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Highly efficient divanadium(V) pre-catalyst for mild oxidation of liquid and gaseous alkanes

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Highlights

New binuclear V(V) complex bearing an NO₂-donor Schiff base ligand is synthesized

This compound is highly active catalyst precursor in the oxidation of alkanes by H₂O₂

2-Pyrazinecarboxylic acid acts as an efficient co-catalyst

High yields (up to 45% based on alkanes) and TONs (up to 7800) are achieved

Oxidation proceeds via radical mechanism with participation of hydroxyl radicals

Abstract

A new binuclear oxovanadium(V) complex bearing an NO_2 -donor Schiff base ligand, [{VO(EtO)(EtOH)}₂(1 $\kappa^2 O, \kappa N: 2\kappa^2 O, \kappa N-L$)]·2H₂O (H₄L = bis(2-hydroxybenzylidene)oxalohydrazonic acid) was prepared and fully characterized by IR, ¹H NMR and electronic spectroscopies, elemental analysis and single crystal X-ray diffraction. In the presence of 2-pyrazinecarboxylic acid (PCA) or another acid promoter, this compound acts as a highly efficient pre-catalyst towards the oxidation of gaseous and liquid alkanes by aqueous H₂O₂ under mild conditions, in aqueous MeCN. Total yields of oxygenates up to 45% and overall turnover numbers up to 7.8 × 10³ are achieved.

Keywords: C-H activation, Schiff bases, Hydrogen peroxide, Hydroxyl radical, 2-Pyrazinecarboxylic acid

1. Introduction

The interest on vanadium chemistry has grown in recent years due to the relevance of this metal in biology [1–5] and catalysis [6–14]. Being involved in many different biological and synthetic processes, vanadium may exist in a variety of oxidation states, what explains the wide application of its compounds as efficient catalysts in different organic reactions [6–38]. For example, vanadium containing compounds are well known to efficiently catalyze oxidative (by H₂O₂ and O₂) transformations of alkanes to alkyl hydroperoxides, alcohols and ketones [11–30], and carboxylations (by the CO/S₂O₈^{2–}/TFA system) of hydrocarbons, including the highly inert methane, to carboxylic acids [30–37]. Such transformations are of industrial significance, since they contribute to the development of synthetic protocols based on alkanes as primary carbon sources [38–40].

Following our interest on alkane functionalization, we have recently reported a number of effective vanadium based catalytic systems towards the carboxylation [30-37] and oxidation [18–30] of alkanes. In the latter reaction, the activity of V catalysts can be dramatically enhanced by addition of a small amount of an acid promoter, such as nitric [18,19], sulfuric [20], oxalic [20] or 2-pyrazinecarboxylic acid (PCA) [21,22,29]. In particular, the use of PCA as an effective promoter for oxidations with H₂O₂-vanadium catalytic systems was discovered by Shul'pin et al. [41]. Further studies have shown that PCA in combination with VO₃⁻ anion provides one of the most efficient and versatile catalytic systems for the mild oxidation of both gaseous and liquid alkanes [12–14,17,21,42]. The promoting effect of PCA in alkane oxidations by H₂O₂ catalyzed by different vanadium derivatives, as well as by other metals (Fe, Mn, Cu and Re), is now well recognized [43]. The role of PCA in VO_3^-/H_2O_2 assisted alkane oxidations has been disclosed on the basis of DFT calculations [21], consisting in stabilizing the transition state of H-transfer in the "water-assisted" mechanism of free radical generation. Moreover, the acidity of the reaction solution leads to the formation of polyvanadates, which exhibit higher catalytic activity in comparison with monovanadium species [22].

