up to 38% [79].

[VO(salen)], salen (**1B**), and [$VO(acac)_2$] (**1A**) have been reported [80] to catalyze the oxidation of isosafrol (**5C**), in acetonitrile and with $H_2O_2$ or TBHP as oxidants. The aldehyde is the major product for the former catalyst, whereas the epoxide is usually the main product in the latter catalyst, but the ketone is also formed in a significant amount [80].



**Scheme 12.** Enantioselective epoxidation of allylic alcohols catalyzed or promoted by oxovanadium complexes.

The oxovanadium complexes with polymeric chelating ligands derived from 5,5′-methylenebis(salicylaldehyde) (**12B**) or 5,5′-dithiobis(salicylaldehyde) (**13B**) and 1,2-diaminocyclohexane in the equimolar ratio, exhibit catalytic activities toward the oxidation, with TBHP, of styrene (overall reaction of Scheme 6), cyclohexene and *trans*-stilbene (**6C**) in acetonitrile at 75 °C [81]. Under the optimized conditions, styrene converts (85% maximum conversion) into benzaldehyde > styreneoxide > 1-phenylethane-1,2-diol > benzoic acid, whereas cyclohexene (98% conversion) gives (see also Scheme 4) 1,2-epoxycyclohexane (the main product), 2-cyclohexene-1-ol, cyclohexane-1,2-diol and 2-cyclohexene-1-one, and *trans*-stilbene forms (47% conversion) benzaldehyde, benzyl and the corresponding *trans* epoxide, as the major products [81].

*3.1.3.1. Epoxidation of allylic alcohols.* Enantioselective epoxidation of allylic (and homoallylic) alcohols to the corresponding epoxy alcohols are promoted by oxovanadium complexes (*e.g.*, Scheme 12). The reaction usually proceeds at room or lower temperatures and a typical oxidant is an aqueous solution of TBHP (it can also be used in nonaqueous solvents). The oxidation of bishomoallylic alcohols promoted by transition metal compounds, including vanadium complexes, was reported [82], but the molar ratio between the substrate and the metal is typically around one, and thus a real catalytical role of the vanadium complex is not disclosed.

$[VO(acac)_2]$ (**1A**) in the presence of TBHP catalyzes the epoxidation (i) of chiral homoallylic alcohols (**7C**) followed by an intramolecular epoxide ring opening of the corresponding 3,4-epoxy alcohols, in anhydrous dichloromethane at −5 °C and under argon atmosphere [83], (ii) of methyl ricinoleate (**8C**) and 13(*S*)-hydroxyoctadeca-9(*Z*),11(*E*)-dienoic acid in dichloromethane at 0 °C, under a dinitrogen atmosphere [84] and (iii) of double bond substituted 2-(2-alkenyl)phenols under mild conditions [85].

The oxovanadium(IV) complexes $[VOL_2]$ of 3-hydroxy-4-pyrone (related with maltol) and 3-hydroxy-4-pyridinone ligands exhibit high activity and selectivity in the epoxidation of geraniol (**2C**) toward 2,3-epoxygeraniol (100% conversion and TOFs up to 200 $h^{-1}$) [86]. The pyrone based complexes are the most efficient ones, with performance similar to that of $[VO(acac)_2]$(**1A**), the reaction being carried out in dichloromethane with TBHP [86]. Vanadium(IV) complexes with bis(aryl)-2-pyridylmethanol ligands (**4A**) catalyze the epoxidation reactions of (**2C**) at 50 °C with TBHP (TONs of 100–400) [87].

Series of chiral hydroxamic acids react with $[VO(OR)_3]$, usually vanadium(V) tri-*i*-propoxy oxide $[VO(OiPr)_3]$ (**2A**), or with $[VO(acac)_2]$ (**1A**), to form vanadium species (**13A**) that are effective for the asymmetric epoxidation of allylic and homoallylic alcohols in a nonaqueous solvent, with good yields and high enantioselectivities [88–97]. The reaction can also take place in water [98,99] or using achiral hydroxamic ligands, but with optically active hydroperoxides [100,101]. Intermediates in the $[VO(OR)_3]$/hydroxamic acid/TBHP catalytic system, bearing a planar chiral hydroxamic acid, include two diastereomeric complexes and their distinct reactivities account for the detected enantioselectivity of the products [34]. The mechanism probably involves the TBHP activation by vanadium(V) centers forming a peroxy intermediate [82].

Another type of reaction promoted by this kind of complex is the oxidation of allylic and propargylic (**9C**) alcohols to the corresponding aldehydes and ketones [102]. However, the presence of hydroxamic acids can constrain the loss of the oxo ligand. Other types of chiral ligand are adequate, namely Schiff bases [103] and terpenoids [104].

## 3.2. In supported systems

### 3.2.1. Alkanes

Both 3-[*N*,*N*-bis-3-(salicylidenamino)ethyltriamine] oxovanadium(IV) anchored on a mesoporous molecular sieve (MCM-41) (**14A**) through a covalent bond and the “free” complex catalyze the oxidation of adamantane (**10C**), in acetonitrile, with urea hydroperoxide or $H_2O_2$, at 60 °C, the two major products being 1-adamantanol and 2-adamantanone (overall reaction of Scheme 8) [105]. The anchored complex allows a higher conversion (22%) than the unsupported one (5%) [105]. An oxovanadium salen complex [salen (**1B**)] anchored on a secondary amino group modified MCM-41 support which is an effective catalyst for the oxidation of cyclohexane using $H_2O_2$, in acetonitrile, at 60 °C, with a 46% conversion into a cyclohexanone and cyclohexanol mixture (overall reaction of Scheme 8) [106].

