



## Oxidation of hydrocarbons with hydrogen peroxide catalyzed by maltolato vanadium complexes covalently bonded to silica gel

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### Abstract

The bis(maltolato)oxo complexes of vanadium(V) and vanadium(IV) both in a soluble form and anchored to chemically modified silica gel, when used in combination with pyrazine-2-carboxylic acid (PCA), catalyze the oxidation of benzene to phenol and alkanes to the corresponding alkyl hydroperoxides with H<sub>2</sub>O<sub>2</sub> at 40–50 °C. Heterogenizing the complexes leads to changes in regioselectivity and bond selectivity parameters of the alkane oxidation, and this opens new routes to the enhancement of the selectivity in oxidation processes.

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Soluble [1–19] and heterogenized [20–35] vanadium complexes are known to catalyze hydrocarbon oxidations with molecular oxygen, hydrogen peroxide and other oxygen donors. It has been demonstrated recently that bis(maltolato)oxovanadium complexes covalently bonded to carbamated modified silica gel catalyze oxidation of cyclohexane [34] and normal alkanes [35] by molecular oxygen typically at 150–175 °C. Here we report that silica-supported vanadium complexes are efficient catalysts in the oxidation under mild conditions (40–50 °C) of benzene and alkanes with hydrogen peroxide if pyrazine-2-carboxylic acid (PCA) is present as a co-catalyst.

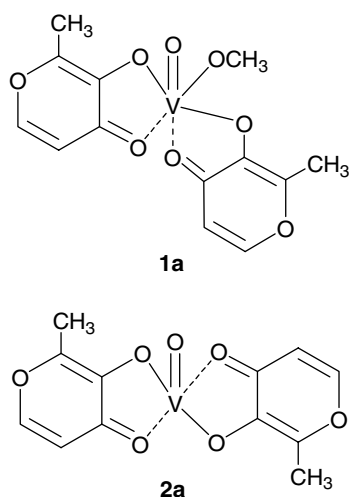
In this work, we used soluble maltolato complexes **1a** and **2a** of vanadium(V) and vanadium(IV), respectively, as well as these complexes covalently bonded to carbamate modified silica gel (**1b** and **2b**, respectively) [34,35]. We have found that both soluble complex **1a** and supported

onto silica gel compound **1b** efficiently catalyze the H<sub>2</sub>O<sub>2</sub> oxidation of benzene to phenol in acetonitrile. Additives of PCA significantly accelerate the reaction (compare curves 1 and 2 in Fig. 1). The oxidation of benzene in the absence of catalysts **1a** or **1b** did not produce even traces of phenol. Some amount of soluble vanadium-containing species is leached to the solution from the heterogenized catalyst **1b** in the course of the reaction. This was demonstrated in special experiments: catalyst **1b** was stirred for 2 h with a solution of hydrogen peroxide in acetonitrile under the conditions of experiments shown in Fig. 1b. After that the catalyst was filtered off at 40 °C and benzene (10 mmol) and H<sub>2</sub>O<sub>2</sub> (20 mmol) were added and the resulting homogeneous solution was stirred at 40 °C for additional 2 h. Only a small amount of phenol (0.007 mmol) was obtained in the experiment carried out in the absence of PCA (which is 10 times lower than the amount obtained after 2 h in the presence of heterogeneous catalyst **1b**). In the presence of PCA leaching of a catalytically active species to the solution was more substantial: the reaction of

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benzene with a homogeneous solution prepared by the preliminary incubation of **1b** with H<sub>2</sub>O<sub>2</sub> in acetonitrile gave 0.04 mmol of phenol (whereas 0.14 mmol was obtained in the reaction with genuine heterogenized catalyst **1b**). Anchored catalyst **1b** is stable and does not decompose in the course of the benzene oxidation. The IR spectrum of the sample obtained after the reaction is identical to the spectrum of the sample before the oxidation. In a special experiment, the sample of **1b** was after the reaction filtered off, washed with acetonitrile, dried in air and used in the second cycle. The initial rate of the benzene oxidation was in this case only ca. 15% lower in the comparison with the rate measured in the first cycle of the catalyst usage.



We have found that the soluble derivative of V(IV) **2a** is a very poor catalyst and rapidly decomposes in the course of the reaction both in the presence and in the absence of PCA giving only traces of phenol. Surprisingly, heterogenizing of complex **2a** on the silica gel produced much more stable and efficient catalyst (catalyst **2b**) although its activity was lower than that of the V(V) derivative **1b** (compare Figs. 1b and 2).