In this context, we report here a new binuclear oxovanadium(V) complex bearing a NO_2 -donor Schiff base ligand, [{VO(EtO)(EtOH)}_2(1\kappa^2O,\kappa N:2\kappa^2O,\kappa N-

L)]·2H₂O (**1**), which is easily synthesized from $[VO(acac)_2]$ and bis(2-hydroxybenzylidene)oxalohydrazonic acid (H₄L). The obtained product **1** was fully characterized by standard methods and by single-crystal X-ray diffraction analysis. Compound **1** was found to efficiently catalyze, in the presence of PCA co-catalyst, the oxidation, by aqueous H₂O₂ under mild conditions, of different alkanes mainly to alkyl hydroperoxides, alcohols and ketones, apart from other minor oxidation products. The effects of catalyst concentration, type of acid promoter and its amount on the reaction rate of cyclohexane oxidation were studied in detail. In order to get some mechanistic information, the KIE (kinetic isotope effect) as well as various selectivity parameters were determined in the oxidations of linear, branched and cyclic alkanes. The catalytic activity of the newly synthesized complex was compared with that of a simple vanadate salt under identical experimental conditions.

2. Experimental

2.1. Materials and general methods

Diethyl oxalate, Hydrazine hydrate (80%, aqueous solution), salicylaldehyde and vanadyl acetylacetonate were all purchased from Aldrich and used as received. Solvents were also used without further purification. The compound H₄L, bis(salicylhydrazone) of oxalyl hydrazide, was prepared by modification of a previously reported method [44]. Infrared spectra (4000–400 cm⁻¹) were recorded on a Nicolet Impact 400D or a BIO-RAD FTS 3000 MX spectrophotometer instrument in KBr pellets; wavenumbers are in cm⁻¹; abbreviations: vs, very strong; s, strong; m, medium. UV-Vis spectra were recorded in 10⁻⁴ M EtOH solutions of the complexes with a Perkin Elmer instrument (Lambda 35). Electrospray mass spectra (ESI-MS) were run with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 p.s.i. nebulizer pressure. Scanning was performed from m/z 50 to 1000 in EtOH or CH₃CN (in the catalytic studies) solution. The compound was observed in both positive and negative modes (capillary voltage = 80–105 V). EPR spectra were recorded with a Bruker ESP 300E X-band spectrometer.

2.2. Synthesis of the H₄L pro-ligand

Synthesis of the oxalyl dihydrazide was carried out from diethyl oxalate and hydrazine hydrate according to a literature method [44]. A modification was made in the preparation of the Schiff base with salicylaldehyde. To an aqueous solution of 236 mg (2 mmol) of oxalyl dihydrazide, 488 mg salicylaldehyde (4 mmol) were added; the obtained suspension was stirred for about 4 h at room temperature. Within this time, a yellowish white precipitate of the Schiff base H₄L appeared. This was filtered off, washed with ethanol and ether and left for slow evaporation at r.t.

Molecular Formula: $C_{16}N_4O_4H_{12}$, Yield 554.2 mg (85%); mp 321–322 °C; ¹H NMR [300.13 MHz, (CD₃)₂SO], δ : 6.79–7.57 (m, 8H), 8.81 (s, 2H), 11.00 (s, 2H), 12.63 (s, 2H).

2.3. Synthesis of complex 1

 $40.75 \text{ mg} (0.125 \text{ mmol}) \text{ of } H_4L \text{ were added to a round bottom flask containing 20 mL of ethanol. Then, 66.25 mg (0.25 mmol) of [VO(acac)_2] were added and the system was left with vigorous stirring for 24 h at 50°C. Within this time a brown transparent solution was obtained, which was filtered off, and left for slow evaporation at r.t. Within a week brown block like crystals appeared which were filtered off, washed with ethanol and dried over fused calcium chloride to give$ **1**.

Complex 1: [{**VO**(**EtO**)(**EtOH**)]₂($1\kappa^2O,\kappaN:2\kappa^2O,\kappaN-L$)]·2H₂O: Yield 63.0 mg (75%). Brown solid soluble in EtOH, CHCl₃, CH₂Cl₂, etc. Anal. Calc. for C₂₄H₃₆ N₄O₁₂V₂ (F.W. = 674.45): C, 42.70; H, 5.33; N, 8.30. Found: C, 42.27; H, 5.06; N, 8.27. MS (ESI): *m/z*: 519.0 [{V₂O₂L(OEt)}₂+H₂O]²⁺ IR (KBr, selected bands, cm⁻¹): 3201 vs v(OH) (coordinated), 1548 s v(C=C), 1605 vs v(C=N), 754 w (Ar), 980 s v(V=O), ¹H NMR (300.13 MHz, CDCl₃), δ : 1.25(t, 12H, <u>CH₃CH₂OH</u> and <u>CH₃CH₂O⁻), 1.80 (broad, H₂O H-bonded and CH₃CH₂O<u>H</u>) 3.7(q, 4H, CH₃<u>CH₂OH</u>,), 5.65(q, 4H, CH₃<u>CH₂O⁻), 7.20–7.60 (m, 8H, Ar-H), 9.22(s, 2H, C(<u>H</u>)=N), UV-vis (EtOH, λ max, nm (ϵ , L M⁻¹ cm⁻¹): 419(18600), 316(41000).</u></u>