The bis(maltolato) complexes of oxovanadium(V and IV) $[VO(ma)_2]$ (**5A**), $[VO(py)(ma)_2]$(ma = maltolato, py = pyridine), *cis*-$[VO(OCH_3)(ma)_2]$ and *cis*-$[VO(OC_2H_5)(ma)_2]$, supported in chemically modified silica gel, act as catalysts in the oxidation of alkanes to the corresponding alkyl hydroperoxides, with $H_2O_2$ at 40–50 °C [107]. Heterogenization of the complexes leads to changes in region-selectivity in comparison with the corresponding homogeneous systems [107].

The oxovanadium(IV) complex of the Schiff base derived from salicylaldehyde (see reagent in Scheme 15) and *o*-aminobenzyl alcohol encapsulated in zeolite-Y, with $H_2O_2$, catalyzes the oxidation of cyclohexane at 70 °C to cyclohexanone and cyclohexanol (overall conversion of 15%) (overall reaction of Scheme 8) [108].

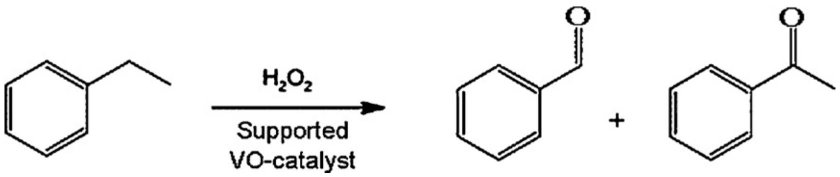
### 3.2.2. Unsaturated organic compounds

The anchored vanadium catalysts mentioned in this section are often recyclable without a substantial loss of their catalytic activities and more efficient than the corresponding nonpolymer-bond complexes. Moreover, when comparisons have been reported, the complexes of vanadium commonly lead to higher conversions than those with other transition metals (such as, copper, nickel, molybdenum and tungsten) [108–113]. Unless stated otherwise, the solvent is acetonitrile and the oxidant is hydrogen peroxide.

The above-mentioned (Section 2.2.1) silica supported bis(maltolato) complexes of [107] behave as catalysts in the oxidation of benzene to phenol (overall reaction of Scheme 10). The salen oxovanadium(IV) [salen (**1B**)] complex anchored on mesoporous silica (SBA-15) matrix catalyzes the oxidation of styrene (see also Scheme 6) mainly to benzaldehyde, at 80 °C [48].

Series of vanadium complexes covalently bonded to chloromethylated polystyrene cross-linked with 5% divinylbenzene (support denoted by PS) have been tested as catalysts for the oxidation of various unsaturated organic species [109–112,114–120].

PS-K$[VO_2$(sal-inh)(im)] and PS-K$[VO_2$(sal-bhz)(im)] [($H_2$sal-inh = Schiff base derived from salicylaldehyde (see reagent in Scheme 15) and isonicotinoylhydrazide (**14B**), $H_2$sal-bhz = Schiff base derived from salicylaldehyde and benzoylhydrazide, im = imidazole)] catalyze the oxidation of benzene with $H_2O_2$



**Scheme 13.** Peroxidative oxidation of ethylbenzene to benzaldehyde and acetophenone, catalyzed by supported oxovanadium complexes.

at 60–80 °C with a maximum 15% conversion and 94% selectivity toward phenol [114] (overall reaction of Scheme 10).

The PS-[VO(fsal-D,L-Ala)($H_2O$)], containing the Schiff-base tridentate ligand obtained from the reaction of 3-formylsalicylic acid (**15B**) (Hfsal) with D,L-alanine, catalyzes the oxidation of *p*-chlorotoluene and cyclohexene at 80 °C [115]. Under the optimized conditions, a maximum of 14% conversion of *p*-chlorotoluene was achieved to the following main products: *p*-chlorobenzaldehyde > *p*-chlorobenzylalcohol > *p*-chlorobenzoic acid > 2-methyl-5-chlorophenol > 3-methyl-6-chlorophenol. The oxidation of cyclohexene with PS-[VO(fsal-D,L-Ala)($H_2O$)] and PS-[VO(fsal-L-Ile)($H_2O$)] (L-isoleucine is the aminoacid in this complex) proceeds with a 79–77% conversion to the following products (see also Scheme 4): 2-cyclohexene-1-ol > 1,2-epoxycyclohexane > cyclohexane-1,2-diol > 2-cyclohexene-1-one [115]. The related polymer bond complex with β-alanine and DMF, *i.e.*, PS-[VO(fsal-β-ala)(DMF)], catalyzes the oxidation of various organic substrates, such as, benzene, cumene, naphthalene, cyclohexane (included in this section for comparative purposes), styrene (see also Scheme 6), cyclohexene and *trans*-stilbene (**6C**), at 60–75 °C [116]. The highest conversion concerns cyclohexane (99%) whereas for the other substrates it is lower than 50% [116].

The use of PS-[VO(saldien)] [$H_2$saldien = *N*,*N*′-bis(salicyledene)diethylenetriamine (**16B**)] leads to only 3% conversion of phenol in water, with 100% selectivity toward *p*-benzoquinone, while in acetonitrile the products are *p*-benzoquinone, hydroquinone and catechol [117]. The selectivity is dependent on the amount and nature of solvent, the temperature and pH [117].

