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Review

Pyrazinecarboxylic acid and analogs: Highly efficient co-catalysts in the metal-complex-catalyzed oxidation of organic compounds

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ABSTRACT

The development of new metal complex catalysts and efficient protocols for the mild and selective oxidation of alkanes, arenes, olefins, alcohols, and other organic substrates is a challenging topic in areas of homogeneous catalysis, coordination, and organic chemistry. In these oxidation reactions, the activity of many metal complex catalysts is dramatically improved upon addition of certain co-catalysts or promoters, which can also act as ligands in simple catalytic systems generated in situ. Given the fact that 2-pyrazinecarboxylic acid (Hpca) and analogous heteroaromatic acids such as 2,3-pyrazinedicarboxylic (H₂pdca), picolinic (Hpic), and dipicolinic (H₂dipic) acids are remarkably efficient and versatile

Abbreviations: 1D, one-dimensional; 3D, three-dimensional; ac, acetate; aq, aqueous; bpy, 2,2'-bipyridine; CyH, cyclohexane; CyOOH, cyclohexyl hydroperoxide; depa, N,N-diethylpicolinamide; dipic, dipicolinate(2–); H₂dipic, dipicolinic acid (2,6-pyridinedicarboxylic acid); dmpa, N,N-dimethylpicolinamide; dpheol, 2-methoxy-1,2-diphenylethanolate(–); equiv, equivalents; gma, an open-shell π radical gma(3–) form of glyoxal-bis(2-mercaptoanil); H₃tea, triethanolamine; Hpca, 2-pyrazinecarboxylic acid; H₂pdca, 2,3-pyrazinedicarboxylic acid; Hpdca, monodeprotonated form of H₂pdca; Hpic, picolinic acid (2-pyridinecarboxylic acid); H₂sae, salicylidene-2-ethanolamine; hptb, N,N',N'.tetrakis(2-benzimidazolylmethyl)-2-hydroxo-1,3-diaminopropane; i-Pr, isopropyl; L¹, 6,7,13,14,15,16,17,18octahydrodibenzo(e,m)-1,4,8,11-dithiadiazacyclotetradecine; L², 7-(2-methylpyridyl)aza-1,4-dithiacyclononane; L³, 1,6-bis(2'-pyridyl)-2,5-dithiahexane; L⁴, 1,4,7trimethyl-1,4,7-triazacyclononane; L⁵, 1-carboxymethyl-4,7-dimethyl-1,4,7-triazacyclononane; mal, maltolate(–) (maltol=3-hydroxy-2-methyl-4-pyrone); mebpa, N-(2-methoxyethyl)-N,N-bis(pyridin-2-ylmethyl)amine; MTO, methyltrioxorhenium; MW, microwave; ox, oxalate(2–); pca, 2-pyrazinecarboxylate(–); pdca, 2,3pyrazinedicarboxylate(2–); phen, 1,10-phenanthroline; pheol, 2-phenoxyethanolate(–); pic, picolinamide; picno, 4-picoline-N-oxide; pinme, monomethyl ether pinacolate(–); py, pyridine; rt, room temperature; salen, (R,R)-N,N-bis(3,5-di-tertbutylsalicylidenato)-1,2-cyclohexanediamine(2–); tacn, 1,4,7triazacyclononane; TBHP, *tert*-butyl hydroperoxide; *t*-Bu, *tert*-butyl; terpy, 2,2',6':2''-terpyridine; TFA, trifluoroacetic acid; TOF, catalyst turnover frequency (TON per hour); TON, catalyst turnover number (moles of products per mol of catalyst); Vipca, vanadium-to-pca molar ratio.

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0010-8545/\$ – see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.ccr.2012.09.012 Keywords: 2-Pyrazinecarboxylic acid (Hpca) Vanadium complexes Iron complexes Homogeneous catalysis Oxidation Alkanes Organic substrates Hydrogen peroxide Reaction mechanism Picolinic acid Dipicolinic acid co-catalysts in a high diversity of oxidation systems, the present review summarizes the state-of-the-art knowledge in this field. In particular, this contribution focuses on the use of Hpca as the most active co-catalyst and describes its coordination chemistry with regard to the oxidative transformations of various organic substrates, providing an overview of isolated vanadium, iron, and some other transition metal complexes derived from Hpca. The review also summarizes the applications of Hpca-assisted and related systems in the oxidation of various organic substrates by different oxidants, and highlights the main selectivity, kinetic, and mechanistic features of these oxidative transformations. The paper covers the application of catalytic systems wherein Hpca, H₂pdca, Hpic, and H₂dipic are used either as co-catalysts (additives) or as ligands within a metal complex catalyst. A special emphasis has been made on the oxidation of alkanes as very inert substrates, and the use of simple and highly efficient [VO₃]⁻/Hpca/H₂O₂ system. The multifaceted roles of Hpca and analogous co-catalysts have been identified and the analysis of main mechanistic pathways and possible intermediates has been performed.

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1. Introduction

The development of new metal complex catalysts and single-pot methods for the oxidative functionalization of various organic substrates continues to be a challenging topic in areas of homogeneous catalysis, coordination, organic, bioinorganic, and green chemistry. The search for atom efficient, mild, and selective oxidation of alkanes, arenes, olefins, and alcohols is an object of particular significance [1–7]. As naturally abundant carbon raw materials, alkanes are particularly attractive substrates for added value organic chemicals, but their high inertness generally constitutes a considerable limitation toward selective oxidative transformations under relatively mild conditions [3–6,8–12]. However, the selection of an appropriate metal catalyst and a suitable oxidizing agent, along with thoroughly tuned reaction conditions, can open up an entry toward mild and efficient oxidative transformations of alkanes and other substrates.

An intensive search for new protocols and metal catalytic systems for the selective oxidation of alkanes [8-12] showed that 2-pyrazinecarboxylic acid (Hpca, Scheme 1) and analogous compounds (2,3-pyrazinedicarboxylic, picolinic, and dipicolinic acids) can be used as highly active co-catalysts in the metal-catalyzed oxidation of alkanes, arenes, alcohols, and other substrates, under mild conditions by peroxides, and typically in the presence of air (O_2) that also takes part in these reactions. Such a type of Hpcaassisted transformations has been pioneered and developed by one of us [9–13], namely using a simple and efficient [VO₃]⁻/Hpca/H₂O₂ system (also referred to as "reagent") that exhibits a broad substrate versatility. In these oxidation reactions, Hpca plays a key role generating catalytically active oxo-peroxo V-pca species [14–16], since $[VO_3]^-$ ion itself is typically not active in the absence of any acid co-catalyst. In recent years, further research has resulted in other interesting catalytic systems based on the combination of various V [17-20], Fe [21-25], Mn [26-28], Re [29,30], and Cu [31-33] complexes with Hpca and analogs. These have not only extended the substrate scope of Hpca-assisted oxidative transformations, but have also been an object of some theoretical and kinetic studies [16,17,34-36].

Although a number of different reviews on the metalcomplex-catalyzed oxidation of organic compounds are available [8–12,38,39], the application of Hpca as a versatile co-catalyst and its coordination chemistry with regard to the oxidative



 $\label{eq:scheme 1. Structure (b) of 2-pyrazinecarboxylic acid (Hpca), C_5H_4N_2O_2 \ [37].$

transformations of alkanes, arenes, alcohols, and other substrates have not yet been reviewed. Hence, the main objectives of the present work consist in (i) providing an overview of isolated vanadium, iron, and some other transition metal complexes derived from Hpca, (ii) summarizing the applications of Hpca-assisted systems in the oxidation of various organic substrates by different oxidants, and (iii) describing the main selectivity, kinetic, and mechanistic features of these oxidation reactions. The present study covers the application of catalytic systems wherein Hpca is used either as a co-catalyst (additive) or as a ligand {pca=2pyrazinecarboxylate(-)} within a metal complex catalyst. The work also describes some selected systems closely related to Hpca, which are based on analogous heteroaromatic carboxylic acids (Scheme 2).

2. Oxidation reactions catalyzed by vanadium compounds

Vanadium oxo and/or peroxo complexes are recognized catalysts, promoters, or stoichiometric oxidants for the oxidative transformation of diverse organic and inorganic substrates. In particular, a considerable number and variety of vanadium derivatives bearing N,O-ligands have been obtained and applied in different organic transformations. Several interesting reviews have been published on this topic [9,38,39].

2.1. Coordination chemistry of vanadium with Hpca and analogs

2-Pyrazinecarboxylic acid (Hpca) is a simple, commercially available, stable, water-soluble, and bioactive pyrazine derivative that is also a metabolite of the first-line anti-tuberculosis drug pyrazinamide (2-pyrazinecarboxamide), the conversion of which to Hpca is achieved by an enzyme called pyrazinamidase [40]. Hpca exhibits rich coordination chemistry [41] and has been widely used as a convenient N,O-building block for the preparation of different metal complexes, coordination polymers, or metal–organic frameworks [42].

With regard to vanadium, there are a dozen isolated mononuclear oxo and/or peroxo complexes bearing 2-pyrazinecarboxylate(-)(pca)ligand (compounds **1–12**, Table 1), in addition to six heterometallic V/M (M = Ag, Co, Ni, Cu) coordination polymers (compounds **13–18**) in which, however, pca is not coordinated to vanadium. In all these compounds pca acts in the N,O-chelating mode.

In a pioneering paper in 1983, Mimoun et al. [43] reported the preparation of vanadium complexes $[VO(O_2)(pca)(picno)(H_2O)](7)$ and $[VO(O_2)(pca)(depa)]$ (8) that bear pca ligands. These compounds were among the peroxo vanadium derivatives active in the stoichiometric oxidation of some hydrocarbons (see below, Section 2.2). In 1999, the first structurally characterized V-pca complexes were synthesized by Süss-Fink et al. [14] via the



Scheme 2. Examples of heteroaromatic carboxylic acids closely related to Hpca: 2,3-pyrazinedicarboxylic (H2pdca), picolinic (Hpic), and dipicolinic (H2dipic) acids.

$$[VO_3]^- + 2Hpca \xrightarrow{MeCN, air, reflux} [VO_2(pca)_2]^-$$

$$[VO_2(pca)_2]^- + H_2O_2 \xrightarrow{MeCN, air, 20-40 \ ^{\circ}C} [VO(O_2)(pca)_2]^-$$

Scheme 3. Simplified formation of the catalytically active species in the $[VO_3]^-/Hpca/H_2O_2$ system.

interaction of $[NBu_4][VO_3]$ or $[NH_4][VO_3]$ with Hpca, namely the dioxo vanadium(V) complex $[NBu_4][VO_2(pca)_2]$ (1) and its oxo-peroxo derivative $[NH_4][VO(O_2)(pca)_2]\cdot 2H_2O$ (2), as well as a double salt of the both $[NBu_4]_2[VO_2(pca)_2][VO(O_2)(pca)_2]$ (3) (Table 1, Scheme 3). These complexes were suspected [14,15] as intermediate compounds in the efficient oxidation of organic substances by the in situ prepared catalytic vanadate anion/Hpca/H₂O₂ system (Scheme 3, see also Section 2.3).

The treatment of [NBu₄][VO₃] with Hpca in MeCN under reflux gave [NBu₄][VO₂(pca)₂] (1) isolated as light yellow crystals (Scheme 4) [14]. It was shown later that [NH₄][VO₃] similarly reacted with Hpca under reflux in MeCN to yield $[NH_4][VO_2(pca)_2]$ (4) as a vellow crystalline solid [44]. An analogous reaction of $[NH_4][VO_3]$ with Hpca and H_2O_2 (30% ag) in H_2O at rt, followed by addition of EtOH, led to the formation of light red crystals of the oxo-peroxo complex [NH₄][VO(O₂)(pca)₂]·2H₂O (2). In addition, treatment of 1 with H₂O₂ (30% aq) in MeCN at 0 °C furnished a double salt $[NBu_4]_2[VO_2(pca)_2][VO(O_2)(pca)_2]$ (3). Interestingly, the oxo-peroxo vanadium(V) moieties $[VO(O_2)(pca)_2]^-$ in 2 and 3 exist in two different isomeric forms, in which the N donor atoms of two pca ligands are in mutual *trans* and *cis* position, respectively [14,15]. Another catalytically active dioxovanadium(V) derivative $[VO_2(pca){O=P(NMe_2)_3}]$ (5) was obtained [18] as yellow crystals from [NH₄][VO₃], Hpca, and O=P(NMe₂)₃ in H₂O/CH₂Cl₂ at rt (Scheme 4).

