

Scorpionate complexes of vanadium(III or IV) as catalyst precursors for solvent-free cyclohexane oxidation with dioxygen*

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Abstract: The V-scorpionate complexes [VCl₃{HC(pz)₃}] (pz = pyrazolyl) and [VCl₃{SO₃C(pz)₃}] catalyze cyclohexane oxidation with dioxygen, to cyclohexanol (the main product) and cyclohexanone, under solvent-free conditions. [VCl₃{HC(pz)₃}] provides the best activity (13 % conversion into the ketone and alcohol, with high selectivity, at the O₂ pressure of 15 atm, at 140 °C, 18 h reaction time). The reaction is further promoted (to 15 % conversion) by pyrazinecarboxylic acid (PCA). The use of C- or O-radical traps supports the involvement of a free-radical reaction mechanism. Several reaction parameters have been varied in a systematic study, directed toward optimization of the process.

Keywords: vanadium; scorpionates; water-soluble complexes; dioxygen; cyclohexane; homogeneous catalysis.

INTRODUCTION

Half-sandwich transition-metal complexes bearing tripodal capping ligands are potentially useful in catalytic processes with biological or industrial significance [1]. In pursuit of our recent investigation of the coordination chemistry of scorpionate-type tris(pyrazolyl)methane ligands [2] toward Re, Fe, V, and Cu centers, we have now focused our attention on the application of some of these compounds as catalyst precursors for alkane partial oxidation.

We have already found [3] that some V complexes with *N,O*- or *N,N*-ligands can catalyze alkane functionalization reactions, under mild or moderate conditions in homogeneous systems using peroxides as oxidants. Hence, Amavadin, i.e., Ca[V(HIDPA)₂] [HIDPA³⁻ = basic form of 2,2'-(hydroxyimino)dipropionic acid], the related Ca[V(HIDA)₂] [HIDA³⁻ = basic form of 2,2'-(hydroxyimino)diacetic acid] or [VO{N(CH₂CH₂O)₃}] compounds [3b,c], and scorpionate complexes [2b] of V can act as homogeneous catalysts for the peroxidative oxidation of some alkanes. The extension of this type of study to hydrotris(1-pyrazolyl)methane and tris(1-pyrazolyl)methanesulfonate V complexes, but using the ideal “green” oxidant (i.e., dioxygen) for oxidative functionalization reactions of alkanes, constitute

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the main aims of the current study. A contribution toward widening the use of V complexes in homogeneous catalysis is also an objective of this work.

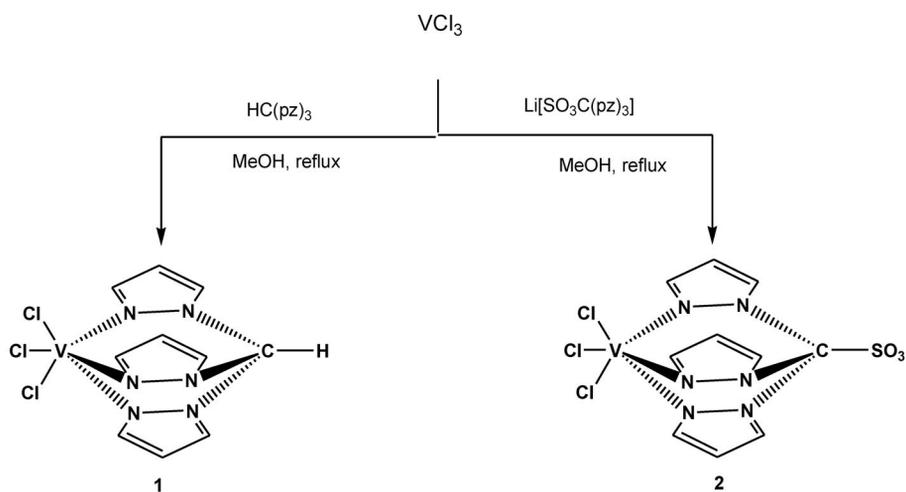
We have selected cyclohexane as the substrate in view of the relevance of its partially oxidized products (cyclohexanol and cyclohexanone) for the production of adipic acid and caprolactam, which are further used in the manufacture of nylon-6,6 and nylon-6, respectively [4,5]. Normally, Co compounds (cobalt naphthenate or cobalt acetate) have been used for the industrial oxidation reaction, with dioxygen as oxidant, at a temperature above 150 °C, and only a low conversion (ca. 4 %) is achieved to obtain a high selectivity (ca. 85 %) toward a mixture of cyclohexanone and cyclohexanol [5]. Thus, commercial cyclohexane oxidation uses inherently inefficient methodology that necessitates repeated recycling of feedstock. The alternative use of peroxides is expensive and is also accompanied by the formation of by-products [6]. The establishment of a greener, more effective and selective cyclohexane oxidation system with atmospheric oxygen is therefore a current need [7].