PS-[VO(hebmz)$_2$] [Hhebmz = 2-(α-hydroxyethyl)benzimidazole (**17B**)] catalyzes the oxidation of benzoin (**3C**) with TBHP in methanol, to benzyl, methylbenzoate, benzoic acid and dimethylacetal [113]. Under optimized reaction conditions, a maximum of 99% conversion of (**3C**) was achieved to those products, with methylbenzoate being the major one (48%). The unsupported complex leads to a higher selectivity toward benzyl than the polymer-anchored complex, although with a lower TOF (59 $h^{-1}$ instead of 68 $h^{-1}$) [118].

PS-K[VO($O_2$)$_2$(L)] [L = 2-(2-pyridyl)benzimidazole (2-pybmz) or 2-(3-pyridyl)benzimidazole (3-pybmz)] catalyze the oxidation of phenol and styrene (see also Scheme 6), typically at 80 °C [109]. The selectivity toward catechol (from phenol) is *ca.* 62% under optimized conditions, whereas the oxidation of styrene leads to the corresponding epoxide, benzaldehyde (the major product, 60–84% selectivity), benzoic acid, phenylacetaldehyde and 1-phenylethane-1,2-diol [109].

[VO(tmbmz)$_2$] [Htmbmz = 2-thiomethylbenzimidazole (**18B**)] and the supported form on chloromethylated polystyrene (PS) (where tmbmz is mostly bond to the polystyrene matrix by the sulfur atom) catalyze the oxidation of styrene (see also Scheme 6), cyclohexene (see also Scheme 4) and ethylbenzene at 80 °C [110]. Under the optimized reaction conditions, styrene gave the following products, ordered according to their selectivity: benzaldehyde > 1-phenylethane-1,2-diol > corresponding epoxide. The oxidation of cyclohexene provided cyclohexane-1,2-diol > 2-cyclohexene-1-one > cyclohexeneoxide, whereas ethylbenzene (see also Scheme 13) oxidation gave benzaldehyde > phenylacetic acid > acetophenone > 1-phenylethane-1,2-diol. The conversions are up to 81%, 86% and 26%, concerning styrene, cyclohexene and ethylbenzene, respectively [110].

PS-[VO(hpbmz)$_2$] [Hhpbmz = monobasic bidentate 2-(2′-hydroxyphenyl)benzimidazole] and the corresponding unsupported complex catalyze the oxidation of styrene (see also Scheme 6) and ethylbenzene at 80 °C [111]. Under the optimized conditions, styrene was oxidized (maximum of 71% conversion) to the corresponding epoxide, benzaldehyde, 1-phenylethane-1,2-diol, benzoic acid and phenylacetaldehyde. The oxidation of ethylbenzene (31% conversion) gave (see also Scheme 13) benzaldehyde, phenyl acetic acid, styrene, 1-phenylethane-1,2-diol and benzoic acid as the major products [111]. PS-[VO(hmbmz)$_2$] [Hhmbmz = 2-(α-hydroxymethyl)benzimidazole] and the unsupported complex catalyze the same substrates at 60 °C [112]. The oxidation of styrene (conversion up to 48%) afforded three major products, *i.e.* the corresponding epoxide, benzaldehyde and benzoic acid, while ethylbenzene gave acetophenone as the main product in a modest conversion [112].

PS-[VO(pimin)$_x$] [Hpimin = 2-(2′-hydroxyphenyl)-1H-imidazoline] provides the maximum conversions of styrene (see also Scheme 6) (100%) and ethylbenzene (31%) at 80 °C [119]. The main products from styrene were benzaldehyde (58%) > 1-phenylethane-1,2-diol > benzoic acid > corresponding epoxide, while acetophenone (20%) > benzaldehyde are those from ethylbenzene (see also Scheme 13) [119].

PS-[VO(fsal-ohyba)(DMF)] [where fsal-ohyba is derived from 3-formylsalicylic acid (**15B**) and *o*-hydroxybenzylamine] and PS-K[VO$_2$(fsal-ohyba)] catalyze the oxidation of styrene (see also Scheme 6) to styrene oxide, benzaldehyde (main product), benzoic acid, phenylacetic acid and 1-phenylethane-1,2-diol at 60–80 °C (conversion up to 80% at optimized conditions, at 80 °C) [120]. Ethylbenzene (see also Scheme 13) affords benzaldehyde, phenylacetic acid, styrene and 1-phenylethane-1,2-diol, whereas phenol is oxidized to catechol and *p*-hydroquinone. The latter catalyst presents the highest activity, with a conversion up to 40% and a maximum of 88% selectivity concerning benzaldehyde from ethylbenzene, at 80 °C. Unsupported complexes exhibit a lower activity [120].

A dioxovanadium(V) complex (with a Schiff base ligand derived from salicylaldehyde (see reagent in Scheme 15) and 2-aminomethylbenzimidazole) encapsulated in zeolite-Y catalyzes the oxidation of phenol and styrene with $H_2O_2$ [113]. Under the optimized reaction conditions, a 44% conversion of phenol in catechol (65% selectivity) and hydroquinone was achieved at 80 °C, whereas styrene (see also Scheme 6) gave (97% conversion at 75 °C) the corresponding epoxide, benzaldehyde, benzoic acid, 1-phenylethane-1,2-diol and phenylacetaldehyde as the major products [113]. The oxovanadium(IV) complex with the Schiff base ligand derived from salicylaldehyde (see reagent in Scheme 15) and *o*-aminobenzyl alcohol, encapsulated in the same support, catalyzes the oxidation of styrene (89% conversion at 80 °C) to benzaldehyde > 1-phenylethane-1,2-diol > benzoic acid > corresponding epoxide > phenylacetaldehyde. In the presence of TBHP as oxidant, styrene oxide is the main product, and the overall conversion is low (20%) [108]. The unsupported complexes present lower catalytic activities [108,113].