2.4. Crystallographic measurements

The X-ray quality single crystal of complex **1** was mounted in a Nylon loop and measured at a temperature of 293 K (Table 1). Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo-K α (λ

0.71073) radiation. Data were collected using omega scans of 0.5° per frame and full sphere of data were obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT [45] on all the observed reflections. Absorption corrections were applied using SADABS [45]. Structure was solved by direct methods by using the SHELXS–97 package [46] and refined with SHELXL–97 [47]. Calculations were performed using the WinGX System–Version 1.80.03 [48]. All hydrogen atoms were inserted in calculated positions. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms were employed.

CCDC-913164 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.5. Peroxidative oxidation of alkanes

The alkane oxidations were typically carried out in air in thermostated (50 °C) Pyrex cylindrical vessels or round bottom flasks with vigorous stirring and using MeCN as solvent (up to 5.0 mL total volume). Typically, the catalyst precursor **1** was introduced into the reaction mixture in the form of a stock solution in acetonitrile (2.5×10^{-4} M). Then PCA (optional) was added as a solid or in the form of a stock solution in MeCN (0.44 M). The alkane substrate, typically cyclohexane (0.25 mL, 2.3 mmol) was then introduced, and the reaction started when hydrogen peroxide (50% in H₂O, 0.68 mL, 11 mmol) was added in one portion. The final concentrations of the reactants in the reaction mixture were as follows: catalyst precursor **1** ($5 \times 10^{-6} - 5 \times 10^{-4}$ M), PCA (0–0.005 M), substrate (0.46 M) and H₂O₂ (2.2 M). The samples were analyzed by GC using nitromethane (0.05 mL) as an internal standard. Attribution of peaks was made by comparison with chromatograms of authentic samples. Chromatographic analyses were undertaken by using a Fisons Instruments GC 8000 series gas chromatograph (He as carrier gas) with a BP20/SGE (30 m × 0.22 mm × 0.25 µm) capillary column (FID detector) and the Jasco-Borwin v.1.50 software.

Since the oxygenation of alkanes often gives rise to the formation of the corresponding alkyl hydroperoxides as the main primary products, the quantification was performed by a method developed by Shul'pin [12–14]. For precise determination of oxygenate concentrations only data obtained after reductions of the reaction sample

with PPh₃ were usually used, taking into account that the original reaction mixture typically contained the three products: alkyl hydroperoxide (as the primary product), ketone and alcohol.

The oxidations of gaseous alkanes were carried out in a 13 mL stainless steel autoclave, equipped with a Teflon-coated magnetic stirring bar. In a typical experiment, after additions of all liquid (in the form of stock solutions in acetonitrile) and solid reagents, the autoclave was closed and pressurized with 0.7-20.0 atm of gaseous alkane (typically 20.0, 6.0, or 0.7 atm of CH₄ and C₂H₆, C₃H₈, or *n*-C₄H₁₀, respectively). The reaction mixture was stirred for 4 h at 50 °C using a magnetic stirrer and an oil bath, whereupon it was cooled in an ice bath, degassed, opened and transferred to a flask for GC analysis. In the oxidations of gaseous alkanes, traces of acetic acid were also detected due to partial oxidation of the MeCN solvent.