We have previously reported cyclohexane oxidation with dioxygen by using various types of metal-supported catalysts, i.e., bis(maltolato)oxovanadium complexes [8], a Schiff-base V complex [9], Co complexes [10], a macrocyclic Co-V complex [11] and some pyrazole rhenium complexes [12] (overall conversions of ca. 15, 13, 20, 15 and 18 %, respectively), which encouraged us to attempt the unprecedented use of V-scorpionate complexes to operate with molecular oxygen (easily available in air) for the functionalization of neat cyclohexane (which is cheaply available from naphtha) to cyclohexanol and cyclohexanone.

EXPERIMENTAL

Materials and instrumentation

The complexes $[\text{VCl}_3\{\text{HC}(\text{pz})_3\}]$ **1** [2b] and $[\text{VCl}_3\{\text{SO}_3\text{C}(\text{pz})_3\}]$ **2** [2b] were prepared according to published procedures (Scheme 1), under a dinitrogen atmosphere, using standard vacuum and inert-gas flow Schlenk techniques. Solvents were purified by standard procedures and freshly distilled immediately prior to use. Picolinic acid, 2-pyrazinecarboxylic acid (PCA), 3-amino-2-pyrazinecarboxylic acid (Aldrich), 2,3-pyridinedicarboxylic acid (Sigma), 2,6-pyridinedicarboxylic acid (Janssen), cyclohexane (Merck), triphenylphosphine (Merck), and dioxygen (Air Liquid Portugal) were used as received.



Scheme 1 Synthetic pathways for the V-scorpionate complexes **1** and **2**.

Gas chromatographic/mass spectrometry (GC/MS) measurements were carried out in a Trio 2000 Fisons mass spectrometer with a coupled gas chromatograph Carlo Erba Instruments, Auto/HRGC/MS. GC measurements were carried out using a Fisons Instruments GC 8000 series gas chromatograph with a flame ionization detector (FID) and a capillary column (DB-WAX, column length: 30 m; internal diameter: 0.32 mm). The temperature of injector was 240 °C. The initial temperature was maintained at 100 °C for 1 min, then raised 10 °C/min to 180 °C and held at this temperature for 1 min. Helium was used as the carrier gas.

Catalytic tests and product analysis

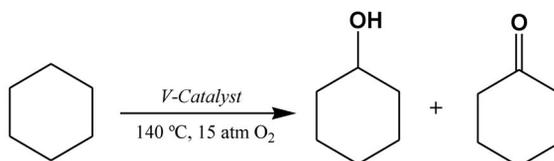
An oscillating-type micro batch reactor (316 stainless steel, 18 ml capacity), provided with a gas delivery inlet and a pressure gauge, was used for conducting the oxidation reactions. The inside temperature was controlled by an on/off controller with a suitable thermocouple. In typical conditions, the reactor was charged with 3.0 ml (27.8 mmol) of neat cyclohexane and 0.019 mmol of catalyst (complexes **1** or **2**) [3.0 mg (0.024 mmol) of PCA were used when the reaction was performed with this cocatalyst]. The reactor was then closed, the inside air was removed by vacuum, the system pressurized by dioxygen at the required pressure, and the reaction was run for 18 h, at the desired temperature. At the end of the reaction, the catalyst, whose color had turned to brown, was separated from the reaction mixture using a filter paper and washed three times with acetonitrile.