Compounds **1a** and **1b** catalyze also the oxidation of cyclohexane under analogous conditions. The oxygenation of cyclohexane gives rise to the formation of the corresponding alkyl hydroperoxide as the main primary product. The formation of alkyl hydroperoxides in addition to the small amounts of the corresponding alcohols and ketones was demonstrated by a method developed in our previous works [4,7,12,36–39] and used further in various metal-catalyzed oxidations [40–45]. This method is based on comparing the intensities of peaks attributed to the alcohol and ketone before and after the reduction of the reaction samples with triphenylphosphine. The cyclohexyl hydroperoxide further gradually decomposes to yield more stable products, the cyclohexanone and cyclohexanol. It can be seen from the data shown in Fig. 3 that the cyclohexane oxidation catalyzed both homogeneously (catalyst **1a**) and heterogeneously (catalyst **1b**) produces almost exclusively cyclohexyl hydroperoxide in quite a consider-

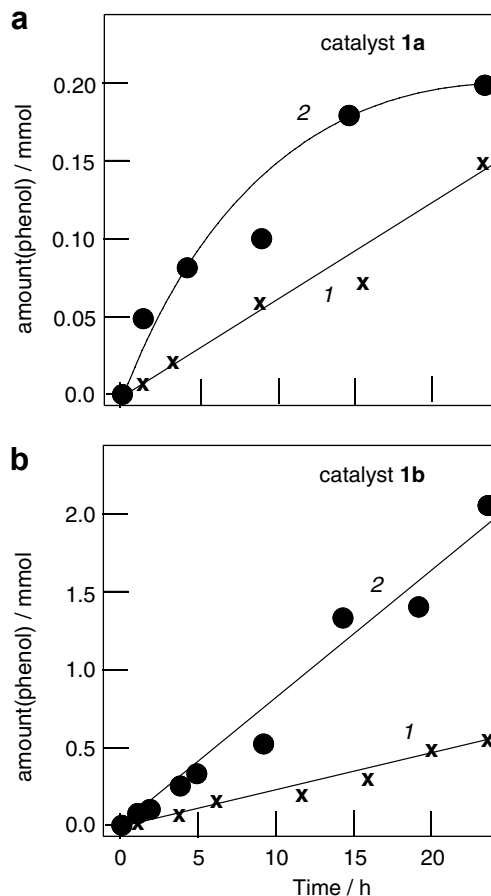


Fig. 1. Accumulation of phenol with time in the oxidation of benzene in acetonitrile at 40 °C in the absence (curves 1) and in the presence of PCA (curves 2). Graph (a): soluble catalyst **1a** ( $5 \times 10^{-4}$  mmol), PCA ( $25 \times 10^{-4}$  mmol), benzene (5 mmol), H<sub>2</sub>O<sub>2</sub> (5 mmol), MeCN (total volume of the reaction solution was 5 mL). Graph (b): heterogenized catalyst **1b** (0.1 g), PCA ( $25 \times 10^{-4}$  mmol), benzene (10 mmol), H<sub>2</sub>O<sub>2</sub> (20 mmol), MeCN (total volume of the reaction solution was 8 mL).

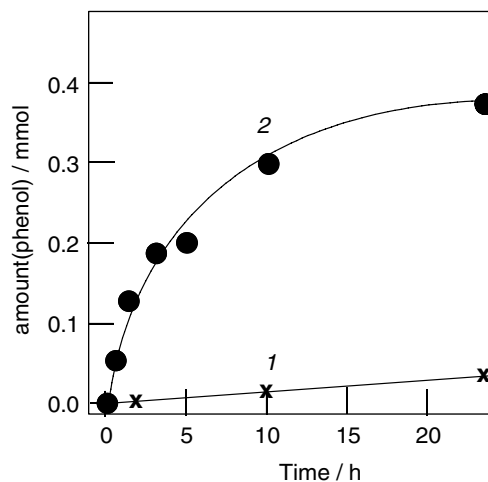


Fig. 2. Accumulation of phenol with time in oxidation of benzene in acetonitrile at 40 °C in the absence (curve 1) and in the presence of PCA (curve 2). Conditions: catalyst **2b** (0.1 g), PCA ( $25 \times 10^{-4}$  mmol), benzene (10 mmol), H<sub>2</sub>O<sub>2</sub> (20 mmol), MeCN (total volume of the reaction solution was 8 mL).