Phthalocyanine vanadium complexes encapsulated in zeolite-Y by the "*in situ* ligand synthesis" method present a distortion from the square planar geometry resulting from encapsulation and exhibit enhanced phenol hydroxylation activity compared to the non-encapsulated ones, in water solution, with a conversion at 175 °C up to 20% and TON 78, the main products being catechol (62%), hydroquinone (24%) and *para*-benzoquinone (6.3%) [121].

Several alumina-supported oxovanadium complexes, with ethylenediamine (en), tetramethylethylenediamine (TMED), bipyridine (bpy), 1,10-phenantroline (phen), acac (**1A**), salen (**1B**) and *N,N′*-phenytenebis(salicylideneiminato) (salophen), catalyze the cyclohexene oxidation with TBHP [122]. The reaction occurs in refluxing solvent (dichloromethane, trichloromethane, acetonitrile or cyclohexene), under dinitrogen (highest 95% conversion). The major products are (see also Scheme 4) 2-cyclohexene-1-one and 1,2-epoxycyclohexane, but 2-cyclohexene-1-ol and 1-(*tert*-butylperoxy)-2-cyclohexene are also formed, and the catalysts can be reused for several times [122].

Oxovanadium(IV) immobilized onto cross-linked polyacylates [copolymer from 1-bromoethylbenzene, methyl acrylate and $N(CH_2CH_2NMe_2)_3$, in the presence of CuBr] (c-PMA$_n$-V). [c-PMA$_n$ (**19B**)] catalyze the oxidative bishydroxylation of several olefins in water with TBHP, at 60–105 °C, with usual conversions (of at least 90%) to the corresponding diols or carboxylate acids [123]. They also catalyze the epoxidation of cyclooctene at 60 °C in high yield [123].

Oxovanadium complexes with acac (**1A**) and Ph–DAB–$(CH_2)_3$R [DAB = 1,4-diazabutadiene, R = $Si(OEt)_3$] ligands, immobilized on a mesoporous molecular sieve (MCM-41) are catalysts for cyclooctene oxidation, with TBHP, at 55 °C and under air, yielding 1,2-epoxycyclooctane as the main product and 1,2-cyclooctanediol as a by-product, with a conversion of at least 60% toward both products and 98% selectivity to the epoxide [124]. They are more active than the corresponding manganese catalysts, and lose activity along consecutive reaction runs [124].

The vanadium complex with the Schiff ligand derived from salicyldehyde and diethylenetriamine, anchored on chloropropyl modified mesoporous silica (CP-MCM-41), behaves as a catalyst for the epoxidation of several olefins, using $H_2O_2$ as oxidant and sodium bicarbonate as a co-catalyst (which can enhance the rate of reaction by many folds) [125]. The system presents a good efficiency and selectivity at room temperature (conversion up to 95% and selectivity concerning the epoxides of at least 90%) [125].

The [VO(saloph)] (saloph = *N,N′*-disalicylidene-*o*-phenylenediaminate) complexes encapsulated in microporous zeolite NaY and mesoporous Al-MCM-41 are more active (three to five times) than the unsupported complexes for the epoxidation of *trans*-stilbene (**6C**) and styrene (see also Scheme 6) [126]. The selectivity is higher for (**6C**) but the TOFs are superior for styrene. The reactions were carried out at 90 °C with TBHP [126]. The water soluble porphyrin-V [*meso*-tetrakis(4-trimethylammoniophenyl)porphyrinato] oxovanadium(IV) tetrachloride (VOTAPP) (**15A**) compounds encapsulated into mesoporous MCM-41, containing different amounts of aluminum or vanadium, catalyze the oxidation of cyclohexene and styrene using iodosylbenzene as oxidant [127]. The catalytic reactions were carried out at room temperature under an inert atmosphere. The heterogeneous VOTAPP system mainly produces the allylic oxidation product (and little epoxide) from cyclohexene, whereas both the epoxide and the allylic oxidation products are obtained from styrene. An increased activity was observed when VOTAPP was supported on Al/V-MCM-41 (highest conversion of 28%) [127]. The supported catalysts, which are more active than the unsupported one, can be recovered easily and reused without significant loss in catalytic activity and in selectivity.

The oxidation of isosafrol (**5C**) with $H_2O_2$ using zeolite–vanadyl composites, VO(salen)Y-1 and VO(salen)Y-3, [salen (**1B**)] as catalysts at 110–130 °C in a microwave reactor allows the synthesis of the corresponding epoxide as the major product with a high selectivity [128].

*3.2.2.1. Epoxidation of allylic alcohols.* [$VO(acac)_2$] (**1A**) anchored onto two different amine-functionalized activated carbons catalyzes the epoxidation of 3-buten-2-ol using TBHP as oxidant, and the system has been compared with that in homogeneous phase, at 0 °C in dichloromethane (see also Scheme 12) [129]. The conversions are similar, but the rate of epoxidation is more than the double in the homogeneous system. The anchored material, upon reuse, shows no significant decrease in the catalytic properties [129].