The oxidation products were analyzed by GC (30 μ l of cycloheptanone added as internal standard to 1.0 ml of the filtered final reaction solution) and further analyzed by GC/MS. Shul'pin's procedure [13,14] for the detection of alkyl hydroperoxide CyOOH (Cy = cyclohexyl) was followed, by treating the final reaction solution with an excess of PPh₃ before the GC analysis. The CyOOH, if present, was deoxygenated by PPh₃ to CyOH (with formation of phosphine oxide); therefore, the CyOOH decomposition to cyclohexanol and cyclohexanone in the gas chromatograph was suppressed. The turnover numbers (TONs) (moles of product per mole of catalyst) and yields (moles of product per mole of cyclohexane) were estimated. Blank experiments were also conducted in the absence of the V catalyst, under the above reaction conditions, and no products were then detected.

RESULTS AND DISCUSSION

Oxidation of cyclohexane to cyclohexanol and cyclohexanone

Complexes **1** and **2** act as catalysts or catalyst precursors for the oxidation of cyclohexane to cyclohexanol and cyclohexanone, with dioxygen (Scheme 2), in an oscillating-type micro batch reactor (typical conditions: V catalyst = 0.019 mmol, cyclohexane = 27.8 mmol, temp. = 140 °C, reaction time = 18 h, $p(\text{O}_2)$ = 15 atm), according to Scheme 2. The tris(1-pyrazolyl)methane complex [VCl₃{HC(pz)₃}] **1** provides the most active catalyst, under optimized conditions (entry 1, Table 1), leading to yields (moles of product/mole of cyclohexane) of cyclohexanol and cyclohexanone of 9.4 and 2.9 % (with a total 13.3 % conversion of cyclohexane, including the by-products).



Scheme 2 Peroxidative oxidation of cyclohexane to cyclohexanol and cyclohexanone catalyzed by the V-scorpionate complexes **1** and **2**.

Table 1 Cyclohexane oxidation with dioxygen catalyzed by V-scorpionate complexes, with or without PCA, under solvent-free conditions.^a

Entry	Catalyst	Conversion (%) ^b						TON ^d
		V catal.			V catal. + PCA			
		Cyclohexanol	Cyclohexanone	Overall ^c	Cyclohexanol	Cyclohexanone	Overall ^c	
1	[VCl ₃ {HC(pz) ₃ }] 1	9.4	2.9	13.3	11.6	3.8	16.0	227
2	[VCl ₃ {SO ₃ C(pz) ₃ }] 2	7.2	2.1	10.1	8.9	2.9	12.1	211

^aReaction conditions: V catal. = 1.9×10^{-2} mmol, PCA (when used) = 24×10^{-3} mmol (3 mg), cyclohexane = 27.8 mmol (3 ml), temp. = 140 °C, time = 18 h, $p(\text{O}_2)$ = 15 atm (measured at 25 °C) (1 atm = 1.0 bar = 101 kPa).

^bMoles of product(s) per 100 moles of cyclohexane.

^cOverall cyclohexane conversion to cyclohexanol, cyclohexanone, and by-products.

^dTON [moles of products (alcohol + ketone)/mole of catalyst] (values refer to the experiments in the presence of PCA).

The strong smell at the end of the oxidation reaction is indicative of the formation of the oxy-functionalized products, which have been analyzed by GC and GC/MS, showing they are mainly cyclohexanol (main product) and cyclohexanone.

The effects of various heteroaromatic carboxylic acids, i.e., PCA, 2,3-pyrazinedicarboxylic acid, 2,6-pyrazinedicarboxylic acid, 3-amino-2-pyrazinecarboxylic acid, and picolinic acid were studied (Tables 1–3 and Figs. 1–5) for the most active catalyst precursor **1**. PCA is the most effective cocatalyst (entry 1, Table 2, Fig. 2). It promotes considerably the cyclohexane oxidation [increase of overall conversion from ca. 13 to ca. 16 % (12 % of cyclohexanol and 4 % of cyclohexanone)] [see entries 1 (Table 1), 1 (Table 2), and 2 (Table 3)], with a good overall TON of 227 (with PCA) (Table 1, entry 1) which is higher than that, 167 (overall TON), previously observed [2b] for the peroxidative oxidation of cyclohexane, by aqueous hydrogen peroxide, catalyzed by **1**. Such a conversion corresponds to overall selectivities toward the cyclohexanol and cyclohexanone of 73 and 24 %, respectively.