The structural fragments **1** and **2** are depicted in Fig. 1 as typical examples of oxo and oxo-peroxo V-pca complexes that are intermediates in the Hpca-assisted catalytic oxidation (see below, Section

Table 1

Isolated vanadium complexes derived from Hpca.

2.3) [14]. In **1**, the six-coordinate vanadium(V) atom possesses a distorted octahedral $\{VO_4N_2\}$ coordination geometry that is filled by two terminal *cis*-oxo ligands and two N,O-chelating pca ligands, the N atoms of which are also in the mutual *cis* positions (Fig. 1a) [14]. In **2**, the seven-coordinate V(V) atom adopts a $\{VO_5N_2\}$ geometry that is better described as a distorted pentagonal bipyramid, the equatorial sites of which are occupied by the O atoms of the peroxo group, two mutually *trans* N atoms of two bidentate pca chelators, and one O atom of pca that is *trans* to the peroxo moiety. The apical positions are taken by the terminal oxo group and the O atom of the second pca ligand (Fig. 1b).

Apart from **1** to **5**, other V-pca compounds have been reported [43,45–48]. These include an oxo complex $[VO(pca)_2(H_2O)] \cdot 2H_2O$ (**6**) generated in the reaction of $VOSO_4 \cdot 5H_2O$ with Hpca in MeOH/Me₂CO medium at 50 °C [45]. Interestingly, this is the only vanadium(IV) derivative within the family of V(V) compounds derived from Hpca (Table 1). A number of oxo-peroxo complexes $[VO(O_2)(pca)(pica)(H_2O)]$ (**7**) [43], $VO(O_2)(pca)(depa)]$ (**8**) [43], $[VO(O_2)(pca)(pica)] \cdot H_2O$ (**9**) [46], $[VO(O_2)(pca)(bpy)]$ (**10**) [47], $[VO(O_2)(pca)(phen)]$ (**11**) [47], and $[H_3N(CH_2)_2NH_3][VO(O_2)(pca)(ox)]$ (**12**) [48] bearing pca and another O-, N,O-, N,N- or O,O-ligand have also been isolated and characterized. In spite of some structural similarity with **2**, these compounds have not yet been tested in catalytic oxidation reactions.

In addition, a series of heterometallic M/V (M=Ag, Co, Ni, Cu) coordination polymers **13–18** (Table 1) has been reported (Table 1) [49–52]. In these hybrid organic-inorganic materials, oxovanadium moieties stabilize and extend the polymeric networks driven by multiple M-pca interactions. A particularly interesting example concerns the hybrid polymer $[Ag_4(\mu_5-pca)_2(V_2O_6)]_n$ (**13**), obtained by a hydrothermal method from Ag_2O , NH₄VO₃, Hpca, and NH₄OH [49]. Apart from featuring a stable three-dimensional $\{[Ag_2(pca)]^+\}_n$ coordination network with channels occupied by $\{VO_3^-\}_n$ chains, this compound exhibits high photocatalytic activity for the decomposition of methylene blue under both ultraviolet

Compound	Formula	V:pca	V coord. number and environment	X-ray structure	Ref.
1	[NBu ₄][VO ₂ (pca) ₂]	1:2	$6 \{VO_4N_2\}$	+	[14]
2	$[NH_4][VO(O_2)(pca)_2] \cdot 2H_2O$	1:2	$7 \{VO_5N_2\}$	+	[14]
3	$[NBu_4]_2[VO_2(pca)_2][VO(O_2)(pca)_2]$	1:2	$6/7 \{VO_{4/5}N_2\}$	a	[14]
4	$[NH_4][VO_2(pca)_2]$	1:2	$6 \{VO_4N_2\}$	-	[44]
5	$[VO_2(pca)] = P(NMe_2)_3$	1:1	5 {VO ₄ N}	+	[18]
6	$[VO(pca)_2(H_2O)] \cdot 2H_2O$	1:2	$6 \{VO_4N_2\}$	+	[45]
7	$[VO(O_2)(pca)(picno)(H_2O)]$	1:1	7 {VO ₆ N}	-	[43]
8	[VO(O ₂)(pca)(depa)]	1:1	$7 \{VO_4N_2\}$	-	[43]
9	[VO(O ₂)(pca)(pica)]·H ₂ O	1:1	$7 \{VO_5N_2\}$	+	[46]
10	$[VO(O_2)(pca)(bpy)]$	1:1	$7 \{VO_4N_3\}$	+	[47]
11	$[VO(O_2)(pca)(phen)]$	1:1	$7 \{VO_4N_3\}$	+	[47]
12	$[H_3N(CH_2)_2NH_3][VO(O_2)(pca)(ox)]$	1:1	$7 \{VO_6N\}$	+	[48]
13	$[Ag_4(\mu_5-pca)_2(V_2O_6)]_n$	1:1	5 ^b {VO ₅ }	+	[49]
14	$[Co_2(\mu_3 - pca)(H_2O)(VO_3)_3]_n$	3:1	$4^{b} \{ VO_{4} \}$	+	[50]
15	$[NH_4]_2[Co_8(\mu_3-pca)_8(VO_3)_{10}]_n \cdot 2nH_2O$	1.25:1	4^{b} {VO ₄ }	+	[51]
16	$[Co_4(\mu_3-pca)_4(V_6O_{17})]_n \cdot 6nH_2O$	1.5:1	4^{b} {VO ₄ }	+	[51]
17	$[Ni_4(\mu_3-pca)_4(V_6O_{17})]_n \cdot 6nH_2O$	1.5:1	4^{b} {VO ₄ }	+	[51]
18	${[Cu_3(\mu-pca)_4(H_2O)_2][V_{10}O_{24}(OH)_4]}_n \cdot 6.5nH_2O$	2.5:1	5/6 ^b {VO _{5/6} }	+	[52]

^a Structure has not been published due to the high *R* factor (>10%).

^b In this heterometallic compound, pca is not coordinated to vanadium atom.



Scheme 4. Structural formulae of complexes 1, 2, and 5.

and visible-light irradiations [49]. Although compounds **14–18** have not been applied in catalytic oxidation of organic substrates, their high thermal stability, hybrid structures, and the presence of a second transition metal apart from vanadium, make them suitable candidates as heterogeneous pca-based oxidation catalysts.

A noteworthy study concerns the investigation of a speciation in a model H⁺/[VO₃]⁻/Hpca system at a metal-to-ligand molar ratio of 1:4 (C_V = 1.0 mM) [16a]. At acidic conditions (pH < 2), the complexation of Hpca to $[VO_3]^-$ starts with the formation of a derivative $[VO_2(pca)(H_2O)_2]$ (S1), which gradually transforms to $[VO_2(pca)_2]^-$ (S2) upon increasing the pH. A parallel process also leads to the deprotonation of one of the water ligands in S1, resulting in $[VO_2(pca)(H_2O)(OH)]^-$ (S3). At pH > 3, the formation of $[VO_2(pca)(OH)_2]^{2-}$ (**S4**) begins, being the main species at pH > 4.5. In all these vanadium(V) derivatives, pca ligands adopt the N,Ochelating mode (Scheme 5). The equilibrium constants calculated for some proton displacement reactions and the analysis of literature data indicate that the binding strength of Hpca is essentially similar to that of picolinic acid [16a]. The anion S2 has been isolated in the solid-state as complexes [NBu₄][VO₂(pca)₂] (1) [14] and $[NH_4][VO_2(pca)_2](4)[44]$. In addition, the formation of related vanadium(IV) compounds can also occur, as attested by the isolation of $[VO(pca)_2(H_2O)] 2H_2O(\mathbf{6})$ and the proposed formation of a dimer $[V_2O_2(pca)_2(\mu-OH)_2(H_2O)_2]$ [45b]. Although the speciation in the [VO₃]⁻/Hpca/H₂O₂ catalytic system has not been studied, it is significantly more complex due to the formation of various peroxo derivatives.

Apart from V-pca complexes, some closely related oxovanadium compounds derived from picolinic (Hpic), dipicolinic (H₂dipic), and 2,3-pyrazinedicarboxylic (H₂pdca) acids have been synthesized and applied in either stoichiometric or catalytic oxidation of various organic substrates [39,43,53–56]. The selected examples are summarized in Table 2.

In an early study [43], Mimoun et al. reported eight neutral oxo-peroxo vanadium(V) complexes of general formula $[VO(O_2)(pic)(LL')]$ (wherein LL' is two monodentate ligands or one bidentate ligand, namely H₂O, MeOH, py, picno, depa, or dmpa), as well as some anionic complexes of the general formula $A[VO(O_2)(pic)_2] \cdot L$ (wherein A is H⁺ or PPh₄⁺, and L is H_2O or $O=P(NMe_2)_3$). The simplest and most studied examples concern the compounds $[VO(O_2)(pic)(H_2O)_2]$ (19a) and $H[VO(O_2)(pic)_2] \cdot H_2O$ (**20a**), the former was also structurally characterized by X-ray diffraction. These derivatives are easily generated from V₂O₅ and Hpic, taken in different molar ratios, in aqueous (30%) solution of H_2O_2 at 0 °C. A related alkylperoxo compound [VO(*t*-BuOO)(dipic)(H₂O)] (**21**) derived from H₂dipic was also reported [54]. A series of oxovanadium(V) dipicolinate complexes of general formula [VO(dipic)(L)] (wherein L are different alcoholate O- or O,O-ligands) were obtained by Thorn and co-workers [56,57]. A particularly interesting example concerns a compound [VO(dipic)(*i*-PrO)] (23) that has been prepared from VO(i-PrO)₃ and H₂dipic in MeCN medium [57a], and used as a convenient precursor for the synthesis of various V-dipic derivatives.

2.2. Stoichiometric oxidation

In regard to stoichiometric oxidation of various organic substrates by peroxovanadium derivatives, there is an important study by Mimoun et al. [43] on the application of oxo-peroxo V-pic complexes **19** and **20** (Table 2) as oxidants in stoichiometric oxidation of olefins, hydroxylation of arenes, and alkanes. This chemistry and particularly the use of complex $[VO(O_2)(pic)(H_2O)_2]$ (**19a**) have been further investigated by Conte and co-workers, also including the development of catalytic oxidation reactions of different substrates, as well as mechanistic studies [39,53a,b]. The oxidation of alkanes and benzene by **19a** in acetonitrile can also be accel-



Fig. 1. Representation of the $[VO_2(pca)_2]^-$ and $[VO(O_2)(pca)_2]^-$ anions in the X-ray crystal structures of **1** (a) and **2** (b). Cations and solvent molecules are omitted for clarity. Color codes: V (green balls), O (red), N (blue), C (cyan), H (pale gray). Adapted from [14].



Scheme 5. V-pca species formed in the H⁺/[VO₃]⁻/Hpca system; pca ligands are schematically shown as N—O groups.

Adapted from [16a].

erated upon irradiation with visible and, especially, UV light [58]. Since a number of reviews covering stoichiometric oxidation have been published [38c,39,59], we are not discussing these studies herein.

In recent years, Thorn and co-workers have reported the application of V-dipic complexes [VO(dipic)(*i*-PrO)] (23), [VO(dipic)(pinme)] (24a), [VO(dipic)(pheol)] (24b), [VO(dipic)(dpheol)] (24c), and analogs in stoichiometric aerobic oxidation of isopropanol, pinacol, and other alcohols as lignin models, namely pinacol monomethyl ether, 2-phenoxyethanol, 1-phenyl-2-phenoxyethanol, and 1,2-diphenyl-2-methoxyethanol [56,57]. Although some catalytic oxidation reactions have also been reported with 23, the catalyst turnover numbers (TONs) have not exceeded 37 [56].