The parent clays laponite and K10-montmorillonite (K10) and those functionalized, or not, with (3-aminopropyl)triethoxysilane (APTES) were used as supports to immobilize [$VO(acac)_2$] (**1A**), and the supported systems were tested for the epoxidation of geraniol (**2C**) with TBHP, at room temperature, in dichloromethane [130]. The [$VO(acac)_2$]APTES@K10 material was the most efficient and stable catalyst upon reuse (5 cycles), with a substrate conversion to 2,3-epoxygeraniol with a regioselectivity comparable to that of the homogeneous phase reaction, but in the latter case the reaction is much faster (0.5 *versus* 48 h). 6,7-epoxygeraniol is the by-product [130] (see also Scheme 12).

[$VO(acac)_2$] (**1A**) immobilized onto a porous clay heterostructure and the mesoporous silica SBA-15 previously functionalized with APTES catalyzes the epoxidation of (**2C**) at room temperature, in $CH_2Cl_2$ with TBHP [131]. The heterogeneous systems present moderate substrate conversion, high selectivity (up to 88%) toward 2,3-epoxygeraniol (see also Scheme 12) and a good stability upon reuse for two cycles. The homogeneous catalyst shows 100% of selectivity after a much shorter reaction time [131].

[$VO(acac)_2$] (**1A**) was also grafted onto a hexagonal mesoporous silica (HMS) using three different methods: direct complex immobilization (A), functionalization of the HMS with APTES pursued by the complex immobilization (B), and treatment of the APTES functionalized support prepared by method B with trimethylethoxysilane (TMS) to deactivate unreacted surface silanol groups, followed by complex grafting (C) [132]. The experimental conditions of the catalytic studies of (**2C**) epoxidation are analogous to those of the previous example. The selectivities of the two epoxides formed in the heterogeneous phase reactions were similar to those observed in the homogeneous phase (1 h reaction time) and the major product was always 2,3-epoxygeraniol. The catalyst which leads to the highest substrate conversion resulted from method B but, by considering the leaching of the active species, method C produced the best catalyst [132]. An alternative system is provided by the immobilization of [$VO(acac)_2$] (**1A**) by covalent bond on the surface of silica-coated magnetic nanoparticles functionalized with amine groups [133]. This magnetic hybrid nanomaterial in the epoxidation of (**2C**) presents a high selectivity toward the 2,3-epoxygeraniol product (96%) (see also Scheme 12) and can easily be recovered by magnetic separation [133].

Microencapsulated [$VO(acac)_2$] (**1A**) in polystyrene, MC-$VO(acac)_2$, prepared without derivatization, acts as catalyst in the epoxidation of several allylic alcohols (see also Scheme 12) using TBHP at room temperature in hexane [134], and is reusable without significant loss of activity [134].

[$VO(acac)_2$] (**1A**) and [VO(salen)] [salen (**1B**)] have also been encapsulated in inorganic (based on hydrolysis/condensation of tetramethylorthosilicate – TMOS) and hybrid matrices (TMOS plus a co-condensation agent) using the sol–gel method [135]. The resulting structures were tested in the epoxidation of allylic alcohols at 70 °C in toluene and with TBHP. When the catalyst was based on [VO(salen)], the hybrid matrix led to higher initial TOFs than the inorganic one, for all tested allylic alcohols (*trans*-3-phenyl-2-methyl-2-propen-1-ol, *trans*-2-hexen-1-ol, *cis*-2-hexen-1-ol, 1-octen-3-ol), (see also Scheme 12) what may be related to its higher pore diameter. *Trans*-2-hexen-1-ol presents the highest conversions, and vanadium leaching was not usually significant during the catalytic reactions [135].

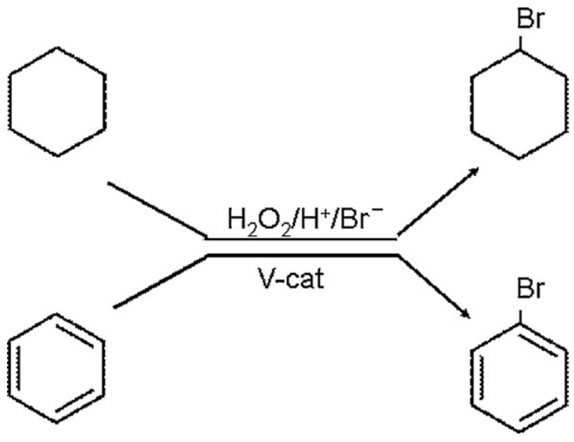
## 4. Halogenations

Halogenated compounds can exhibit important biological activities and the incorporation of halogen atoms in drugs can be a strategy to modify the bioactivities and specificities of some products [2,6,136–138]. Vanadium occurs in haloperoxidases, enzymes accepted to be responsible for the biosynthesis of a significant amount of the widely distributed halogenated products of natural origin. The haloperoxidases of vanadium occur in some marine algae, fungi and lichen, and their active centers bear oxovanadium(V). The plausible oxidizing agent is the $H_2O_2$ and the substrate is an halide, except fluoride [2,4,6,139,140]. The haloperoxidases present peroxidative, haloperoxidative, epoxidative and sulfoxidative activity, and oxovanadium(V) complexes with a mixed *O*- and *N*-donor atoms coordination sphere are structural models of the vanadate-dependent haloperoxidases. Chemical halogenation usually requires harsh reaction conditions and forms by-products, in contrast with the biocatalyzed processes [138,141]. The search of new vanadium complexes able to catalyze more efficiently the halogenation reactions is an endeavour to modern chemistry.