The kinetic isotope effect (KIE) was calculated as a ratio between the reaction rates W_0 of C₆H₁₂ and C₆D₁₂ oxidations under the following reaction conditions: $[C_6H_{12}]_0$ or $[C_6D_{12}]_0 = 0.46$ M, $[\mathbf{1}]_0 = 5 \times 10^{-5}$ M, $[PCA]_0 = 5 \times 10^{-3}$ M, $[H_2O_2]_0 = 1.1$ M in CH₃CN (up to 5 mL of the total reaction volume) at 50°C.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

The H₄L pro-ligand was prepared (Scheme 1) by a modification of a method described in the literature [44]. For this Schiff base condensation reaction we have used water as the reaction medium, therefore breaking the general procedure of using methanol or ethanol. Moreover, the preparation of complex **1** has been carried out using $[VO(acac)_2]$ as the metal precursor, water and ethanol as solvents, and mild reaction conditions (50 °C). The molecular structure of complex **1** has been established by X-ray diffraction analysis (see below) and in this section we report its spectroscopic characterization.

Scheme 1 here

The IR spectrum of the complex shows a single strong peak for the V=O stretching at 980 cm⁻¹ [49–53]. The presence of H-bonded water is evident by a broad peak at 3201 cm⁻¹. v(C=N) appears at 1605 cm⁻¹, a little higher in energy than that of the

free ligand [44], whereas the aromatic v(C=C) at 1548 cm⁻¹ is unperturbed in the complex as compared to the free ligand. The pro-ligand H₄L loses hydrogen from both NH and OH functionalities upon coordination to the VO³⁺ centre, in accord with the disappearance in the complex of the broad v(NH) band at 3405 cm⁻¹.

The ¹H NMR spectrum of **1** in CDCl₃ shows the characteristic resonances of the ligand: the proton of the azomethine nitrogen at δ 9.2 [54]; the aromatic protons as multiplets in the δ range of 7.2–7.6 [55]; the CH₂ protons of the coordinated ethoxide at δ 5.65 [56], while those of the coordinated ethanol occur at δ 3.7; the CH₃ protons of both the coordinated ethoxide and ethanol at δ 1.25 [57]. The H-bonded OH proton of the coordinated ethanol and the protons of the water molecule appear as a broad peak at δ 1.80.

The electronic spectrum of **1** in EtOH shows two bands at 419 and 316 nm assigned to $L(p_{\pi})-V(d_{\pi})$ LMCT charge transfer bands [58]. Other bands in the high energy region are due to intra-ligand charge transfer processes [58]. An ethanol solution of the complex **1** was found to be EPR silent, as expected on the basis of the +5 metal oxidation state. Mass spectral analysis by ESI-MS shows an ion peak at m/z 519.0 in the positive mode assigned to [{V₂O₂L(OEt)} + H₂O]⁺.

3.2. Description of the structure

The X-ray structural analysis of **1** confirmed that the complex is binuclear in the solid state (Figure 1) and contains a crystallographically imposed centre of inversion in the middle of the C8–C8^{*i*} bond. The complex crystallizes in the centrosymmetric triclinic space group *P*-1 with half a molecule in the asymmetric unit and one molecule of water. The tetranegative L^{4-} ligand binds the two oxovanadium(V) species through the two tridentate binegative O_2N donor sites; the other two coordination positions of the metal cation are occupied by one ethoxide ion and an ethanol molecule. The coordination sphere of the 6-coordinate vanadium is distorted octahedral with the vanadium atom 0.303 Å above the basal least-square plane defined by O1-N1-O2-O20, and shifted towards the apical position which is occupied by the O3-oxo atom. This deviation is comparable to the data concerning related vanadium complexes [55,56]. The vanadium cation belongs to two fused five and six-membered metallacycles, V1-O1-C1-C6-C7-N1 and V1-N1-N2-C8-O2. Accordingly, the O1-V1-N1 and the N1-V1-O2 angles are of 83.50(11) and 74.07(10)^o, respectively, and represent the major deviations

from the octahedral geometry around the metal. The bond distances in the coordination sphere of vanadium are comparable to those of related monoxo alkoxo V(V) complexes [59]. However, the V=O bond length of 1.579(3) Å is shorter than that previously reported for the dioxovanadium(V) complex with the same ligand [1.616(4) and 1.630(3) Å] [60], what also occurs with the other metal-L ligand bonds. The shortest V-O bonds in the coordination sphere of vanadium pertain to those involving the O20 ethoxide oxygen atoms, indicating a stronger binding of this group as compared to that of phenolate or ethanol oxygens.