2.3. Catalytic oxidation with H_2O_2

Given the obvious limitations of stoichiometric reactions, the development of new catalytic processes and systems for efficient oxidation of organic substrates continues to be an important research topic. Some catalytic oxidation reactions based on the use of isolated vanadium picolinate complexes and hydrogen peroxide have been found [39], however their efficiency in terms of product yields and/or turnover numbers is low. In 1993, Shul'pin and coworkers [13,60,61] reported that the system consisting of hydrogen peroxide and air as oxidants, a vanadate ion as a catalyst and 2pyrazinecarboxylic acid as a co-catalyst, very efficiently oxidizes various organic compounds under mild conditions (temperature 20–70°C, atmospheric pressure). The proposed simple, cheap, and commercially available vanadate anion/Hpca/H₂O₂/O₂ reagent was applied to the oxygenation of saturated and unsaturated hydrocarbons and oxidation of alcohols [6,9-12]. The substrate scope of this and closely related catalytic systems is described in the following sections.

Table 2

Selected vanadium complexes derived from Hpic, H2 dipic, and H2 pdca.ª

2.3.1. Alkanes

2-Pyrazinecarboxylic acid and related compounds (e.g., H₂pdca) can act as co-catalysts (additives) which dramatically increase the efficiency and rate of vanadium-catalyzed alkane oxidation by hydrogen peroxide [6,9-13,60,61]. Thus, the combination of the $[VO_3]^-$ ion (either in a form of $[NBu_4][VO_3]$ or $NaVO_3$) with Hpca in a typical molar ratio of 1:4, in the presence of H_2O_2 and air (O_2) in MeCN medium, provides the catalytic system that is capable of oxidizing even methane, which is the most inert hydrocarbon. This reaction proceeds at 40–50 °C leading to the formation of methyl hydroperoxide as a primary (intermediate) oxidation product, which decomposes to methanol and formic acid as final products (Scheme 6) [62,63]. Their total yield reached 13% based on CH₄ (or 50% based on H₂O₂), also with TON of 630 [62]. Hereinafter, yields are defined as moles of products per mol of substrate or oxidant, while TONs are expressed as moles of products per mol of catalyst. The achieved levels of activity are very high considering the exceptional inertness of methane and rather mild reaction conditions.

2-Pyrazinecarboxylic acid is the most powerful co-catalyst among other pyrazinecarboxylic acids (Table 3), although somewhat comparable activity has been observed when using 2,5-pyrazinedicarboxylic acid [62]. Thus, when a substituent is situated in proximity to the COOH group of functionalized Hpca, almost no oxidation of methane is observed. When the methane oxidation is carried out in an aqueous solution at high temperature (90 °C), it is accompanied by the intense parallel degradation of the Hpca co-catalyst [64]. Therefore, relatively high yields of methane oxidation products (largely, formic acid) cannot be attained unless a rather high Hpca concentration is used. Addition of sulfuric acid to the solution containing Hpca increases the yield of the products, whereas TONs can attain values of 150.

Alkyl hydroperoxides are very common primary products in alkane oxidation by peroxides and dioxygen. Since they can be quantitatively transformed to the corresponding alcohols by the

Compound	Formula	V coord. number and environment	X-ray structure	Application	Ref.
19a	[VO(O ₂)(pic)(H ₂ O) ₂]	$7 \{VO_6N\}$	+	Stoichiometric oxidation of olefins, hydroxylation of arenes and alkanes ^b	[39,43,53]
19b	[VO(O ₂)(pic)(depa)]	$7 \{VO_5N_2\}$	-		[43]
20a	$H[VO(O_2)(pic)_2]H_2O$	$7 \{VO_5N_2\}$	-		[43]
20b	$H[VO(O_2)(pic)_2] \{O=P(NMe_2)_3\}$	$7 \{VO_5N_2\}$	-		[43]
21	[VO(t-BuOO)(dipic)(H ₂ O)]	7 {VO ₆ N}	+	Stoichiometric hydroxylation of arenes and alkanes	[54]
22	[VO(pic) ₂] – NaY zeolite	$5 \{VO_3N_2\}$	-	Catalytic oxidation of alkanes	[55]
23	[VO(dipic)(i-PrO)]	5 {VO ₄ N}	_	Catalytic oxidation of pinacol and lignin models, stoichiometric oxidation of isopropanol	[56,57]
24a	[VO(dipic)(pinme)]	6 {VO ₅ N}	+	Stoichiometric oxidation of lignin models	[56]
24b	[VO(dipic)(pheol)]	6 {VO ₅ N}	+		[56]
24c	[VO(dipic)(dpheol)]	6 {VO ₅ N}	+		[56]
25	[VO(Hpdca) ₂ (H ₂ O)]	$6 \{VO_4N_2\}$	_	Catalytic oxidation of alkanes ^c	[45]

^a This table is not comprehensive and concerns only selected examples of vanadium compounds that were applied in stoichiometric or catalytic oxidation.

^b Some catalytic oxidation reactions have also been developed with **19a**.

^c Although **25** as such has not been applied in catalysis, it is presumably one of the catalytically active species formed in situ in the [VO₃]⁻/H₂pdca/H₂O₂ system [36a].



Scheme 6. Oxidation of methane by the [VO₃]⁻/Hpca/O₂/H₂O₂ reagent.



Scheme 7. Oxidation of propane by the [VO₃]⁻/Hpca/H₂O₂ reagent.

Effect of acid co-catal	yst on the oxidation of me	thane by the [NBu4][VO	3]/H ₂ O ₂ /O ₂ system in MeCN. ^a

Entry	Acid co-catalyst	Total yield (MeOH + HCOOH) based on H ₂ O ₂ (%)	TON
1	2-Pyrazinecarboxylic acid (Hpca)	32	375
2	2,5-Pyrazinedicarboxylic acid	29	325
3	5-Methylpyrazine-2-carboxylic acid	5	50
4	2,3-Pyrazinedicarboxylic acid monoamide	4.5	45
5	2,3-Pyrazinedicarboxylic acid (H2pdca)	0	0
6	3-Aminopyrazine-2-carboxylic acid	0	0

Adapted from [62a].

Table 3

^a Temperature 40 °C, [co-catalyst]:[vanadate] = 4:1.

treatment with a reducing agent (e.g., PPh₃, NaBH₄), a convenient method for the determination and quantification of real concentrations of all products in alkane oxidation has been developed by one of us [10,11,65]. This method is based on the gas chromatographic comparative analyses of the reaction mixtures before and after reduction of the reaction samples containing alkyl hydroper-oxides with PPh₃.

The $[VO_3]^-/Hpca/H_2O_2$ reagent is also active in the oxidation of other gaseous alkanes (ethane, propane, *n*-butane, and *i*-butane) to the corresponding alkyl hydroperoxides, alcohols, ketones, aldehydes, and/or carboxylic acids [36,62,66]. Their overall yields can attain 8–12% based on the substrate, while the best TONs span from 330 to 2130 in the oxidation reactions of propane and ethane, respectively. The selectivity and efficiency characteristics of these transformations significantly depend on the reaction parameters. Under certain conditions, C₃H₈ can be oxidized rather selectively to a mixture of 2-propanol and 1-propanol (molar ratio of 2:1) with the total yield of 27% based on H₂O₂ (Scheme 7) [36].

The linear and branched C_5-C_7 alkanes (*n*-hexane, *n*-heptane, 2-methylhexane, and 3-methylhexane) are also oxidized by the $[VO_3]^-/Hpca/H_2O_2/O_2$ system into the corresponding alcohols and carbonyl compounds (after reduction with PPh₃, see Scheme 8) [13,36,66,67], with maximum overall yields in the 9–13% range based on the substrate (TONs 200–310) [13]. Higher conversions can potentially be reached upon optimization of the reaction



Scheme 8. Oxidation of C₅-C₇ alkanes by the [VO₃]⁻/Hpca/H₂O₂/O₂ reagent.

conditions. Using the analogous catalytic system, *n*-pentane can be transformed at 75 °C exclusively to 2-pentanone and 3-pentanone with the overall yield of 52% (based on H_2O_2) and TON of 700 (Scheme 9). Interestingly, pentyl hydroperoxides have not been detected in the reaction mixture [66].

Among various cycloalkanes, cyclohexane has extensively been studied as a recognized model substrate in the development of mild and selective catalytic oxidation processes [6,9-12,68], particularly in view of the importance of the products, since cyclohexanol and cyclohexanone are intermediates in the production of nylon-6,6' and polyamide-6 [68,69]. Hence, $c-C_6H_{12}$ has been oxidized by the $[VO_3]^-/Hpca/H_2O_2/O_2$ and related systems [13,15,36,62,66,70], resulting in a mixture of cyclohexyl hydroperoxide (CyOOH, major primary product), cyclohexanol and cyclohexanone (final products), with the total product yield of 35% (based on $c-C_6H_{12}$) and TON of 800 (Scheme 10) [13]. The relative amounts of all three products depend significantly on the reaction parameters, such as time, temperature, concentrations of the [VO₃]⁻ catalyst, Hpca cocatalyst, and H₂O₂. For example, cyclohexanol can be produced almost exclusively (30% yield, TON 1200) under certain reaction conditions (40 °C, 25 h) and after reduction with PPh₃ of the primarily formed CyOOH [36]. An urea-hydrogen peroxide adduct can also be employed as an oxidizing agent with the $[VO_3]^-/Hpca$ system (40°C, 6h, stepwise addition of oxidant) giving, upon treatment with PPh₃, cyclohexanol as a major product (32% yield based on $c-C_6H_{12}$) with a minor amount of cyclohexanone (1% yield) [70]. Addition of pyridine to the [VO₃]⁻/Hpca catalytic system has a slight positive effect on the activity and selectivity parameters in alkane oxidation by H₂O₂ [71].

Following a successful application of Hpca as a co-catalyst in the oxidation of cyclohexane, a promoting role of other heteroaromatic carboxylic acids has been tested [11,14], and the selected results are given in Table 4. Although these analogs of 2-pyrazinecarboxylic acid are usually less active co-catalysts, rather efficient and simple catalytic systems based on the combination of [NBu₄][VO₃] with 2,3-pyrazinedicarboxylic acid (H₂pdca) or picolinic acid (Hpic)



Scheme 9. Oxidation of *n*-pentane by the $[VO_3]^-/Hpca/H_2O_2/O_2$ reagent.



Scheme 10. Oxidation of cyclohexane by the [VO₃]⁻/Hpca/H₂O₂/O₂ reagent.

have also been developed. For example, the $[VO_3]^-/H_2pdca/H_2O_2$ system can furnish (after reduction with PPh₃) cyclohexanol and cyclohexanone in up to 33% total yield (TON 1300) [36].

The complex $[NBu_4][VO_2(pca)_2]$ (1) also catalyzes the oxidation of cyclohexane by aqueous 30% H₂O₂ at 40 °C (Scheme 11) [15]. Although 1 shows inferior activity than that of the precursor $[VO_3]^-/Hpca$ (molar ratio of 1:4) system, the total product yields (based on $c-C_6H_{12}$) increase from 5% to 20% upon addition of Hpca (2 equiv) that acts as a co-catalyst accelerating the proton transfer steps (see Section 2.3.4) [15,36]. A similar behavior is observed when using related catalysts $[NH_4][VO(O_2)(pca)_2]\cdot 2H_2O$ (2) and $[VO_2(pca){O=P(NMe_2)_3}]$ (5), the latter being the most active leading to the total product yield of 30% and TON of 1370 (Scheme 11) [15,18]. Other systems composed of Hpca and different vanadium complexes have also been applied for cyclohexane oxidation [17,19,36].

The combination of Hpca and bis(maltolato)oxo vanadium complexes, used either in a soluble form or anchored to chemically modified silica gel, has been applied for the selective oxidation of $c-C_6H_{12}$ by H_2O_2 to cyclohexyl hydroperoxide [20]. The best yields of CyOOH attain 27% based on substrate (TON 2600) when using soluble vanadium(V) catalyst [VO(OMe)(mal)₂] (**26**) and oxidant excess. In a heterogenized form, the same catalyst leads to a slightly inferior product yield (25%). Other heterogeneous catalytic systems based on supported vanadium oxides in combination with Hpca have been reported for cyclohexane oxidation, although

Table 4

Effect of acid co-catalyst on the oxidation of cyclohexane by the $[\rm NBu_4][\rm VO_3]/\rm H_2O_2$ system in MeCN.^a

Entry	Acid co-catalyst	TON
1	2-Pyrazinecarboxylic acid (Hpca)	1100
2	2,3-Pyrazinedicarboxylic acid (H ₂ pdca)	1100
3	Picolinic acid (Hpic)	970
4	4,5-Imidazoledicarboxylic aid	430
5	Perchloric acid	380
6	4-Imidazolecarboxylic acid	70
7	Acetic acid	65
8	3,5-Pyrazoledicarboxylic acid	30
9	3-Aminopyrazine-2-carboxylic acid	20
10	2,6-Bis(pyrrolidin-2-yl)-pyridine	20
11	Anthranilic acid	9
12	5-Methyl-2-phenyl-1,2,3-triazole-4-carboxylic acid	8

Adapted from [14]

^a Temperature 40 °C, [co-catalyst]:[vanadate]=4:1; total TONs (moles of cyclohexanol and cyclohexanone per mol of catalyst) were measured after reduction with PPh₃. resulting in very low product yields based on substrate [72a]. Later, a modified system consisting of a MgO-supported vanadium oxide catalyst and Hpca as co-catalyst has been described [72b].