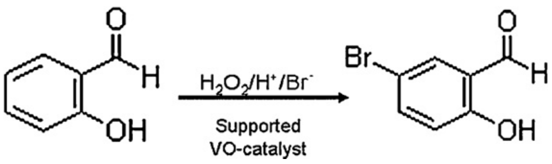
### 4.1. *In liquid systems*

[VO(acac)(BMIMAPY)][$ClO_4$] [BMIMAPY (**9B**)] catalyzes the oxidation, with $H_2O_2$, of bromide (hexadecyltrimethylammonium salt) in acetonitrile with $HClO_4$ to acidify the medium toward the formation of $Br_3^-$ [60] that can be used as a bromination agent of organic compounds.

The oxovanadium(V) complex [VO(tea)] (**7A**) has been used as a catalyst for the peroxidative halogenation of cyclohexane and benzene [57–59] under mild experimental conditions (20 °C), to obtain organohalides (bromocyclohexane and bromobenzene, respectively, Scheme 14) by a plausible involvement of radical mechanisms. These reactions occur in mixed aqueous solution with acetonitrile, in acidic medium (nitric acid), the oxidizing agent being an aqueous solution of $H_2O_2$ in the presence of KBr. The same reaction is catalyzed by the Amavadin complex (**8A**) and by its model (**9A**) (TON values up to 17) [58].



**Scheme 14.** Peroxidative bromination of cyclohydrocarbons catalyzed by vanadium complexes.



**Scheme 15.** Peroxidative bromination of salicylaldehyde catalyzed by supported oxovanadium complexes.

The oxovanadium(V) aminetriphenolate complex (**16A**) catalyzes efficiently the bromination and chlorination of 1,3,5-trimethoxybenzene at 28 °C to give the corresponding 1-halo-2,4,6-trimethoxybenzene {[VO(acac)$_2$] (**1A**) was also applied for bromination}, using the respective tetrabutylammonium salt as the halide source, in DMF with perchloric acid [142]. Concerning the bromination, the TONs and TOFs are up to 1260 and 220 $h^{-1}$, respectively [142]. The oxovanadium(v) complex [VO($O_2$)(HSalhyhb)($H_2O$)] [$H_2$Salhyhb = Schiff-base derived from salicylaldehyde (see reagent in Scheme 15) and γ-hydroxybutanoic acid hydrazide] participates in the oxidative bromination of 1,3,5-trimethoxybenzene in the presence of tetrabutylammonium bromide, in the same solvent/acid medium, leading also to the formation of 1-bromo-2,4,6-trimethoxybenzene [143]. [VO{N(DMBO)$_3$}] [N(DMBOH)$_3$ = tris(2-hydroxy-3,5-dimethylbenzyl)amine] acts as a bromination catalyst in the presence of $AlBr_3$ and molecular oxygen, in 1,4-dioxane at 80 °C [144]. $AlBr_3$ behaves as the bromide source and also as a Lewis acid inducing the bromination, and the above substrate is converted to the same product (1-bromo-2,4,6-trimethoxybenzene, 90% yield) [144].

Dinuclear oxovanadium complexes [145,146] with hydrazones as ligands, mononuclear complexes with the same type of ligand [63,147], and polymeric and insoluble oxovanadium(IV) complexes [with Schiff bases resulting from 5,5′-methylenebis(salicylaldehyde) (**12B**) and 1,2-diaminoethene, 1,2-diaminopropane or 1,3-diaminopropane (**6B**)] [68] catalyze in water the oxidative bromination of salicylaldehyde (see reagent in Scheme 15), in the presence of $H_2O_2$, KBr and $HClO_4$, to 5-bromosalicylaldehyde, 3,5-dibromosalicylaldehyde (and 2,4,6-tribromophenol, in [146]) at room temperature. The maximum overall conversion is 94% [146] and 87% selectivity toward 5-bromosalicylaldehyde [147].

Schiff base oxovanadium(V) complexes, where the Schiff base can be 3,5-di-*tert*-butyl-*N*-(2-hydroxyphenyl)salicylidenimine or (2S)-3,5-di-*tert*-butyl-*N*-[1-hydroxy-4-(methylsulfinyl)butyl]-salicylidenimine, dissolved in a non-aqueous solvent (acetonitrile, chloroform or dichloromethane), with TBHP as oxidant and a source of bromine, promote the conversion of bis(homoallylic) alcohols into bromocyclized ethers [148].

### 4.2. *In supported systems*

The immobilized PS-[VO(hmbmz)$_2$] [Hhmbmz = 2-(α-hydroxymethyl)benzimidazole] [112], PS-K[VO$_2$(sal-inh)(im)] and PS-K[VO$_2$(sal-bhz)(im)] [114] and the encapsulated in zeolite-Y NH$_4$[VO$_2$(sal-inh)]-Y and NH$_4$[VO$_2$(sal-oap)]-Y [$H_2$sal-inh = *N*-isonicotinamidosalicylaldimine, $H_2$sal-oap = *N*-(2-hydroxyphenyl)salicylideneamine] [149] are catalysts for the oxidative bromination of salicylaldehyde using $H_2O_2$/KBr in acid ($HClO_4$) aqueous solution, to afford 5-bromosalicylaldehyde with 100% selectivity [112] (Scheme 15).