The crystal packing diagram of **1** (Fig. 2) is organized forming parallel chains of the dimetallic moieties, with crystallization water molecules hosted between the parallel chains of the complexes and involved in strong intermolecular contacts (Fig. 1) leading to the assembly of the vanadium units into 1D chains (running along the crystallographic *a* axis). The shortest *intra-* and *interchain* metal---metal separations are of 6.820 and 8.316 Å, respectively, which correspond, in this order, to the unit cell parameters *a* and *b* (Table 1), whereas the intramolecular V···V separation is equivalent to 7.023 Å.

Figure 1 here Figure 2 here Table 1 here

3.3. Oxidation of liquid alkanes

In the present work, we have found that **1** in the presence of PCA efficiently catalyzes the oxidation of alkanes by aqueous H_2O_2 . In the absence of co-catalyst, the oxidation of cyclohexane to the mixture of cyclohexanol and cyclohexanone (Scheme 2) catalyzed by **1** (5×10^{-5} M) is slow (Fig. 3, curve *1*) affording, after 4 h of reaction, the overall 2.4% yield of oxygenates (TON 224) with an equal content of alcohol and ketone in the reaction mixture after its treatment by PPh₃. The presence of PCA (0.005 M) noticeably increases the oxidation rate, leading to 29% total yield and TON of 2.64 $\times 10^3$ after 4 h (Fig. 3, curve *3*).

Scheme 2 here Figure 3 here

In the cyclohexane oxidation catalyzed by $1 (5 \times 10^{-4} \text{ M})$ in the presence of PCA (0.005 M), the detailed analysis of kinetic curves (Fig. 4) of product accumulation shows that in the beginning of the reaction cyclohexanol is predominantly formed, although cyclohexanone is also present in the solution. After 30 min of the reaction, the concentration of alcohol falls slightly, but that of ketone continues to grow, while the total amount of oxygenate products remains constant. This observation, together with the fact that a difference in the alcohol/ketone molar ratio in the reaction solution was observed before and after its treatment by PPh₃ (in order to reduce ROOH to ROH), points out the presence of cyclohexyl hydroperoxide in the reaction mixture as a primary product of cyclohexane oxidation [12–14] which, however, decomposes to the corresponding alcohol and ketone. After 1 h of the reaction, the concentrations of alcohol and ketone become close and practically no difference in the product composition was observed by GC before and after the treatment with PPh₃ (i.e., cyclohexyl hydroperoxides are not present any more in the solution).

Figure 4 here

The addition of another strong acid co-catalyst such as trifluoroacetic acid (TFA, 0.005 M) also improves the catalytic performance of **1** (Fig. 3), but the oxidation of cyclohexane proceeds slower and less efficiently than that in the presence of PCA, leading to 12% total yield (alcohol/ketone molar ratio = 2) and TON of 1.12×10^3 .

The increase of the PCA amount results in the growth of the catalytic activity of **1** (Fig. 5). In the absence of PCA, the reaction rate of the cyclohexane oxidation with **1** is rather low. The maximum reaction rate W_{max} increases up to the PCA concentration of 25×10^{-4} M (Fig. 3 B), thus testifying the direct involvement of PCA in the formation of catalytically active vanadium containing species. The W_{max} does not depend on the content of PCA upon further addition beyond 25×10^{-4} M, indicating that at these conditions the rate of the formation of the intermediate active PCA containing species is constant.

Figure 5 here

The rate of cyclohexane oxidation is directly proportional to the concentration of complex **1** in the 5×10^{-6} M – 5×10^{-4} M range, in the presence of a constant amount of PCA (0.005 M) (Fig. 6). Moreover, monomeric species conceivably are involved in the

reaction mechanism, as suggested by ESI-MS analysis of the acetonitrile solution containing complex $1 (3 \times 10^{-6} \text{ M})$, PCA $(2.7 \times 10^{-5} \text{ M})$ and H₂O₂ (1 mL). The negative scan showed a single peak in the mass range of 50–500 at m/z 345.1. This corresponds to a monoperoxo vanadium species with two coordinated pca ligands [VO(O-O)(pca)₂]⁻ (pca = monodeprotonated form(1–) of PCA). Such a complex was earlier synthesized [61] and fully described [17], and its formation was also observed in other PCA-assisted V-based catalytic systems [21].