Moreover, Hpca acts as a co-catalyst in the V-catalyzed oxidation reactions of other cycloalkanes (cyclopentane, cyclooctane, methylcyclohexane, *cis*- and *trans*-decalin), which typically result in moderate product yields [73,74]. The V-pca derivative **2** can catalyze the oxidation of *cis*- and *trans*-decalin, 1,2- and 1,4-dimethylcyclohexane, but without stereoselectivity [36]. Interestingly and in contrast to the $[VO_3]^-/Hpca$ system, 2-pyrazinecarboxylic acid only accelerates the oxidation of cyclooctane catalyzed by vanadium-containing polyphosphomolybdates, without enhancing an overall product yield (30% of oxygenates based on *c*-C₈H₁₆, TON 1000) [74].

Iwasawa and co-workers applied the encapsulated oxovanadium(IV) picolinate complex $[VO(pic)_2]$ -NaY zeolite (**22**) and related derivatives, including a soluble oxo-peroxo vanadium(V) complex H[VO(O₂)(pic)₂]·H₂O (**20a**), as active catalysts for the oxidation of various alkanes by the urea-hydrogen peroxide adduct, at 30–40 °C in MeCN, under heterogeneous or homogeneous conditions [55]. Thus, cyclohexane, 2,5-dimethylhexane, and *n*-octane are transformed to the corresponding alkyl hydroperoxides, alcohols, and ketones, with overall product yields up to 32% in the oxidation of *c*-C₆H₁₂ catalyzed by **22**. In spite of some leaching, this catalyst showed preferable oxidation of smaller substrates and increased selectivity toward the oxidation of terminal methyl groups [55].

2.3.2. Arenes, olefins, and acetylenes

The $[VO_3]^-/Hpca/H_2O_2$ reagent [13,70,75] and other Hpcaassisted systems [20] have been applied for the oxidation of benzene and its derivatives (toluene, ethylbenzene, and cumene) by H_2O_2 in MeCN medium. Typically benzene is hydroxylated to phenol, whereas alkylbenzenes are preferably oxidized to sidechain oxidation products. Although the conversions are generally not high in these transformations, the yields of phenol up to 20% based on C_6H_6 have been achieved when using complex $[VO(OMe)(mal)_2]$ (**26**) supported onto silica gel (Scheme 12) [20]. The hydroxylation of benzene and substituted benzenes XC_6H_5 $(X = CH_3, F, Cl, Br, NO_2)$ to give the corresponding monophenols, by H_2O_2 and in the presence of catalytic amounts of $[VO(O_2)(pic)(H_2O)_2]$ (**19a**), has also been reported [53b]. However, the efficiency of these reactions in terms of yields and TONs was significantly lower than that of the Hpca-assisted transformations.



Scheme 11. Oxidation of cyclohexane by the V-pca complex/Hpca/H₂O₂/O₂ reagent.



Scheme 12. Hydroxylation of benzene by the 26-SiO₂/Hpca/H₂O₂/O₂ system.

Moreover, the $[VO(acac)_2]/Hpca/H_2O_2/O_2$ and $[VO_3]$ -/Hpca/H_2O_2/O_2 systems exhibit good activity for the mild oxidation of various unsaturated hydrocarbons, namely cyclohexene, styrene, α -methylstyrene, *trans*-stilbene, α -methyl*trans*-stilbene, and phenylacetylene [73,76]. Thus, cyclohexene can be transformed into cyclohex-2-enyl hydroperoxide (10% yield based on C₆H₁₀) as a main primary product, along with a number of other products in lesser amounts [73]. On the contrary, styrene is more reactive and can be oxidized quite selectively to benzaldehyde as the main product (Scheme 13), obtained in 30–35% yields based on the substrate (TONs 350–600) [76]. In an analogous reaction, the $[VO_3]^-/Hpca/H_2O_2/O_2$ reagent has been used for a practically important transformation of isoeugenol to vanillin (Scheme 14) [77]. Similarly, an oxidative cleavage of *trans*-stilbene leads to the formation of benzaldehyde (Scheme 15) in up to 75% yield (TON 1500) [76]. Furthermore, α -methylstyrene and α -methyl*trans*-stilbene are oxidized by the $[VO(acac)_2]/Hpca/H_2O_2/O_2$ system to produce acetophenone (41% based on substrate, TON 810) or a mixture of acetophenone and benzaldehyde (20% overall yield), respectively. 2-Pyrazinecarboxylic acid is an essential co-catalyst in all these oxidation processes since in its absence the reactions are less efficient and rather slow [76].

The $[VO(acac)_2]/Hpca/H_2O_2/O_2$ system is also active for the oxidation of acetylenes [76]. However, the oxidation of phenylacetylene is less efficient in comparison with that of styrene (Scheme 13), leading to lower overall yield of benzoic acid and benzaldehyde (17%, TON 310). Interestingly, the selectivity to



Scheme 13. Oxidation of styrene by the $[VO_3]^-/Hpca/H_2O_2/O_2$ reagent.



Scheme 14. Oxidation of isoeugenol to vanillin by the [VO₃]⁻/Hpca/H₂O₂/O₂ reagent.



Scheme 15. Oxidation of trans-stilbene by the [VO₃]⁻/Hpca/H₂O₂/O₂ reagent.



Scheme 16. Oxidation of isopropanol by the [VO₃]⁻/Hpca/H₂O₂/O₂ reagent.

benzoic acid can be increased by lowering the reaction temperature from 60 to 23 °C. Diphenylacetylene can also be oxidized to benzoic acid under similar reaction conditions, although in a low yield [76].

2.3.3. Alcohols

Apart from hydrocarbons, Hpca in combination with vanadium catalysts have also been applied for the oxidation of various alcohols to corresponding carbonyl compounds [13,16,17,70]. Hence, the versatile $[VO_3]^-$ /Hpca/H₂O₂/O₂ reagent can selectively convert isopropanol to acetone with 100% yield based on H₂O₂ (TON 500). In this oxidation, *i*-PrOH acts as both substrate and solvent (Scheme 16), and no reaction occurs in the absence of Hpca [16]. The same reagent is also capable of oxidizing 1-propanol and cyclohexanol, although giving only moderate product yields [13,70]. The application of V-pic derivatives in alcohol oxidation by H₂O₂ has also been reported [55b,78].

2.3.4. Mechanistic studies

A number of discussions have been devoted to mechanisms of oxidation by the $[VO_3]^-/Hpca/H_2O_2$ reagent and other vanadium containing systems [9,16,17,35,36,73,75,76,79], also including early publications [10,11,13,61,74,80,81]. Thus, based on selectivity parameters, EPR, and kinetic studies, Shul'pin and co-workers proposed a mechanism of oxidation of various organic compounds by the $[VO_3]^-/Hpca/H_2O_2$ reagent [36]. A crucial oxidizing species is hydroxyl radical generated from hydrogen peroxide and vanadium catalyst via two consecutive stages. The initial vanadium(V) derivative (for example, in vanadate anion) is reduced by the first H_2O_2 molecule to give a derivative of vanadium(IV) and hydroperoxo radical.

$$V^{V} + H_{2}O_{2} \rightarrow V^{IV} + HOO^{\bullet} + H^{+}$$

The low-valent vanadium derivative reacts with the second H_2O_2 molecule via Fenton-like mechanism [82] to generate the active hydroxyl radical.

$$V^{IV} + H_2O_2 \rightarrow V^V + HO^{\bullet} + HO^{-}$$

Two alternative mechanisms have been tentatively proposed to explain the accelerating role of Hpca in this reaction [36a,76]. Both of them assume that Hpca facilitates proton transfer from the H_2O_2 molecule coordinated to vanadium to an oxygen-containing ligand. In the first case, Hpca can take part either in the form of a zwitterion (structure **A**, Scheme 17) or as an amino acid with an intramolecular hydrogen bond (structure **B**, Scheme 17). Proton transfer occurs via six-membered transition states, giving rise to the formation of a hydroperoxo complex **C**. In the alternative "robot's arm mechanism", the coordinated via N atom pca ligand can transfer a proton from coordinated H_2O_2 in the structure **D** (Scheme 18) to the V=O fragment with the participation of the protonated (**E** and **F**) and deprotonated (**D** and **G**) carboxylic groups.

Bell and co-workers [35] studied the generation of free radicals in the $[VO_3]^-/Hpca/H_2O_2$ system by DFT method and found that the direct transfer has a higher barrier than the pca-assisted indirect transfer. "Indirect transfer occurs by migration of hydrogen $10^4 \times W_0$ (acetone), Ms⁻¹



Fig. 2. (Graph A) Oxidation of 2-propanol by the $[VO_3]^-/Hpca/H_2O_2$ reagent in 2-propanol solution. Dependences of the initial rate W_0 of acetone accumulation in the reactions catalyzed by $[NBu_4][VO_3]$ (curve 1) and [VO(tea)](curve 2) on the initial concentration of Hpca ([V] = 1 mM). Dashed curve is a theoretical curve calculated in accord with the proposed kinetic scheme. (Graph B) Dependence of the initial oxidation rate W_0 on initial concentration of Hpca in the cyclohexane oxidation in acetonitrile catalyzed by [VO(tea)]([V] = 0.1 mM). Adapted from [17].

from coordinated H_2O_2 to the oxygen of a pca ligand connected to the vanadium atom. The proposed mechanism demonstrates the important role of the co-catalyst in the reaction and explains why H_2O_2 complexes without pca are less active" [35]. In a more recent publication [17], the mechanism of oxidation catalyzed by vanadate anion or an oxovanadium(V) triethanolaminate complex [VO(tea)] in combination with Hpca was studied by kinetic and DFT methods. The oxidation reactions of alkanes and 2-propanol catalyzed by both vanadium catalysts proceed via the same mechanism. Thus, similar character of dependences of the initial rate on the initial concentration of Hpca when using these catalytic systems in the oxidation of 2-propanol and cyclohexane [17] is demonstrated in Fig. 2. In both cases the dependences have the maximum. A common kinetic scheme of the isopropanol oxidation has been



Scheme 17. Hpca-assisted mechanism of proton transfer to produce a hydroperoxo complex C.



Scheme 18. Proton transfer from D to produce hydroperoxo complex G ("robot's arm mechanism") assisted by the pca ligand coordinated to vanadium via N atom.

proposed on the basis of spectroscopic and kinetic data as well as DFT calculations [17].