PS-[VO(fsal-ohyba)(DMF)], where fsal-ohyba is derived from 3-formylsalicylic acid (**15B**) and *o*-hydroxybenzylamine, and PS-K[VO$_2$(fsal-ohyba)] catalyze the same reaction (but using $H_2SO_4$

instead of $HClO_4$) of salicylaldehyde toward the formation of 5-bromosalicylaldehyde (73% conversion and 80% selectivity) (Scheme 15), but the supported dioxomolybdenum(VI) complex PS-[$MoO_2$(fsal-ohyba)(DMF)] is more efficient [120].

The peroxovanadate complex anchored to poly(acrylate) (PA) $Na_3[V_2O_2(O_2)_4$(carboxylate)]-PA mediates the bromination of several activated aromatics into their corresponding monobromo-organics, in acetonitrile/water (1:1) at room temperature, with tetraethylammonium bromide as the bromide source [150]. The preferential addition in *ortho* or *para* positions of the aromatic ring leading to monohalogenated products suggests an electrophilic bromination mechanism [150].

## 5. Carboxylations

Although carboxylations (which involve C–C bond formation) are not typical oxidation reactions, they are treated herein briefly in view of the possible use of common types of catalyst and also of their synthetic relevance. They allow to synthesize carboxylic acids (bearing one more carbon atom than the substrate) and their derivatives, which have several applications in modern life, namely in the production of polymers and solvents, and in pharmaceutical and food industries [151].

Vanadium complexes have been used as catalysts for the carboxylation of alkanes via single-pot conversions [51,57,152–163]. These syntheses of carboxylic acids are much simpler than those used in industry. For instance, in the case of the conversion of methane into acetic acid, the current industrial routes involve commonly three distinct stages and use more expensive catalysts and harder experimental conditions (*e.g.* the Mosanto and BP-Amoco Cativa processes of carbonylation of methanol, at the third stage, based on Rh and Ir catalysts, respectively) [57,164].

The complexes tested successfully include oxovanadium(IV or V) compounds with *N*,*O*- or *O*,*O*-ligands, *i.e.*, [VO(tea)] (**7A**), [$VO(CF_3SO_3)_2$], Ba[$VO(nta)(H_2O)]_2$ (nta = nitrilotriacetate), [$VO(ada)(H_2O)$] (ada = *N*-2-acetamidoiminodiacetate), [$VO(Hheida)(H_2O)$] (Hheida = 2-hydroxyethyliminodiacetate), [VO(bicine)] [bicine = basic form of *N*,*N*-bis(2-hydroxyethyl)glycine], [$VO(dipic)(OCH_2CH_3)$] (dipic = pyridine-2,6-dicarboxylate), and the dioxovanadium(V) compounds [$VO_2\{SO_3C(pz)_3\}$] (pz = pyrazolyl), [$VO_2\{HC(pz)_3\}$][$BF_4$], [$VO_2\{HB(3,5\text{-}Me_2pz)_3\}$] (3,5-$Me_2$pz = 3,5-dimethyl-1-pyrazolyl) and [$VO_2(3,5\text{-}Me_2Hpz)_3$][$BF_4$], bearing pyrazole or scorpionate ligands (**8B**) [51,57,152–159]. A few non-oxovanadium(IV) complexes are also good catalysts(or catalyst precursors), namely the closely related models of Amavadin (**8A**,**9A**) and other V-compounds [152–159] which can mimic its reactivity.

The alkane carboxylation reactions are typically undertaken in trifluoroacetic acid (TFA) at 80 °C with a vanadium complex catalyst and peroxydisulfate as the oxidant, under a CO atmosphere, and lead to the corresponding carboxylic acids with one more carbon (Scheme 16).

This methodology with vanadium complexes concerns both gaseous (methane [152–155], ethane [156,157] and propane [158]) and liquid (linear and cyclic C-5 and C-6) [159] alkanes. CO acts as the carbonylating agent, but in its absence TFA can play such a role, although less effectively [152]. Remarkably high TONs (up to above $10^4$) and yields (up to 92%) were achieved [152,156], mainly for the carboxylation of gaseous alkanes. Hence, *e.g.*, Ca[$V(HIDA)_2$] ($Ca^{2+}$ salt of **9A**) leads to a 92% yield of propionic and acetic acids from ethane [156], whereas with Ca[$V(HIDPA)_2$] ($Ca^{2+}$ salt of **8A**), [$VO(CF_3SO_3)_2$] and [VO(tea)] (**7A**) acetic acid is obtained in 54%, 45% and 29% yields, respectively, from methane [155]. These appear to be the most effective systems so far reported for any alkane functionalization reaction under mild/moderate conditions.

The dioxo-scorpionate-V(V) complexes are usually more active than the monooxo-discorpionate-V(IV) ones and than the non-oxo catalysts [$VCl_3\{HC(pz)_3\}$] and [$VCl_3\{SO_3C(pz)_3\}$], with yields up to 40% and TONs up to 157, using methane and ethane [51]. Additionally, the sulfonate derivativeis water soluble, which is favorable for application as a green catalyst [51].