Table 2 Effect of various heteroaromatic carboxylic acids (as cocatalysts) on the cyclohexane oxygenation with dioxygen catalyzed by [VCl₃{HC(pz)₃}] **1**, under solvent-free conditions.^a

Cocatalyst	Entry	Conversion (%) ^b		
		Cyclohexanol	Cyclohexanone	Overall ^c
Pyrazinecarboxylic acid (PCA)	1	11.6	3.8	16.0
2,3-Pyrazinedicarboxylic acid	2	9.5	3.8	14.4
2,6-Pyrazinedicarboxylic acid	3	9.5	3.6	13.7
3-Amino-2-pyrazinecarboxylic acid	4	8.6	3.3	12.8
Picolinic acid	5	8.3	2.7	11.9

^aSame conditions as those indicated in Table 1; amount of cocatalyst = 24×10^{-3} mmol.

^bMoles of product(s) per 100 moles of cyclohexane (compare with the obtained conversion in the absence of cocatalyst, first columns of entry 1, Table 1).

^cOverall cyclohexane conversion to cyclohexanol, cyclohexanone, and by-products.

Table 3 Effects of various parameters on the cyclohexane oxidation with molecular oxygen catalyzed by compound **1** with PCA under solvent-free conditions.^a

Run no.	Catal. (mg)	PCA (mg)	Temp. (°C)	$p(\text{O}_2)$ (atm) ^b	Time (h)	Conversion (%) ^c		
						Cyclohexanol	Cyclohexanone	Overall ^d
1	5	3	140	15	18	4.1	1.2	6.3
2	7	3	140	15	18	11.6	3.8	16.0
3	9	3	140	15	18	13.2	4.3	18.3
4	11	3	140	15	18	14.5	4.6	20.1
5	13	3	140	15	18	15.1	4.4	21.5
6	7	1	140	15	18	10.4	3.5	14.1
7	7	2	140	15	18	10.9	3.9	15.4
8	7	5	140	15	18	12.0	3.9	16.8
9	7	10	140	15	18	10.7	2.7	17.3
10	7	3	80	15	18	1.2	0.4	1.9
11	7	3	100	15	18	2.8	0.8	4.2
12	7	3	120	15	18	6.7	2.0	9.7
13	7	3	160	15	18	12.7	4.2	17.7
14	7	3	200	15	18	13.0	4.3	20.4
15	7	3	140	5	18	3.0	0.9	4.7
16	7	3	140	10	18	7.4	2.3	11.2
17	7	3	140	20	18	13.4	4.3	19.2
18	7	3	140	25	18	13.1	4.5	21.9
19	7	3	140	15	6	1.5	0.5	2.5
20	7	3	140	15	12	3.9	1.4	6.4
21	7	3	140	15	24	13.6	4.4	18.7
22	7	3	140	15	30	13.8	4.3	20.3

^aFor the other reaction conditions, see Table 1 or experimental section.^bMeasured at room temperature (1 atm = 1.0 bar = 101 kPa).^cMoles of product(s) per 100 moles of alkane.^dTotal cyclohexane conversion to cyclohexanol, cyclohexanone, and by-products.

A promoting effect of PCA was also observed by us [12,15] for oxidation of cyclohexane and of related alkanes catalyzed by supported V complexes, and by Shul'pin and Süß-Fink [16] in the peroxidative oxidation of alkanes, in various homogeneous systems with V species. In our system, 2,3-pyrazinedicarboxylic acid (overall conversion ca. 14 %) acted as a weaker promoter, while the other tested heteroaromatic carboxylic acids had no significant effect or even showed a slight inhibition (Table 2). Thus, we have used PCA as a promoter for the following further cyclohexane oxidation studies.