At the concentration of complex **1** of 5×10^{-4} M, the reaction is fast (Fig. 6) and the maximum yield of ca. 28% with the corresponding TON of 254 was achieved already after 45 min (Table 2). Further decrease of the catalyst amount to 5×10^{-5} M results in some deceleration of the oxidation, but leading to the identical 29% yield after 4 h, with a TON of 2.64×10^{3} . The reaction rate is reduced at a lower concentration of **1** $(5 \times 10^{-6}$ M) leading to 8.5% of oxygenates after 8 h of the reaction, although with a remarkably high turnover number of 7.83×10^{3} (Table 2).

Although the role of the *NO*₂-donor Schiff base ligand could not be fully established, we propose that it can stabilize a peroxo vanadium species formed during the catalytic cycle (as suggested by theoretical studies performed on other vanadium catalysts [21]). Besides, the bi or multinuclearity can be a favourable feature for oxovanadium catalysts, as recently demonstrated by us [22,29]. In accord, oxidation of cyclohexane catalyzed by **1**/PCA proceeds faster (maximum initial reaction rate W_0 = 4.5×10^{-6} M/s) and more efficiently than that in the presence of (Bu₄N)VO₃/PCA (W_0 = 3.3×10^{-6} M/s) under identical reaction conditions, that were found to be optimal for vanadates: ([catalyst]₀ = 10^{-5} M), [PCA]₀ = 6×10^{-4} M, [C₆H₁₂]₀ = [H₂O₂]₀ = 0.40 M, 50 °C), leading to the higher TOF of 1612 h⁻¹ vs. 805 h⁻¹ for the vanadate/PCA system.

Figure 6 here

Table 2 here

In order to get some information about the nature of the mechanism, we have performed the oxidation of other alkanes apart from cyclohexane (Table 3) and measured various selectivity parameters. Hence, in the oxidation of linear *n*-heptane and branched methylcyclohexane (MCH) by the $1/PCA/H_2O_2$ system, the regio-[C(1):C(2):C(3):C(4) = 1:6:6:6] and bond selectivity $[1^\circ:2^\circ:3^\circ = 1:8:19]$ parameters are rather low, being close to those (Table 3) previously determined for systems that are

known to oxidize alkanes with participation of hydroxyl radicals, e.g., the well studied $VO_3^{-}/PCA/H_2O_2$ system. In addition, a low normalized 3°/2° C–H selectivity (3) was observed in the oxidation of adamantane, being again consistent with the presence of nonselective oxidizing species [62]. However, the oxidations of *cis*- and *trans*-dimethylcyclohexanes (*cis*- and *trans*-DMCH) proceed with some stereoselectivity, resulting in the *trans/cis* ratio of isomeric alcohols of 0.38 and 0.34, respectively.

The competitive oxidation of cyclohexane / cyclohexane- d_{12} catalyzed by 1/PCA in the presence of H_2O_2 reveals a low kinetic isotope effect (KIE = 1.3), which is indicative of a powerful and rather indiscriminate oxidizing species, such as the hydroxyl radical [62].

Table 3 here

Summarizing the abovementioned kinetic and selectivity data, we can conclude that the PCA co-catalyst reacts with vanadium complex **1** to form catalytically active species that participate in the generation of HO[•] radicals from H_2O_2 , possibly via the formation of a V-peroxo complex containing PCA. The HO[•] abstracts hydrogen from alkane with formation of R[•], which then reacts with O_2 (e.g. from air) affording ROO[•] and leading to the formation of ROOH. However, alkyl hydroperoxide ROOH rapidly decomposes (conceivably by V-catalyzed processes) [12–14,19–22] to the corresponding alcohol and ketone.