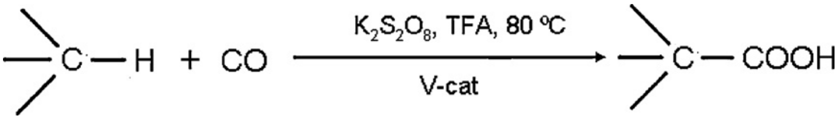
Radical trap experiments, essays with $^{13}C$-enriched alkanes and $^{13}CO$ and theoretical studies [155,156] prove the involvement of radical mechanisms for the carboxylations. The carboxylation of linear alkanes occurs preferentially at a secondary carbon than at a primary one, also supporting a radical mechanism [159].

A recent development concerns the replacement of TFA by mixed water/acetonitrile solvent, and the resulting $CO/H_2O/S_2O_8^{2-}$ system can operate under rather mild conditions (at 30–60 °C, without any acid additive) [153,160–163]. Water has a relevant role, not only as solvent but also as a reagent, behaving as the hydroxylating agent, as proved by $H_2{}^{18}O$ experiments and accounted for by DFT studies which also disclose detailed radical mechanisms [160–162]. This alkane hydrocarboxylation route to carboxylic acids proceeds efficiently (yields up to 72%, in presence of a metal promoter) and selectively even without any metal catalyst (metal-free), but is promoted by various metal complex promoters, namely, in some cases, the Amavadin model [$V(HIDA)_2]^{2-}$ (**9A**), although less efficiently than a tetracopper(II) promoter [163].

## 6. Other types of oxidation

Vanadium compounds have also been used as catalysts or promoters in other types of oxidation. Hence, the above V-catalyst/TFA/$S_2O_8^{2-}$ systems for carboxylation of gaseous $C_n$-alkanes also produce, as by-products, $C_n$-carboxylic acids upon alkane oxidation (*e.g.*, acetic acid from ethane) apart from the corresponding $C_{n+1}$-carboxylic acids derived from alkane carboxylation (*e.g.*, propionic acid from ethane) [156]. Methane oxidation in the hydrogen peroxide/vanadate anion/PCA system, in water at 50–90 °C, leads mainly to formic acid [165]. The presence of a strong acid (sulfuric, trifluoroacetic or perchloric) promotes the oxidation and perchloric acid can even be used as a co-catalyst instead of PCA. The maximum TON obtained was 294 (yield less than 15%) in the presence of perchloric acid, for an initial $CH_4$ pressure of 75 atm [165].

Other examples of types of V-catalyzed or -promoted oxidation include the conversion of benzylamines to imines by atmospheric oxidation with [$VO(Hhpic)_2$] as catalyst [166], the hydroamination of styrene and vinyl pyridine by polymer-bond oxovanadium(IV) and dioxovanadium(V) complexes [167], the oxidation of tertiary amines to the corresponding *N*-oxides with $H_2O_2$ by the silica supported vanadium catalyst $V_xSi_{4x}O_{6.4x}$ [168], the selenide oxidation by [$VO(acac)_2$] (**1A**) with either cumene hydroperoxide or TBHP as oxidants [169], the oxidation of phosphines with vanadium(V) ions



**Scheme 16.** Alkane carboxylation catalyzed by vanadium complexes.

and $H_2O_2$ in acidic aqueous acetonitrile [170], and some enantioselective oxidations, such as, coupling of 2-naphthols using achiral oxovanadium complex under mild conditions [171].

## 7. Final remarks

Diverse applications in oxidation catalysis for a variety of organic substrates have already been found for oxovanadium complexes, namely those of the types discussed above. The substrates include not only olefins and aromatics (to form different types of derived oxygenate) but also the very inert alkanes which thus can be converted, under mild conditions, to added value organic derivatives, such as alcohols, ketones, organohalides and carboxylic acids. Various oxidants have also been used, including molecular oxygen and hydrogen peroxide, the most convenient ones under green chemistry and economical perspectives.

Within the vanadium catalyst precursors, the common metal oxidation states are the highest ones (IV and V), and *O*- and *N*-ligands (or *N*,*O*-combinations) are particularly suitable. However, the real active vanadium species (conceivably bearing oxo and/or peroxo ligands), generated in the oxidation reaction media, are unknown in most of the cases, kinetic and mechanistic studies are scant, and structure-activity relationship are yet to be established. Hence, further progresses on the clarification of these matters are crucial for the design of more efficient and selective vanadium catalysts.

Nevertheless, mechanistic proposals have been put forward in some cases, *e.g.*, on the basis of theoretical calculations which provide promising methods to disclose the roles of the vanadium complexes, and deserve a higher attention in future studies.

The typical solvents for typical oxidations and carboxylations are acetonitrile and trifluoroacetic acid, respectively, but attempts to replace them by water have been undertaken. In a limited number of the cases they were (in part) successful providing an important step toward the development of environmentally friendly catalytic systems. In this regard, the recent recognition [54,160–162] that water can behave not only as a solvent, but also as a promoter and a reagent, open a rather promising perspective and should be further explored.

The use of unconventional microwave heating, of supercritical fluid media and of ionic liquids in oxidation catalysis with vanadium complexes still remains little explored and is also encouraged.

The overall field is promising and multi- and interdisciplinary approaches should lead to developments toward a better understanding of the chemistry involved and the promotion of fruitful applications in organic synthesis with industrial significance. In particular, oxovanadium complexes can effectively catalyze or promote the functionalization of alkanes under mild or moderate conditions, a challenging topic in modern Chemistry that can lead to the future use of these natural rich C-sources as alternative feedstocks for chemical industry.

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