$[V(0)(00)_2(H_20)]^- + Solvent \Rightarrow [V(0)(00)_2(Solvent)]^- + H_20$	K_1
$[V(O)(OO)_2(H_2O)]^- + Hpca = [V(O)(OO)(OOH)(pca)]^- + H_2O$	K_2
$[V(O)(OO)_2(Solvent)]^- + Hpca \Rightarrow [V(O)(OO)(OOH)(pca)]^- + Solvent$	K ₃
$[V(O)(OO)(OOH)(pca)]^{-} + Hpca \Rightarrow cis - [V(O)(OO)(pca)_{2}]^{-} + H_{2}O_{2}$	K_4^{cis}
$[V(O)(OO)(OOH)(pca)]^{-} + Hpca \Rightarrow trans - [V(O)(OO)(pca)_{2}]^{-} + H_{2}O_{2}$	K_4^{trans}
cis -[V(0)(00)(pca) ₂] ⁻ + H ₃ O ⁺ \Rightarrow [V(0)(00)(H ₂ O)(pca)] + Hpca	K_5^{cis}
$trans-[V(O)(OO)(pca)_2]^- + H_3O^+ \Rightarrow [V(O)(OO)(H_2O)(pca)] + Hpca$	K_5^{trans}
$[V(0)(00)(00H)(pca)]^{-} + H_3O^{+} \Rightarrow [V(0)(00)(H_2O_2)(pca)] + H_2O$	K_6
$[V(0)(00)(H_2O_2)(pca)] + H_2O \Rightarrow [V(0)(00)(H_2O)(pca)] + H_2O_2$	K_7
$[V(O)(OO)(H_2O_2)(pca)] \Rightarrow [V(OH)(OO)(OOH)(pca)]$	K _H
$Hpca + H_2O \rightleftharpoons pca^- + H_3O^+$	Ka
$[V(OH)(OO)(OOH)(pca)] \rightarrow HOO^{\bullet}$	$k_{\rm obs}$

The observed initial reaction rate W_0 is in accord with the following equation:

$$W_0 = k_{obs} \left[V(OH)(OO)(OOH)(pca) \right]$$

$$= k_{\text{obs}} \frac{K_{\text{H}}K_{6}[\{cis-[V(O)(OO)(\text{pca})_{2}\}^{-}][H_{2}O_{2}]_{0}K_{a}^{1/2}}{K_{a}^{cis}\{[\text{Hpca}][H_{2}O]\}^{1/2}}$$

A theoretical curve calculated in accordance with the kinetic scheme (dashed curve in Fig. 2A) satisfactorily coincides with the experimental points. The calculated distribution of various vanadium species in moist 2-propanol is shown in Fig. 3.

On the basis of the DFT calculations [17], another pathway for proton migration in the vanadium complex has been proposed, which counts with direct involvement of water. The molecule of H₂O is a part of a six-membered transition state **H** (Scheme 19). A water-assisted mechanism of proton transfer turned out to be even more effective than the "robot's arm" mechanism. The most favorable catalytic cycle including the steps of proton transfer is depicted in Scheme 20. Thus, the formation of the reactive hydroxyl radicals occurs via the addition of H₂O₂ to the V^{IV} complex [V(OO)(OH)(pca)] to furnish [V(OO)(OH)(pca)(H₂O₂)], followed by water-assisted H-transfer to the HO-ligand (the rate-limiting stage of the overall process), isomerization, and O–OH bond cleavage. In this mechanism, the pca ligand plays a key role as a stabilizer of transition state V(IV) species involved into the rate-limiting stage [17].

Moreover, polyvanadates formed in situ via the interaction of a strong acid (sulfuric, trifluoroacetic, or oxalic acid) with monovanadate in acetonitrile are much more active catalysts in comparison with starting monovanadate anion in the absence of a strong acid or Hpca [34,83]. The key factor of the higher activity of oligovanadates is the modification of the reaction mechanism upon the introduction of the second vanadium fragment. Thus, as supported by the DFT calculations, the model divanadate catalyst is more active, by 4.2 kcal/mol (i.e., by a factor of ca. 1200), than the simple monovanadate species [34]. This occurs because H-transfer to the oxo ligand in the rate-limiting step is opened for the di(poly)vanadate catalysts but not accessible for the monovanadate catalyst. The second vanadium fragment such as the pca ligand in the case of complexes derived from Hpca, plays the role of a stabilizer of key transition states due to the formation of 6-membered cyclic structures [34].

2.4. Oxidation with TBHP

tert-Butyl hydroperoxide (TBHP) is generally less efficient oxidant than H_2O_2 in cyclohexane oxidation catalyzed by the $[VO_3]^-/Hpca$ combination [84a]. The reaction can also undergo in the absence of Hpca. An oxovanadium(V) dipicolinate derivative can also catalyze the selective epoxidation of *cis*-cyclooctene with TBHP [84b].

As an intermediate in the $[VO_3]^-/Hpca$ system, the isolated dioxovanadium(V) complex $[NH_4][VO_2(pca)_2]$ (**4**) has been applied as a catalyst for the oxidation of various alcohols with TBHP (70% aq) in acetonitrile at 70 °C. Thus, cyclohexanol (Scheme 21) and 1-phenylethanol (Scheme 22) are converted into cyclohexanone and acetophenone with 89 and 95% yields (based on substrate), respectively [44].

Similarly, benzyl alcohol (Scheme 23) is oxidized to a mixture of benzaldehyde (26%) and benzoic acid (73%). All these oxidative



Scheme 19. A water-assisted mechanism of proton transfer.

transformations also undergo in toluene but result in inferior product yields (Scheme 23). However, the oxidation of benzyl alcohol in toluene is very selective, giving benzaldehyde (87%) as the sole product without any over-oxidation to benzoic acid [44]. For all the substrates tested, the activity of **4** was superior to that of other vanadium catalysts $[V_2O_5, VO(acac)_2, (VO)_2P_2O_7]$ [44].

2.5. Oxidation with molecular oxygen

Although molecular oxygen and air are the oxidants of choice for the oxidative transformations of organic substrates due to their availability and low price, under mild conditions they are usually less reactive than peroxides. In addition, the reactions with O_2 or air typically require more elevated temperatures and show inferior selectivities. Nevertheless, the Hpca-assisted oxidation by peroxides is significantly more efficient in the presence of O_2 as a co-oxidant [9–15].

Interestingly, the $[VO_3]^-/Hpca$ system also exhibits moderate activity in the aerobic oxidation reactions of alkanes and arenes [85] that undergo under mild conditions but require the presence of reducing agents such as ascorbic acid or zinc. The oxidation of cyclohexane by air, in acetonitrile at 30 °C, catalyzed by $[VO_3]^-$ in the presence of Hpca [85], pyridine, acetic acid, and zinc metal gave cyclohexanol, cyclohexanone and only negligible amounts (due to the presence of Zn as a reducing agent) of cyclohexyl hydroperoxide (total TON 78), as determined after the reduction with PPh₃ and subsequent GC analysis [10,11,65]. In this oxidation, the dependence of the concentration of oxygenates on the initial concentration of Hpca has a maximum (Fig. 4) [85]. In this system Hpca most likely acts as a mediator of proton and electron transfer.

A number of soluble and supported vanadium complexes have been reported to catalyze the oxidation of saturated hydrocarbons with molecular oxygen at relatively high temperatures [86a-e]. For example, the activity of the [VO(mal)₂] catalyst in cyclohexane oxidation is noticeably promoted by Hpca, while Hpic was almost inactive co-catalyst [86a]. The addition of Hpca similarly accelerates the alkane oxidation with O₂ catalyzed by supported complexes of palladium [86f] and copper [86g,h]. The rate of vanadate-catalyzed oxidation of 2-methylcyclohexanone with O_2 in the presence of *p*-toluenesulfonic acid to produce 6-oxoheptanoic acid is practically not enhanced when Hpca is added [87a]. Mono- and tetravanadium(IV) complexes derived from 3-hydroxypicolinic acid are active catalysts for the oxidation with O₂ of various primary and secondary benzyl alcohols to the corresponding carbonyl compounds [87b].



Scheme 20. The formation of radicals in the most favorable catalytic cycle. Color codes: formation of H₂O₂ adducts (red), H-transfers (blue), radical generation (green). Adapted from [17].



Fig. 3. Distribution of vanadium complexes formed from [VO(tea)] in moist 2propanol at different concentrations of added Hpca. Adapted from [17].



Scheme 21. Oxidation of cyclohexanol with TBHP catalyzed by complex 4.



Scheme 22. Oxidation of 1-phenylethanol with TBHP catalyzed by complex 4.



Fig. 4. Dependence of the total concentration of cyclohexanol and cyclohexanone (after 2 h at 30 °C) on the concentration of added Hpca in the oxidation of cyclohexane by air in MeCN, catalyzed by $[VO_3]^-$ in the presence of zinc powder, pyridine, and acetic acid. Adapted from [85].

3. Oxidation reactions catalyzed by iron compounds

As a naturally abundant metal with a recognized biological function and relevance in active sites of various oxidation enzymes, iron and its complexes have been widely used in different oxidation reactions [82a,88]. In the present section, we describe (i) the isolated Fe-pca derivatives and their catalytic applications, and (ii) the effect of added Hpca and analogs as co-catalysts on the oxidation of various substrates catalyzed by Fe-containing systems.

3.1. Isolated Fe-pca complexes as catalysts

Although the coordination behavior of Hpca toward iron centers has been investigated in a number of studies [89,90], there are only a few structurally characterized Fe–pca complexes reported up to date [42,90–93]. These are summarized in Table 5 and briefly described below.

Hence, a simple combination of aqueous solutions of FeCl₂ and Hpca (equimolar amounts) results in the formation of $[Fe(pca)_2(H_2O)_2]$ (27) [90]. A similar reaction but in the presence of KOH furnishes a 1D polymer [Fe(µ-pca)(pca)(H₂O)]_n (28a) [91], in which one of the pca ligands acts as a spacer. An analogous compound **28b** can be obtained by treatment of Fe(ClO₄)₃·10H₂O with Hpca and [NBu₄][OH] at rt in MeCN/H₂O solution [92]. If iron powder is mixed with a two-fold molar excess of Hpca in pyridine under an inert atmosphere, a derivative $[Fe(pca)_2(py)_2] \cdot py$ (29) is isolated [92]. In the same study, the reaction of $Fe(ClO_4)_3 \cdot 10H_2O$ with a three-fold molar excess of Hpca and NaOH, at rt and in MeCN/H₂O medium, led to the generation of a 1D Fe(III)/Na coordination polymer { Na_2 [Fe₂(μ_3 -O)(μ_3 -pca)₃(μ -pca)(pca)₂(μ - H_2O_2]_n·2nCH₃CN(**30**) that is a unique iron(III) compound derived from Hpca [92]. Yet another 3D heterometallic Fe(II)/Ag polymer $[Fe_2Ag_2(\mu_3-pca)_4(Hpca)(MeOH)_2]_n(ClO_4)_{2n} \cdot 3nMeOH(31)$ was synthesized by the reaction of Hpca with Fe(ClO₄)₂.6H₂O and AgNO₃ in MeOH [93]. In all these structurally characterized Fe-pca compounds, pca is rather versatile ligand acting in N,O- (27, 29), N,O- and N₂O- (**28**, **30**), or N₂O₂-coordination (**31**) modes.

The mononuclear Fe(II) complex **29** (Fig. 5a) and the 1D Fe(III)/Na polymer **30**, composed of repeating diiron $[Fe_2O(pca)_6]^{2-}$ cores (Fig. 5b) that are further arranged into $[Fe_2Na_2(\mu_3-O)(\mu_3-pca)_3(\mu-pca)(pca)_2(\mu-H_2O)_2]$ cluster nodes, are particularly interesting examples because they have been applied as biomimetic catalyst precursors for the oxidation of various hydrocarbons by H₂O₂ [94]. Thus, Reedijk and co-workers have studied the solution



Scheme 23. Oxidation of benzyl alcohol with TBHP catalyzed by complex 4.

Table 5

Structurally characterized iron complexes derived from Hpca.

Compound	Formula	Fe:pca	Fe coord. number and environment	X-ray structure	Ref.
27	$[Fe(pca)_2(H_2O)_2]$	1:2	$6 \{VO_4N_2\}$	+	[90]
28a	$[Fe(\mu-pca)(pca)(H_2O)]_n$	1:2	6 {VO ₃ N ₃ }	+	[91]
28b	$[Fe(\mu-pca)(pca)(H_2O)]_n \cdot nH_2O$	1:2	$6 \{VO_3N_3\}$	+	[92]
29	[Fe(pca) ₂ (py) ₂]·py	1:2	$6 \{VO_2N_4\}$	+	[92]
30	[Fe ₂ Na ₂ (μ ₃ -O)(μ ₃ -pca) ₃ (μ-pca)(pca) ₂ (μ-H ₂ O) ₂] _n ·2nCH ₃ CN	1:3	$6 \{VO_4N_2\}$	+	[92]
31	$[Fe_2Ag_2(\mu_3-pca)_4(Hpca)(MeOH)_2]_n(ClO_4)_{2n}\cdot 3nMeOH$	1:2	$6 \{VO_4N_2\}$	+	[93]



Scheme 24. Oxidation of adamantane by the $29/H_2O_2$ system.

and redox behavior of **29** and **30**, as well as their reactivity toward H_2O_2 . These compounds catalyze the oxidation of cyclohexane, cyclooctane, and adamantane (Scheme 24) to the corresponding cyclic alcohols and ketones, determined by GC after direct injection of the reaction sample to the chromatograph [94]. The maximum overall product yields based on H_2O_2 reach 31 ($c-C_6H_{12}$ with **29**), 23 ($c-C_8H_{16}$ with **30**), and 37% ($c-C_{10}H_{16}$ with **29**). In spite of modest TONs, these levels of activity are higher than those reported for related oxidative transformations in the presence of a Fe-pic derivative [95].