3.4. Oxidation of gaseous alkanes

We have also found that complex **1** in the presence of PCA efficiently catalyses the oxidation of gaseous alkanes by aqueous H_2O_2 at 50 °C into the corresponding carbonyl compounds (Table 4). Hence, the oxidation of ethane leads after 4 h to the formation of acetaldehyde (main product after PPh₃) and ethanol, in addition to a smaller amount of acetic acid presumably generated via the oxidation of the formed acetaldehyde. The total yield of the products based on ethane reaches 8.1%, corresponding to the total TON of 1.98×10^3 . In contrast to ethane, propane is more reactive due to the presence of the secondary carbon atom, leading to the 35.7% total yield of oxygenates (TON 2.67×10^3). Among them, acetone and isopropanol are the main products although some minor amounts of propanal, propanol and propionic acid have also been detected. The oxidation of *n*-butane by the **1**/PCA/H₂O₂ system results in

the formation of butanone-2 and butanol-2 as major products, whereas butanal, 1butanol and butyric acid are formed in minor amounts. In the n-C₄H₁₀ oxidation, a high total yield of oxygenates (45.3% based on *n*-butane) has been obtained, with the corresponding TON of 562. In contrast, methane oxidation undergoes to a much lower extent (TON 63, 0.3% yield of MeOH, Table 4).

Table 4 here

4. Conclusion

The present study reported the synthesis, full characterization and X-ray crystal structure of the new divanadium(V) Schiff-base complex **1**. It was found that this compound, in the presence of 2-pyrazinecarboxylic acid co-catalyst, efficiently catalyzes the oxidation of liquid and gaseous alkanes by aqueous H_2O_2 into the corresponding alkyl hydroperoxides, alcohols and ketones. Thus, the oxidation of cyclohexane to the mixture of cyclohexanol and cyclohexanone proceeds with a high yield of ca. 30% and turnover numbers of ca. 8.0×10^3 . The oxidation of light gaseous alkanes leads to 45% total products yield (*n*-butane oxidation) and to the TON of ca. 2.7×10^3 (ethane oxidation). The oxidations appear to proceed with participation of hydroxyl radicals, which are generated from H_2O_2 upon catalytic action of vanadium species containing PCA. Among the reported vanadium and other transition metal catalysts applied for alkane oxidations by H_2O_2 , the achieved herein efficiency of the 1/PCA system is remarkably high, both in terms of product yields and TONs, especially concerning the oxidations of inert gaseous alkanes under rather mild conditions in aqueous MeCN.

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Figure / scheme captions

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Scheme 1. Synthetic procedure for the preparation of complex 1.

Scheme 2. Peroxidative oxidation of cyclohexane (model substrate) to cyclohexyl hydroperoxide (main primary product), cyclohexanol and cyclohexanone (major final products).

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	$\mathbf{I} \cdot \mathbf{H}_2 \mathbf{O}$	
Molecular Formula	C ₂₄ H ₃₂ N ₄ O ₁₀ V ₂ ,2(H ₂ O)	
Formula Weight	674.45	
Crystal System	Triclinic	
Space group	P-1	
a (Å)	6.8197(6)	
b (Å)	8.3164(7)	
c (Å)	14.9479(14)	
α (°)	97.756(3)	
β (°)	92.413(2)	
γ (°)	110.001(3)	
$V(A^3)$	785.80(12)	
Z	1	
pcalc (Mg/m ³)	1.425	
μ (Mo K α) (mm ⁻¹)	0.658	
F(000)	350	
Refls collected	6963	
Refls unique/obs.	2820/1927	
R _{int}	0.0508	
$R1^{a}_{I}(I \leq 2\sigma)$	0.0498, 0.0858	
wR2 ^b (I I $\leq 2\sigma$)	0.1136, 0.1316	
GOF	1.024	

Table 1 Crystallographic data and refinement parameters for complex 1.

^a RI = $\sum ||Fo| - |Fc|| / \sum |Fo|$.

^b wR2 = $\left[\sum [w(Fo^2 - Fc^2)2] / \sum [w(Fo^2)^2]\right]^{1/2}$

Table 2

Oxidation of cyclohexane by H₂O₂ catalyzed by **1** in the presence of PCA.^a

Catalyst		Reaction	Yield [%] ^b				
Entry amount [M]	time [min]	Cyclohexanol	Cyclohexanone	Total	TON ^c		
1	5×10^{-4}	45	20.6	7.0	27.6	254	
2	5×10^{-5}	240	19.4	9.3	28.7	2.64×10^3	
3	$5 imes 10^{-6}$	500	3.9	4.6	8.5	7.83×10^{3}	

^a Reaction conditions: cyclohexane (0.46 M), PCA (0.005 M), H₂O₂ (50% aqueous, 2.2 M), CH₃CN (up to 5 mL total volume), 50°C.