Optimization of the reaction conditions

Effects of the amounts of catalyst and of promoter

The conversion of cyclohexane into the oxidation products markedly increases with the amount of catalyst **1** (Fig. 1) up to the $n(\text{catalyst})/n(\text{C}_6\text{H}_{12})$ molar ratio of ca. 0.07 %. A further increase of this amount leads only to a relatively low promotion of the conversion. The product selectivity does not appreciably change with the catalyst amount (Fig. 1).

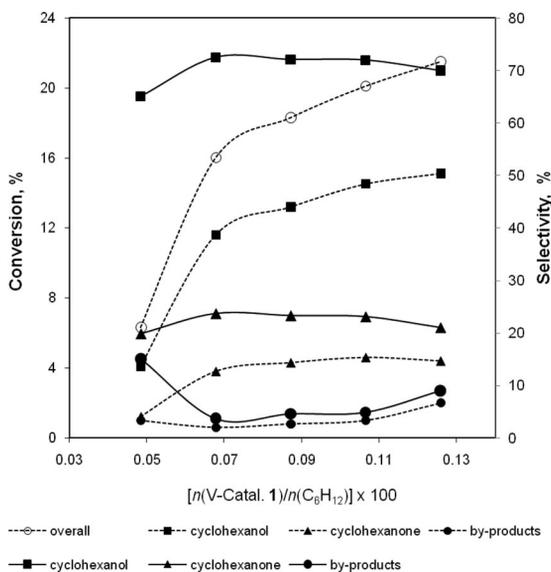


Fig. 1 Effect of the amount of catalyst precursor **1** (molar ratio relatively to C_6H_{12}) on the conversion of C_6H_{12} (---) or on the selectivity (—), upon oxidation by O_2 , in the presence of PCA [140°C , $p(\text{O}_2) = 13.6$ atm, 18 h, $\text{PCA} = 24 \times 10^{-3}$ mmol].

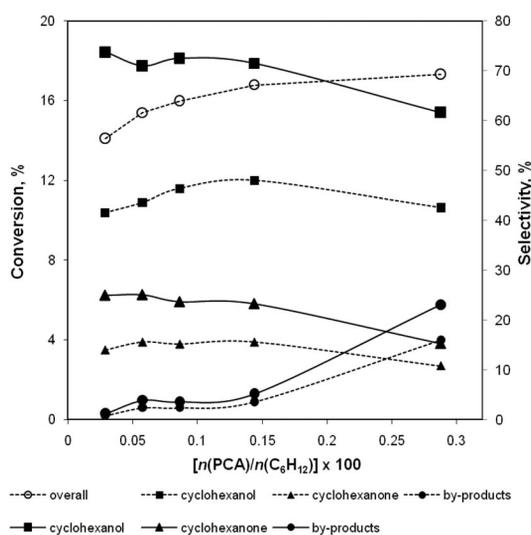


Fig. 2 Effect of the amount of PCA promoter (molar ratio relatively to C_6H_{12}) on the conversion of C_6H_{12} (---) or on the selectivity (—), upon oxidation by O_2 , catalyzed by catalyst precursor **1** [catal. = 1.9×10^{-2} mmol, 140°C , $p(\text{O}_2) = 13.6$ atm, 18 h].

The overall cyclohexane conversion increases with the amount of PCA (essentially up to $n(\text{PCA})/n(\text{C}_6\text{H}_{12})$ of 0.15 %) on account of the increase of the conversion into cyclohexanol (Fig. 2). A higher amount of PCA is discouraged in view of the decrease of the selectivities toward both the alcohol and the ketone (Fig. 2), due to the enhanced formation of by-products.

Effect of temperature

The temperature effect on the oxidation of cyclohexane was examined in the range 80–200 °C (Fig. 3). An increase of temperature up to ca. 140 °C leads to enhancement of the conversions and the selectivities to the main products (cyclohexanol and cyclohexanone). A higher temperature is not favorable since such conversions do not increase further and, moreover, the selectivities toward the alcohol and the ketone tend to decrease (Fig. 3). The reaction temperature was not allowed to go beyond 200 °C since an unidentified black charring material is then formed.