The compound **30** has also been applied for the oxidation of alkylbenzenes that undergo at the alkyl group [94]. The products have been determined by GC after direct injection of the reaction sample to the chromatograph. Thus, toluene is transformed to benzyl alcohol and benzaldehyde with the overall yield of 28% based on H_2O_2 , whereas ethylbenzene is converted to a mixture of 2-phenylethanol, 1-phenylethanol, and acetophenone with the overall yield of 46% (Scheme 25). Similarly, the oxidation of cumene (Scheme 26) leads to 2-phenyl-2-propanol and acetophenone (54% overall yield) [94]. One can assume the formation of the alkyl



Fig. 5. Fragments of the X-ray crystal structures of **29** (a) and **30** (b) showing the $[Fe(pca)_2(py)]$ and $[Fe_2O(pca)_5]^{2-}$ cores, respectively. H atoms and crystallization molecules (in **29** and **30**), as well as $[Na_2(\mu-H_2O)_2]^{2+}$ moieties (in **30**) are omitted for clarity. Color codes: Fe (purple balls), O (red), N (blue), C (cyan). Adapted from [92].



Scheme 25. Oxidation of ethylbenzene by the 30/H₂O₂ system.





Scheme 27. Cyclooctane ketonization by the Gif-system $FeCl_3/H_2O_2/O_2/py$ in the presence of Hpca or H_2 pdca.

hydroperoxides in all these cases. The hydroperoxides are decomposed in the chromatograph to produce the corresponding alcohols and ketones [10,11,65].

Although other Fe-pca derivatives (Table 5) have not been tested in oxidation catalysis, the recently reported metal–organic framework **31** can act as a heterogeneous catalyst for the cyanosylilation of aldehydes [93]. In addition, various simple Fe-pca complexes related to **27** and **28** can potentially be generated in situ from iron salts and 2-pyrazinecarboxylic acid in the course of Hpca-assisted oxidation reactions of different substrates, which are discussed in the following sub-section.

3.2. Hpca-assisted catalytic oxidation

As in the case of vanadium-catalyzed oxidation processes, the addition of Hpca or analogs to iron-based systems can significantly increase the rate and efficiency of oxidative transformations of various substrates. Barton et al. showed that Hpca and H₂pdca accelerate the cyclooctane ketonization to cyclooctanone in the Gif-system FeCl₃/H₂O₂/O₂/py, namely by partially suppressing the generation of O₂ from H₂O₂ (Scheme 27) [96]. Although the maximum yield of cyclooctanone reached 23% based on H₂O₂, the system is barely catalytic due to the use of high loadings of FeCl₃, Hpca, or H₂pdca.

Bianchi et al. [97] have applied Hpca or H_2 pdca as co-catalysts in the biphasic ($H_2O/MeCN/C_6H_6$) hydroxylation of benzene and toluene that proceed in the Fenton's type system composed of aq H_2O_2 , Fe_2SO_4 , and CF_3COOH (Scheme 28). Phenol can be obtained in 47–55% yields based on H_2O_2 with 78–81% selectivity relative to converted benzene. The catalytic system (aqueous phase) can potentially be reused in several consecutive cycles [97a].

The role of heteroaromatic carboxylic acids, especially picolinic acid (Hpic), in the Gif systems was described in a number of state-of-the-art reviews by Barton et al. [98] and others [99], and therefore this topic is not discussed in the present work. A few more recent studies on the oxidative functionalization of different substrates by the Gif and related iron(III) picolinate systems in the presence of different oxidants have been reported [100-104]. These include oxidation of cyclohexane [100], cyclooctane [101], cyclododecane [100b], and 1,3-dimethyladamantane [102], hydroxylation of octahydronaphthalene derivatives [103], and stereoselective allylic hydroxylation of cholesteryl acetate [104]. An interesting approach consisted in the synergic oxidation of cycloalkanes and hydrogen sulfide by O₂ at rt under the Gif conditions (FeCl₃/Hpic system) [100b]. Moreover, the Fe(III) picolinate and dipicolinate complexes supported on kaolinite were applied in combination with H_2O_2 for the heterogeneous oxidation of cyclohexane, epoxidation of cis-cyclooctene, and the Baeyer-Villiger oxidation of



Scheme 28. Hydroxylation of benzene by the Fe₂SO₄/Hpca/CF₃COOH/H₂O₂ system.



Scheme 29. Structural formula of complex 32.

cyclohexanone [100f]. Oxidation of alcohols with periodic acid catalyzed by the Fe(III)/Hpic system was also described [100g].

Beller and co-workers developed a catalytic system based on the combination of $FeCl_3 \cdot 6H_2O$ with dipicolinic acid (H₂dipic) and various amines, which showed good activity and selectivity toward epoxidation of different olefins by H₂O₂ [105a,b]. In addition, the in situ generated iron chloride complexes bearing 6-(N-phenylbenzimidazoyl)-2-pyridinecarboxylic acid and related Hpic derivatives were applied for the selective oxidation of various benzyl and allyl alcohols, by H₂O₂ at rt, to give the corresponding aldehydes and ketones [105c].

Apart from simple iron salts, a number of systems composed of various iron complexes and Hpca or analogs have been developed for the oxidation of hydrocarbons and alcohols by peroxides [19,21-25,106]. For example, a diiron(III) complex $[Fe_2(hptb))(\mu$ -OH)(NO₃)₂](NO₃)₂·CH₃OH·2H₂O (**32**) (Scheme 29) is not active as such but, upon addition of Hpca, H₂pdca, or Hpic as a co-catalyst, **32** can catalyze the oxidation of alkanes by H₂O₂, at rt and in MeCN medium, to give alkyl hydroperoxides as main primary products [106]. Although the efficiency is modest in case of using CH₄ and C₂H₆ as substrates (TON 21), better levels of activity have been achieved in the oxidation of cyclohexane (TON 140 and overall product yield of 12% based on substrate). Among all the tested cocatalysts, Hpca has been the most active. These oxidation reactions are believed to proceed with the participation of hydroxyl radicals [106].

In a series of recent studies [19,23–25], Pombeiro and coworkers showed that various iron complexes bearing N_2S_2 macrocycles [23] or intricate bis- and tris-pyridyl amino-thioether N_3S/N_4S ligands [19,24], in combination with Hpca and other cocatalysts, can catalyze the oxidation of benzene, cycloalkanes, and alcohols. The selected examples of these iron catalysts are given in Scheme 30 and include a Fe(III) complex $[Fe(gma)(PBu_3)]$ (33) [25] and Fe(II) compounds $[FeCl_2(L^1)]$ (34) and $[FeCl_2(L^2)]$ (35) [23].

Thus, the **33**/Hpca/H₂O₂ system is active for the hydroxylation of benzene to phenol (13% yield based on C_6H_6 , TON 70), as well as for the oxidation of cyclopentane and cyclohexane to the corresponding alcohols and ketones (up to 17% overall yield based on substrate measured after treatment with PPh₃, TON 80). The reactions proceed in MeCN medium at 25 °C. Higher TONs (up to 490) can be achieved on decreasing the catalyst concentration, although resulting in lower product yields [25]. The related systems based on the combination of Hpca with **34**, **35**, and similar iron(II) complexes [19,23,24] are also active for the mild oxidation of cyclohexane by H₂O₂, leading to the maximum overall yields of the oxygenates in the 17–21% range. However, other acid co-catalysts such as HNO₃, HCl, and TFA exhibit comparable or even superior activities than those of the Hpca-assisted systems [19,23,24].

In addition, the iron(II) complexes 34, 35, and some closely related derivatives in combination with Hpca have been used for the oxidation of 1-phenylethanol to acetophenone by TBHP [19,23,24]. This model reaction typically undergoes at 80°C in a solvent-free medium and is drastically accelerated by a low microwave (MW) irradiation power (10W), leading to 75-92% yields of acetophenone after 15-30 min (Scheme 31), in addition to high values of turnover numbers (TONs up to 1000) and turnover frequencies (TOFs up to $4500 h^{-1}$). The same reaction is much slower in the absence of MW-irradiation, leading to the maximum acetophenone yield of 65% after 6 h [23]. Picolinic acid can act as a guite efficient co-catalyst in such oxidative transformations [24]. Apart from 1-phenylethanol, a related Fe(II) complex $[FeCl_2(L^3)]$ (36) is also capable of catalyzing the oxidation of cyclohexanol, 2-hexanol, and 3-hexanol to the corresponding ketones (28-36% yields based on substrate), while 1-hexanol is transformed to hexanoic acid (17% yield) [19].

The behavior of iron-based catalysts in the oxidation of alkanes by H_2O_2 in the absence and in the presence of Hpca can be opposite for different iron compounds [21,107]. Thus, the addition of Hpca depresses cyclohexane (CyH) oxidation in MeCN catalyzed by Fe(ClO₄)₃ or FeCl₃ [21]. Similarly, addition of 2 equiv of Hpca results in the complete inhibition of alkane oxidation with H_2O_2 catalyzed by an amino-pyridine complex {[Fe(mebpa)Cl]₂O}}(ClO₄)₂ (**37**) [108]. In the absence of Hpca, the FeCl₃/bpy/H₂O₂ system efficiently oxidizes alkanes in MeCN to give predominantly alkyl





Scheme 31. Solvent-free oxidation of 1-phenylethanol by TBHP catalyzed by the 34/Hpca or 35/Hpca systems.



Scheme 32. Structural formula of complex 38.

hydroperoxides. The turnover numbers attained 400 after 1 h at $60 \degree C$ [109].

In contrast to the "simple" Fe(ClO₄)₃ and FeCl₃ salts, iron(III) diacetate hydroxide Fe(OAc)₂(OH) and the binuclear iron(III) complex containing 1,4,7-triazacyclononane [Fe₂(μ -O)(μ -OAc)₂(tacn)₂]I₂·0.5Nal 3H₂O (**38**) require the addition of Hpca, since no alkane oxidation occurs in the absence of this acid co-catalyst. The synthesis and structure of **38** (Scheme 32) were described by Wieghardt et al. [110]. The oxidation of methane, in D₂O at 60 °C with H₂O₂, catalyzed by a tetranuclear complex [Fe₄(L⁵)₄(μ -O)₂](PF₆)₄ bearing triazacyclononane derivative L⁵ leads to the total TON of 19, which increases to 41 upon addition of Hpca [22].

The examples of dependences of the initial rates W_0 of the cyclohexyl hydroperoxide formation and dioxygen evolution on the initial concentration of Hpca in the oxidation of cyclohexane by the **38**/Hpca/H₂O₂ system are given in Fig. 6. Based on the kinetic study, the following scheme was proposed [21] for the cyclohexane oxidation catalyzed by **38**/Hpca.