^b Based on cyclohexane, calculated from GC analysis after treatment of the reaction mixture with PPh₃.

^c Total TON corresponds to moles of products (cyclohexanol and cyclohexanone) per mol of catalyst.

Table 3

Selectivity parameters in the oxidation of linear and branched cyclic alkanes.^a

Catalytic system	Regioselectivity	Bond	Stereoselectivity	
	$(n-C_7H_{16})$	selectivity	trans/cis	
	C(1):C(2):C(3):C(4)	(MCH)	cis-	trans-
		1°:2°:3°	DMCH	DMCH
1/PCA/H ₂ O ₂ /CH ₃ CN	1:6:6:6	1:8:19	0.38	0.34
VO ₃ ⁻ /PCA/H ₂ O ₂ /CH ₃ CN (40°) ^b	1:9:7:7	1:6:18	0.75	0.80
$[VO{N(C_2H_4O)_3}]/PCA/H_2O_2/CH_3CN (40^{\circ})^{b}$	1:5.5:6.0:5.1	1:4:10	0.70	0.75
hv/H ₂ O ₂ /CH ₃ CN (20°) ^b	1:7:6:7		0.9	_

^a Reaction conditions: catalyst **1** (5 × 10⁻⁵), PCA (0.005 M), substrate (0.46 M), H₂O₂ (50% aqueous, 2.2 M), MeCN (up to 5 mL total volume), 50 °C. All parameters were measured after reduction of the reaction mixtures with PPh₃ before GC analysis and calculated based on the ratios of isomeric alcohols. The calculated parameters were normalized, i.e., recalculated taking into account the number of H atoms at each carbon atom. Parameters C(1):C(2):C(3):C(4) are relative reactivities of hydrogen atoms at carbons 1, 2, 3 and 4 of the *n*-heptane chain. Parameters 1° : 2° : 3° are relative normalized reactivities of the hydrogen atoms at primary, secondary and tertiary carbons of methylcyclohexane. Parameter *trans/cis* is determined as the ratio of the formed tertiary alcohol isomers with mutual *trans* and *cis* orientation of the methyl groups. Abbreviations: MCH is methylcyclohexane; *cis*-DMCH and *trans*-DMCH are isomers of 1,2-dimethylcyclohexane.

^b Taken from reference [21].

Table 4

Oxidation of gaseous alkanes by the 1/PCA/H₂O₂ system.^a

Alkane	Products (M) ^b	Total TON ^c	Total
(pressure, atm; mmol)			Yield [%] ^d
Ethane (20; 6.23)	acetaldehyde (0.069), ethanol	1.98×10^{3}	8.1
	(0.0225), acetic acid (0.0075) ^[e]		
Propane (6; 1.87)	acetone (0.059), isopropanol	2.67×10^{3}	35.7
	(0.028), propanal (0.028), <i>n</i> -		
	propanol (0.015), propionic acid		
	(0.0037)		
Butane (1; 0.31)	2-butanone (0.0176), 2-butanol	562	45.3
	(0.0059), butanal (0.0029), 1-		
	butanol (0.001), butyric acid		
	(0.0007)		
Methane (20; 6.23)	MeOH (0.0031 M)	63	0.3

^a Reaction conditions: complex **1** (5 × 10⁻⁵ M), PCA (0.005 M), H₂O₂ (50% aqueous, 2.2 M), MeCN (up to 5 mL total volume), 50 °C, 4 h in a 13 mL stainless steel autoclave.

^b Determined by GC (after reduction of the reaction mixtures with PPh₃).

^c Total moles of products / mol of catalyst.

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^d Yield (%) (moles of products / 100 moles of alkane).

^e After deduction of the acetic acid amount (0.002 M) generated from MeCN solvent in a blank test.

Figures



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Schemes



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Graphical Abstract