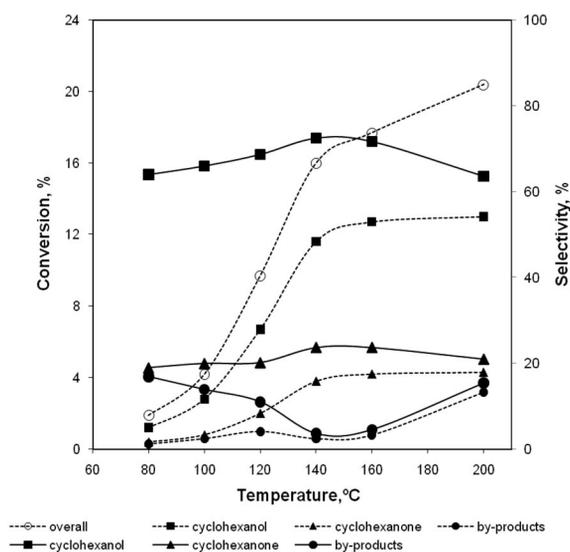


Fig. 3 Effect of temperature on the conversion of C_6H_{12} (---) or on the selectivity (—), upon oxidation by O_2 , catalyzed by catalyst precursor **1** in the presence of PCA [catal. = 1.9×10^{-2} mmol, $p(\text{O}_2) = 15$ atm, 18 h, PCA = 24×10^{-3} mmol].

Effect of dioxygen pressure

The effect of dioxygen pressure was studied (Fig. 4) in the range 5–25 atm. The overall conversion of cyclohexane markedly increases with the pressure of O_2 (which is consistent with the increase of the solubility of this gas), but for pressures above 20 atm, the conversions to cyclohexanol and cyclohexanone do not increase. The selectivities toward these products (mainly to the former) lower for O_2 pressures above 15 atm on account of the increasing amount of by-products (Fig. 4). Hence, the application of an O_2 pressure above 15 atm is usually not advisable.

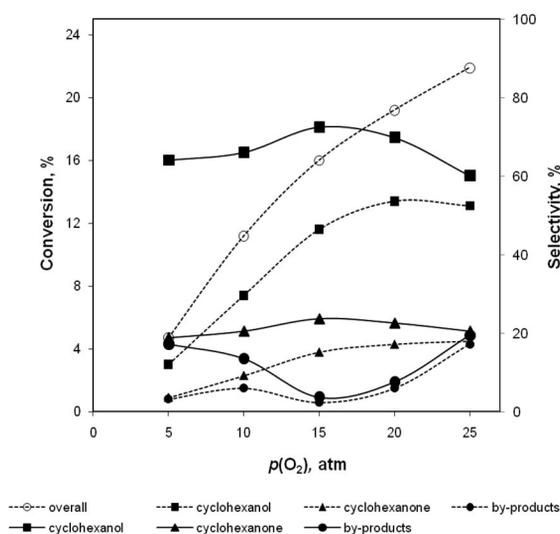


Fig. 4 Effect of the dioxygen pressure on the conversion of C_6H_{12} (---) or on the selectivity (—), upon oxidation by O_2 , catalyzed by catalyst precursor **1** in the presence of PCA (catal. = 1.9×10^{-2} mmol, 140°C , 18 h, PCA = 24×10^{-3} mmol).

Effect of reaction time

The effect of reaction time (in the 6–30 h range), at 140°C , is shown in Fig. 5. The conversions to the desired main products (mainly cyclohexanol) highly increase up to ca. 18 h, beyond which the growing is remarkably slower, although the overall conversion continues to grow on account of the increased formation of by-products (Fig. 5). The maximum selectivity toward cyclohexanol is achieved for a reaction time of 18 h, which thus has been the typical value used for our experiments.