 $38 + Hpca \approx 38 \cdot Hpca$ (K₁)

38·Hpca + Hpca \Rightarrow **38**·(Hpca)₂ (K_2)

 $38 \cdot \text{Hpca} + \text{H}_2\text{O}_2 \rightleftharpoons 38 \cdot \text{Hpca} \cdot \text{H}_2\text{O}_2$ (*K*₃)

38·Hpca·H₂O₂ + H₂O₂ \rightleftharpoons **38**·Hpca·(H₂O₂)₂ (*K*₄)

 $38 \cdot \text{Hpca} \cdot (\text{H}_2\text{O}_2)_2 \rightarrow 38 \cdot \text{Hpca} + \text{H}_2\text{O} + \text{HOO}^{\bullet} + \text{HO}^{\bullet} \qquad (k_5)$

 $CyH \,+\, HO^{\bullet} \,\rightarrow\, Cy^{\bullet} \,+\, H_2O$

$$Cy^{\bullet} + O_2 \rightarrow CyOO^{\bullet} \rightarrow \cdots \rightarrow CyOOH$$

 $38 \cdot \text{Hpca} \cdot (\text{H}_2\text{O}_2)_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 38$

This kinetic scheme was used to obtain the equation for the stationary rate of CyOOH formation:

$$W_0 = -\frac{d[CyH]}{dt} = \frac{d[CyOOH]}{dt} = \frac{k_5 K_1 K_3 K_4 [H_2 O_2]_0^2 [Hpca]_0 [\mathbf{38}]_0}{1 + \Sigma}$$

where

 $\Sigma = K_1[\text{Hpca}]_0 + K_1K_2[\text{Hpca}]_0^2 + K_1K_3[\text{Hpca}]_0[\text{H}_2\text{O}_2]_0$ $+ K_1K_3K_4[\text{Hpca}]_0[\text{H}_2\text{O}_2]_0^2.$

The following constant parameters (the almost overlapping experimental and simulated curves are shown in Fig. 6) have been obtained: $k_5 = 0.13 \text{ s}^{-1}$, $K_1 = 16 \text{ M}^{-1}$, $K_2 = 6250 \text{ M}^{-1}$, $K_3 = 12.5 \text{ M}^{-1}$, $K_4 = 10 \text{ M}^{-1}$.

Moreover, in the presence of Hpca ferrocene catalyzes the oxygenation of alkanes by H_2O_2 to give predominantly alkyl



Fig. 6. Dependences of the initial rates W_0 of CyOOH formation (curve 1) and O_2 evolution (curve 2) on the initial concentration of added Hpca in the cyclohexane oxidation by the **38**/Hpca/H₂O₂ system. The simulated curve for W_{ROOH} *1a* is dashed. Conditions: [**38**]₀ = 2.5 × 10⁻⁴ M, [Cyclohexane]₀ = 0.46 M, [H₂O₂]₀ = 0.59 M, in acetonitrile in air, 25 °C. Adapted from [21,107].

hydroperoxides, while benzene can be transformed to phenol [111]. The oxidation reaction does not occur in the absence of Hpca, whereas Hpic is much less efficient co-catalyst. The reaction is first order with respect to H_2O_2 and second order relative to ferrocene (Fig. 7a) [111].

The dependence of the initial oxidation rate W_0 on the concentration of added Hpca has a maximum (Fig. 7b), thus suggesting the possible formation of adducts with Hpca. On the basis of the experimental data (Fig. 7), a simplified kinetic scheme of the process has been proposed [111]. In the first stage, ferrocene is oxidized to ferricenium cation, which in turn is transformed into a **Fe** species – a fragment containing one iron ion.

$$FeCp_2 + H_2O_2 \xrightarrow{H^+} Fe^+Cp_2$$
 (ferricenium cation)

 $Fe^+Cp_2 \to \textit{Fe}$

The *Fe* species produced in these two consecutive reactions interacts with a Hpca molecule to form a *Fe*(pca) complex:

$$Fe + Hpca \Rightarrow Fe(pca)$$
 (K₁)

The obtained complex can react with the second Hpca molecule giving a derivative containing two pca ligands per one Fe ion:

$$Fe(pca) + Hpca \Rightarrow Fe(pca)_2$$
 (K₂)

Two **Fe**(pca) moieties can dimerize to afford a dinuclear **Fe**₂(pca)₂ complex:

$$Fe(pca) + Fe(pca) \Rightarrow Fe_2(pca)_2$$
 (K₃)



Fig. 7. Dependences of the initial rate W_0 of oxygenate accumulation in the cyclohexane oxidation with H_2O_2 , catalyzed by ferrocene in MeCN, on the initial concentration of ferrocene (a, curve 1) or Hpca (b). Further details: (a): dependences at [Hpca]₀ = 3×10^{-3} M, curve 2 is the linearization of curve 1 in coordinates [FeCp₂]₀– $W_0^{1/2}$; (b): dependences at [FeCp₂]₀ = 5.0×10^{-4} M, dotted curve presents the simulated dependence; (a and b): general reaction conditions: [H₂O₂]₀ = 0.32 M, [cyclohexane]₀ = 0.37 M, 50 °C. Adapted from [111].

The $Fe_2(pca)_2$ complex is presumably a catalytically active species that produces hydroxyl radicals when interacting with H_2O_2 :

$$Fe_2(pca)_2 + H_2O_2 \rightarrow HO^{\bullet}$$
 $(k_4)_2$

Hydroxyl radicals react in parallel routes with solvent (acetonitrile) and substrate (cyclohexane, RH):

$$HO^{\bullet} + MeCN \rightarrow products$$
 (k_5)

 $HO^{\bullet} + RH \rightarrow ROOH$ (k₆)

The last reaction is the rate limiting step in the cyclohexane transformation into cyclohexyl hydroperoxide. The following equation has been proposed for the initial reaction rate:

$$W_{0} = \frac{\alpha [\text{Hpca}]_{0}^{2}}{\left(1 + \beta [\text{Hpca}]_{0}^{2}\right)^{2}}$$

here $\alpha = \frac{k_{4}[\text{H}_{2}\text{O}_{2}]_{0}(K_{1}[\text{FeCp}_{2}]_{0})^{2}}{1 + k_{5}[\text{MeCN}]/k_{6}[\text{RH}]_{0}}$ and $\beta = K_{1}K_{2}$.



Scheme 33. Structural formula of complex 39.

For the performed experiments [111], the values $\alpha = 30 \text{ M}^{-1} \text{ s}^{-1}$ and $\beta = 1.1 \times 10^5 \text{ M}^{-2}$ were obtained. Using these parameters, the initial reaction rates (dotted curve, Fig. 7b) were calculated at different concentrations of Hpca. The simulated curve coincides closely with the experimental curve.

4. Oxidation reactions catalyzed by manganese compounds

The catalytic application of manganese complexes in combination with Hpca and analogs has been investigated in a few recent studies [26-28]. In 1998, Shul'pin and Lindsay Smith [112,113] discovered that a dinuclear trioxomanganese(IV) complex $[(L^4)Mn(\mu-O)_3Mn(L^4)](PF_6)_2$ (**39**, Scheme 33) { $L^4 = 1,4,7$ trimethyl-1,4,7-triazacyclononane} very efficiently catalyzes the oxidation of alkanes if a carboxylic acid is present in low concentration as a co-catalyst. In addition, this system is capable of oxidizing not only alkanes but also alcohols, olefins, sulfides, and dyes [114]. A study of the effect of various acids [26] (Table 6) has revealed that 2,3-pyrazinedicarboxylic acid (Table 6, entry 7) is a unique co-catalyst, while the following carboxylic acids with similar composition and structure are less efficient in the oxidation of cyclohexane by H₂O₂: 2pyrazinecarboxylic (entry 8), 3,5-pyrazoldicarboxylic (entry 9), and anthranilic (entry 10) acids. Some other acids are much less active co-catalysts, namely phthalic (entry 11), pyridine-2,6dicarboxylic (entry 12), and picolinic (entry 13) acids. Thus, only a heteroaromatic carboxylic acid with a specific structure can interact with the catalyst reaction center enhancing its activity. The system consisted of complex **39** and 2,3-pyrazinedicarboxylic acid demonstrated good efficiency in the oxidation, by aqueous 70% H₂O₂ at 25 °C, of cyclohexane to cyclohexyl hydroperoxide, cyclohexanol, and cyclohexanone (total yield of 20% based on c-C₆H₁₂, TON 1000) [27]. Trifluoroacetic acid can also increase the rate of cyclohexane oxidation by the **39**/H₂pdca/H₂O₂ reagent [26].

The mild oxidation of stereoisomeric 1,2-dimethylcyclohexanes and toluene by TBHP catalyzed by a manganese(III) Schiff-base complex [Mn(salen)Cl] (**40**), used as such in a soluble form or immobilized on a polydimethylsiloxane-based membrane, has been studied by Pombeiro and co-workers [28]. These reactions proceed with the participation of free radicals and are markedly promoted by Hpca that also alters the stereoselectivity parameters. The remarkably high TONs (up to 1500) have been achieved in the selective oxidation of toluene to benzaldehyde (87% selectivity) and benzyl alcohol by the **40**/Hpca/TBHP system. Apart from Hpca, other co-catalysts (i.e., nitric, benzoic, and oxalic acid) can exhibit comparable levels of activity, although with different stereoselectivities [28].

The combination of $Mn(ClO_4)_2$ with picolinic acid as a cocatalyst and H_2O_2 as an oxidant furnishes a highly efficient, selective, and readily accessible catalytic system for the *cis*dihydroxylation of different electron-deficient alkenes such as diethyl fumarate, N-alkyl and N-aryl-maleimides [115,116]. Thus, diethyl fumarate can be selectively transformed to the corresponding *cis*-diol as the sole product (Scheme 34), isolated

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Table 6

Effect of carboxylic acid co-catalyst on the initial (W_0) and maximum (W_{max}) rates of the cyclohexane oxidation with H_2O_2 catalyzed by complex **39**.

Entry	Co-catalyst	Reaction rate $W \times 10^6$, M s ⁻¹	
		W ₀	W _{max}
1 2 3 4	CH ₃ CO ₂ H (CO ₂ H) ₂ CH ₂ (CO ₂ H) ₂ (CH ₂) ₃ (CO ₂ H) ₂ (CH ₂) ₃ (CO ₂ H) ₂	0.7 1.4 1.5 1.4	0.7 1.4 1.5 1.4
5	CF ₃ CO ₂ H CCI ₂ CO ₂ H	2.0	16.0 8.3
7	$\sim 10^{-100}$ $\sim 10^{-10}$ $\sim $	8.3	8.3
8	N CO ₂ H	2.6	2.6
9	N HN CO ₂ H	1.0	2.1
10	CO ₂ H NH ₂	0.5	1.2
11	CO ₂ H CO ₂ H	0.5	0.5
12	CO_2H	0.6	0.6
13	CO ₂ H	0.3	0.3

Adapted from [26].

in up to 95% yield (TON up to 1000). Similarly, electron-rich alkenes (*cis*-cyclooctene, cyclohexene, 1-methylcyclohexene, 1- octene, styrene, *trans*- β -methylstyrene, and 2-methyl-2-pentene) can undergo simultaneous epoxidation and *cis*-dihydroxylation (up to 100% conversions) by the same catalytic system (Scheme 35) [115a]. An improved protocol for the multigram scale selective epoxidation of electron-rich alkenes (34 substrates) by the Mn(II)/Hpic/H₂O₂ system has recently been reported [115b], allowing to achieve remarkably high values of TONs (up to 3 × 10⁵) and TOFs (up to 40 s⁻¹).

The effect of molecular structure of the co-catalyst in the *cis*dihydroxylation of diethyl fumarate has been studied, revealing that apart from picolinic acid full conversions can also be achieved with 2,5-pyridinedicarboxylic and 2-pyridineacetic acids, whereas 3-pyridinecarboxylic, 2,6-pyridinedicarboxylic, and quinoline-8carboxylic acids are inactive [115a]. Interestingly, Hpic is a degradation product formed in situ from various pyridyl ligands used as co-catalysts in the oxidative transformations of alkenes by the $Mn(ClO_4)_2/pyridyl$ ligand/NaOAc/H₂O₂ system [116]. Finally, manganese complexes with pyridine-2,6-dicarboxylic acid







Scheme 35. Epoxidation and *cis*-dihydroxylation of *cis*-cyclooctene by the Mn(ClO₄)₂/Hpic/NaOAc/H₂O₂ system.

$$C_{2}H_{6} \xrightarrow[TFA, 80 \circ C, 20 h]{3 equiv K_{2}S_{2}O_{8}} CH_{3}CH_{2}COOH + CH_{3}COOH$$

Scheme 36. Carboxylation of ethane by the 42/CO/K₂S₂O₈/TFA system.

[117] catalyze the disproportionation of H_2O_2 , whereas a dinuclear Mn(II) complex $[Mn_2(dipic)_2(H_2O)_6] \cdot (H_2dipic)_2$ (**41**) acts as an oxygen evolving complex with Oxone as a primary oxidant [118].

5. Oxidation reactions catalyzed by rhenium complexes

2-Pyrazinecarboxylic acid in combination with methyltrioxorhenium (MTO) and anhydrous H_2O_2 form a versatile system for the oxidation of alkanes (cyclohexane, cyclooctane, and *n*-heptane) and arenes (benzene, toluene, and ethylbenzene) [29a]. The system operates at 80 °C in MeCN under air (the optimal MTO:Hpca ratio is 1:4), resulting in the overall product yields up to 15% (based on H_2O_2) and TONs up to 290 in the oxidation of cyclooctane [29a]. In the absence of Hpca, the rates of oxidation of cycloalkanes are approximately three times lower in comparison with the reaction catalyzed by the MTO/Hpca system. Phenol [29b] and hydrocarbons containing tertiary C–H bonds have been oxidized in the absence of Hpca [29c–f]. However, in the oxidation of purine and uracil derivatives to the corresponding 1-oxides and 5,6-epoxides by the MeReO₃/H₂O₂ and MeReO₃/H₂O₂-urea catalytic systems the best yields were obtained in the presence of Hpca [29g].

An oxorhenium(V) complex [ReOCl₂(pic)(PPh₃)] (**42**) derived from Hpic has been applied for the single-pot carboxylation of ethane by the CO/K₂S₂O₈/TFA system to give a mixture of propionic and acetic acids in up to 29% overall yield based on C₂H₆ (Scheme 36) [30]. Interestingly, the activity of **42** cannot be improved further by addition of "free" picolinic acid. In addition, a closely related compound derived from dipicolinic acid showed almost no activity in the present type of transformations [30].

6. Oxidation reactions catalyzed by copper complexes

Diverse copper complexes in combination with various acid additives [119] are frequently used as biomimetic models of certain Cu-based enzymes [120] in oxidative transformations of organic substrates. However, there are only a few copper containing catalytic systems that employ 2-pyrazinecarboxylic acid either as a ligand [31,32] or a co-catalyst [19,23,24]. Nevertheless, pca is a versatile ligand toward copper centers, as attested by a large number of structurally characterized Cu-pca complexes and coordination polymers [42].

Satokawa and co-workers prepared a mononuclear complex [Cu(pca)₂] (43) and some derived materials obtained upon its encapsulation into zeolite-Y or immobilization on alumina and organically modified silica supports [31]. The parent complex and supported materials therefrom catalyze the oxidation of cyclohexene, by H_2O_2 in acetone at 75 °C, to give cyclohexene oxide, 2-cyclohexen-1-ol, 2-cyclohexen-1-one, and 1,2-cyclohexanediol. Although good cyclohexene conversions (up to 85%) have been reported, the workup and product analysis procedures are not clear. In addition, the analogous Co(II)-pca derivatives have been synthesized and shown similar features in cyclohexene oxidation [31]. Another study concerns two new 3D copper(I/II) coordination polymers $[Cu_6(\mu_3 - pca)_5(H_2O)_2(XW_{12}O_{40})] \cdot H_2O$ based on μ_3 -pca and polyoxotungstates, where X=Si (44a) or Ge (44b). These compounds were applied as heterogeneous catalysts in the photocatalytic decomposition of aq MeOH to produce H₂ and HCOH [32]. Furthermore, a water-soluble 2D Cu(II)/Na coordination polymer $[Cu(\mu_4-dipic)_2 {Na_2(\mu-H_2O)_4}]_n \cdot 2nH_2O$ (45) derived from dipicolinic acid can act as a promising bioinspired catalyst precursor for the mild oxidation of cyclopentane and cyclohexane by H₂O₂, without requiring the presence of any acid promoter [33].

With regard to oxidation in the presence of 2pyrazinecarboxylic acid, a series of copper(II) complexes bearing N₂S₂ macrocycles [23] or amino-thioether N₃S/N₄S ligands [19,24] were tested as catalysts for the oxidation of cyclohexane by H_2O_2 and of 1-phenylethanol by TBHP. Interestingly and in sharp contrast to closely related Fe(II) compounds (e.g., complexes 34-36), the addition of Hpca or Hpic to such Cu(II) catalysts has a strong inhibiting effect in oxidation of $c-C_6H_{12}$ and 1-phenylethanol [19,23,24]. In fact, a Cu-pca product isolated from the catalytic reaction mixture and tentatively formulated as [Cu(pca)₂] was almost inactive in the oxidation of 1-phenylethanol [24]. On the contrary, various N-bases (e.g., pyridazine, 3,5-dimethyl-1H-pyrazole, pyridine, and triethylamine) are highly efficient additives in such Cu-catalyzed oxidation of 1-phenylethanol by the TBHP/MW system, resulting in the acetophenone yields up to 99% (TOFs up to $5220 h^{-1}$) [24].

7. Miscellaneous systems

Apart from the V, Fe, Mn, Re, and Cu containing catalysts described above, a few other systems that involve Hpca or analogs have been reported [121–123,125–136]. In particular, Chatterjee

et al. applied [121a,b] some ruthenium(III) complexes containing picolinate ligands as catalysts in the oxidation of various saturated and unsaturated hydrocarbons by TBHP, H₂O₂, and other oxidants. A mechanism involving the formation of an intermediate highvalent Ru(V)-oxo species has been proposed [121a,b]. In addition, Beller and co-workers developed a Ru(II) catalytic system based on the [Ru(dipic)(terpy)] complex for the selective oxidation of naphthalenes and phenols by hydrogen peroxide to give the corresponding quinones in high yields [121c]. The same catalytic system is also highly efficient (TON > 10,000, TOF up to $14,800 \text{ h}^{-1}$) for the oxidation of aliphatic and benzyl alcohols to the corresponding carbonyl products, without the use of co-catalysts or organic solvents [121d]. Moreover, a number of Ru complexes derived from dipicolinic acid were applied in (i) the epoxidation of olefins by H_2O_2 [121e] or TBHP [121f], (ii) the oxidation of alcohols by NaIO₄ [121g] or the air/N-methylmorpholine-N-oxide system [121h], and (iii) the Ce(IV)-driven water oxidation [121i,j].

Barrett and co-workers have described [122] a rare application of non-transition metallic bismuth(0) in the oxidation catalysis, namely toward oxidation of alkyl and cycloalkyl arenes, with TBHP and in the presence of Hpic as an additive, to give the corresponding benzyl ketones (48–99% yields). Alternatively, oxidation of methylated arenes results in the corresponding substituted benzoic acids (50–95% yields). The optimized procedure involved the use of bismuth(0)(20 mol%), picolinic acid (20 mol%), and TBHP (6 equiv, 70% aq), in pyridine and acetic acid (9:1) at 100 °C [122]. In this system, Hpic either acts as a ligand facilitating the solubilization of the bismuth(III) species, or it could be oxidized to the corresponding N-oxide, allowing its direct involvement in the oxygen transfer. Preliminary mechanistic studies suggested a radical mechanism [122].

The influence of Hpca has also been studied in the oxidation of cycloheptane [123] by the OsCl₃/H₂O₂ system. Interestingly, in this case the addition of Hpca has a negative effect, reducing the total yield of cycloheptanol and cycloheptanone from 15 to 7%. In contrast, pyridine shows a clear promoting effect, leading to the total yield of 28%. Pyridine also dramatically accelerates alkane oxidation catalyzed by other osmium complexes [65a,124a]. Although in the presence of Hpca the heterometallic complex [Co₄Fe₂O(sae)₈]·4DMF·H₂O (H₂sae is salicylidene-2ethanolamine) is not active as a catalyst in oxidation of alkanes with H_2O_2 at rt, nitric acid is a good co-catalyst in this reaction [124b]. The selective oxidation of thymol to thymoquinone by the system composed of H_2O_2 and the dichromium(III) catalyst, $[Cr_2(\mu -$ OH)(dipic)₂(H₂O)₂], has also been reported [124c]. Yet another system concerns the application of a Pd-dipicolinate complex as cocatalyst in the homogeneous oxidation of n-butenes to 2-butanone by O2 in the presence of the Mo/V-phosphoric heteropolyacid catalyst [124d].

An interesting feature of Hpca, Hpic, and some other heteroaromatic carboxylic acids consists in the fact that they can act as organocatalysts in some oxidative transformations. For example, Hpca and its derivatives are active photocatalysts in metal-free oxygenation of alkanes [125]. Thus, irradiation of cyclohexane in acetonitrile with visible light in the presence of methylpyrazinecarboxylate gave cyclohexyl hydroperoxide, cyclohexanol, and cyclohexanone (1.5:1:1 molar ratio) with the total TON of \sim 100. In addition, Hpca catalyzes the oxidation of primary and secondary alcohols by a mixture of sodium dichromate and perchloric acid [126]. Moreover, Hpic catalyzes the oxidation by chromic acid of organic compounds, including maleic [127], citric [128], malic and lactic acids [129], indole [130], trans-stilbene [131], D-galactose [132], glycerol [133] and primary alcohols [134], among a diversity of other substrates. A derivative of dipicolinic acid, 2,6-dicarboxypyridinium fluorochromate, was applied as a new oxidant for the efficient solvent-free oxidation of diverse substrates including various alcohols, phenols, and hydroquinones [135]. Various pyrazinium salts were recently reported as highly active organocatalysts for the mild oxidation by H₂O₂ of different sulfides to sulfoxides, and the Baeyer–Villiger oxidation of cyclobutanones to lactones [136].

8. Conclusions and outlook

In the present work, we have reviewed the use of 2-pyrazinecarboxylic acid (Hpca) and analogs (H₂pdca, Hpic, and H₂dipic) as highly efficient and versatile co-catalysts in metal-complex-catalyzed oxidation of various organic substrates. The most active V, Fe, Mn, Re, Ru, and Cu based catalytic systems have been identified, wherein Hpca or analogs are added either as co-catalysts or already present as ligands within the metal complexes. Their catalytic performance with respect to different substrates (alkanes, arenes, olefins, and alcohols) and oxidizing agents (H₂O₂, O_2 , *t*-BuOOH) has been analyzed, and the main selectivity, kinetic, and mechanistic features of these oxidative transformations have been highlighted.

In particular, we have considered examples of various catalytic oxidation processes when the reaction either proceeds noticeably less efficiently or does not occur at all if certain co-catalysts are not present in the reaction mixture. Although 2-pyrazinecarboxylic acid is one of the most powerful promoters that dramatically enhances the efficiency of vanadium and iron containing catalysts, some catalytic systems wherein Hpca does not affect the reaction rate or even plays the role of an inhibitor have also been reported [19,23,24,87a,123].

In spite of a number of studies, the mechanisms of the accelerating role of Hpca in oxygenation reactions are still not completely clear. However, pca as a chelating ligand can stabilize a catalyst precursor and transient species, it can also facilitate proton transfer (see Schemes 17 and 18), as well as can play the role of a stabilizer of key transition states due to the formation of 6-membered cyclic structures (see Schemes 19 and 20). In addition, the heteroaromatic carboxylic acids including Hpca can mimic the protein environment around an enzyme reaction center. It is important to emphasize that in many cases only specific molecules can act as efficient co-catalysts, whereas other compounds with very similar structures and properties turn out to be much less reactive or completely inactive in the catalytic transformations. We clearly see this comparing the promoting effects of Hpca with those of other similar heteroaromatic carboxylic acids.

We expect that the research on the application of Hpca, H₂pdca, Hpic, H₂dipic, and analogs as convenient and highly efficient cocatalysts in oxidative transformations of various organic substrates continues to grow rapidly in the near future. Thus, further developments should focus on (1) the synthesis and catalytic application of new vanadium and other transition metal complexes derived from Hpca and related acids, (2) design of simple catalytic systems generated in situ from cheap metal sources and acid co-catalysts, (3) widening the spectrum of Hpca-assisted oxidation reactions and improving their substrate versatility and selectivity, (4) transition from homogeneous to heterogeneous catalytic systems through heterogenization of the most active pyrazinecarboxylate metal complexes or heteroaromatic carboxylic acid co-catalysts on various supports, and (5) optimization of the most efficient catalytic protocols and deeper investigation of their reaction kinetics and mechanisms. We also believe future research will have implications in the development of new and the understanding of known oxidative processes that occur in biological and natural systems, especially given the recognized biological functions of 2-pyrazinecarboxylic, picolinic, and dipicolinic acids.

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