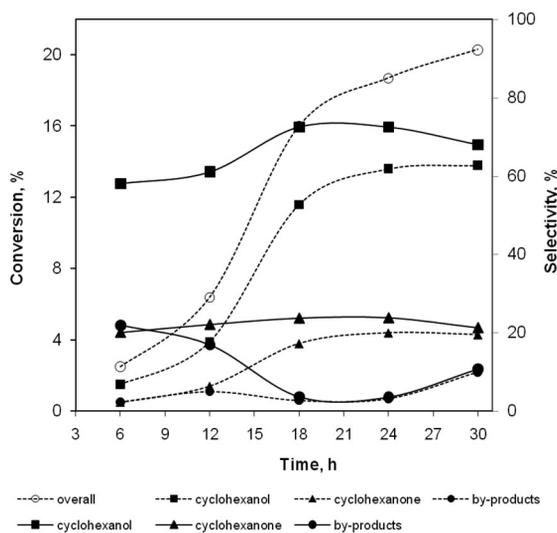


Fig. 5 Effect of the reaction time on the conversion of C_6H_{12} (---) or on the selectivity (—), upon oxidation by O_2 , catalyzed by catalyst precursor **1** in the presence of PCA [catal. = 1.9×10^{-2} mmol, 140°C , $p(\text{O}_2) = 13.6$ atm, PCA = 24×10^{-3} mmol].

Effect of radical traps

The effect of the presence of a radical trap on the oxidation reaction was studied for the conditions of entry 2, Table 3. The catalytic activity of the cyclohexane oxidation system is almost suppressed when performing the reactions in the presence of a liquid carbon-radical trap (trichlorobromomethane) or an oxygen-radical trap (diphenylamine), in a stoichiometric amount relative to cyclohexane. Common solid radical traps cannot be used, in view of their insolubility in cyclohexane.

The same type of effect was observed by us [2b,3,12,17] for the peroxidative oxidation of cyclohexane by H_2O_2 , which proceeds mainly by a type of mechanism that involves both carbon- and oxygen-centered radicals.

CONCLUSIONS

We have found an unprecedented use of V-scorpionate complexes as catalysts for the cyclohexane oxidation to cyclohexanol and cyclohexanone, with molecular oxygen, in a one-pot process and under solvent-free conditions. The study of the effects of a variety of factors indicates that the most appropriate operating conditions are 140 °C, $p(\text{O}_2)$ of ca. 15 atm and ca. 18 h reaction time.

The V complexes are more active in the presence of PCA, which acts as a promoter and, with complex **1** (the most effective one), a 15 % conversion cyclohexane into cyclohexanol and cyclohexanone, with a high selectivity, was achieved under optimized conditions.

Although the mechanistic details are not yet established, a free-radical mechanism appears to occur since, when the reaction is carried out in the presence of the radical traps CBrCl_3 or Ph_2NH , the above products are formed only in very small amounts.

The cyclohexyl radical (Cy^\bullet) could be initially formed by the reaction (slow induction period) of dioxygen (O_2) with the alkane upon homolytic C–H bond rupture. The oxidation of Cy^\bullet with O_2 would form the cyclohexylperoxy radical (CyOO^\bullet) which could further react as follows [8,12,15,16,18]: by decomposition, to the final products, i.e., the corresponding alcohol and ketone; or by hydrogen-abstraction from cyclohexane to form the hydroperoxide CyOOH . Homolytic decomposition of the latter to CyO^\bullet (O–O bond rupture) and CyOO^\bullet radical (O–H bond cleavage) could be catalyzed by the V catalyst. The PCA cocatalyst could promote these bond cleavages, by assisting hydrogen transfer from the CyOOH ligand to an oxo (or hydroxo) ligand, yielding the coordinated alkylperoxo CyOO species which could undergo homolytic bond rupture, following a process similar to that proposed by Shul'pin [16] for oxovanadium/ H_2O_2 systems.

CyOH could be formed either upon hydrogen abstraction from cyclohexane (CyH) by CyO^\bullet or upon decomposition of CyOO^\bullet leading also to the ketone. The possible involvement of CyOOH is substantiated by the increase of the detected amount of the alcohol with a decrease of that of the ketone, when the final reaction mixture is treated, prior to the GC analysis, with triphenylphosphane (which reduces CyOOH to CyOH , thus eliminating the CyOOH decomposition to alcohol + ketone in the gas chromatograph), according to a method reported by Shul'pin [13,14].

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