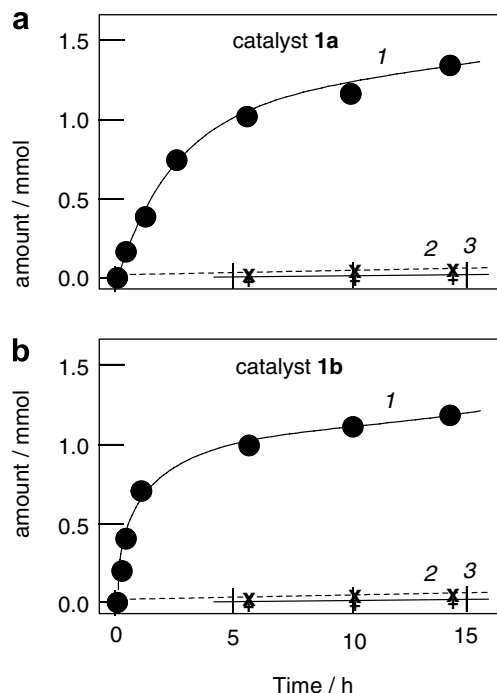


Fig. 3. Accumulation of cyclohexyl hydroperoxide (1), cyclohexanol (2) and cyclohexanone (3) with time in the oxidation of cyclohexane (4.8 mmol) with  $\text{H}_2\text{O}_2$  (20 mmol) in acetonitrile (total volume of the reaction solution was 5 mL) at 50 °C in the presence of PCA ( $20 \times 10^{-4}$  mmol). Graph (a): soluble catalyst **1a** ( $5 \times 10^{-4}$  mmol). Graph (b): heterogenized catalyst **1b** (0.02 g).

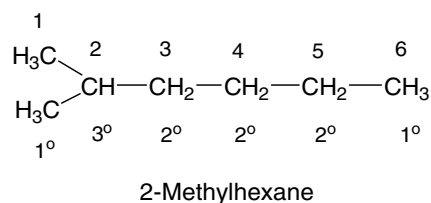
able yield (27% or 25%, respectively). A remarkably high TON of  $2.6 \times 10^3$  (mol product per mol catalyst) is achieved by the homogeneous system after 14 h reaction time.

It was interesting to compare selectivity parameters obtained for linear, branched and cyclic alkanes in the oxidations catalyzed on the one hand by soluble vanadium complexes in combination with PCA (as well as some other homogeneous oxidizing systems) and on the other hand by the heterogenized catalyst **1**. These parameters are summarized in Table 1. It can be seen (entries 1–9) that selectivity parameters for oxidations of linear hexane and octane are low [the C(1):C(2) ratio is approximately 1:8] for both **1a** and **1b** and these are close to the values obtained for the corresponding oxidations catalyzed by vanadate anion (entries 4 and 8) or by photochemical oxidations with hydrogen peroxide (entries 5 and 9). Decomposition of hydrogen peroxide under the action of UV light or the “vanadate–PCA” combination is known to occur with the formation of free hydroxyl radicals [2,4,6,7,10,12,19,38] and we can propose that in the case of catalysts **1a** and **1b** the oxygenation reaction begins from the attack of hydroxyl radicals at C–H bonds of the alkanes.

It is, however, noteworthy that the reaction of *n*-hexane catalyzed by relatively small vanadate ion (as well as the photochemical oxygenation) exhibits some predominance in the functionalization of position 2 over position 3, whereas oxidations catalyzed by more bulky compounds

**1a**, **1b** and **2a** (entries 1–3) give a C(2):C(3) ratio below unity, i.e.  $\text{C}(2) < \text{C}(3)$ . The *n*-octane oxidations induced by light (entry 9) or the “vanadate–PCA” combination (entry 8) give a  $\text{C}(2) > \text{C}(3) > \text{C}(4)$  relationship that contrasts to the  $\text{C}(2) < \text{C}(3) > \text{C}(4)$  order determined in the case of catalysis by **1a** (entry 6) and **1b** (entry 7). These differences can be explained if we assume that C–H bonds of methylenes in position 3 are a bit more accessible for the interaction with the bulky oxidizing centers of the catalysts **1a** and **1b** than those of the other methylene groups. It would be apparently possible if the alkane chains adopt a U-shape (hairpin) or clew conformation [47]. It is interesting to note that Lindsay Smith and coworkers [48] found recently in the oxidation of *n*-pentane with iodosylbenzene that the ratio of pentan-2-ol to -3-ol and of pentan-2-one to -3-one were close to the statistical value of 2:1 when catalyzed by manganese(III) tetrakis[tetrafluoro-4-(trimethylammonium)phenyl]porphyrin, both a soluble form in homogeneous solution and supported on modified silica surfaces. With more hindered manganese(III) tetrakis(2,6-dichloro-3-sulfonatophenyl)porphyrin as a catalyst the ratios were slightly larger (3 or 4:1) showing that there is a small selectivity for the less hindered 2-position of pentane. The authors concluded that the influence of the supports on the regioselectivity of the oxidations is very small, thus it appears that anchoring the porphyrin to the support by electrostatic (coordinative) interactions has little effect on the catalyst’s reactivity. No obvious dependence of the regioselectivity of the oxidation on the solvent has been found [48].

In the oxidation of 2-methylhexane the bond selectivity parameter  $1^\circ:2^\circ:3^\circ$  decreases on passing from the catalyst (*n*-Bu<sub>4</sub>N)VO<sub>3</sub>–PCA with less sterically hindered reaction center (entry 12) to the catalyst **1a** with the more bulky ligand (entry 10) and finally to the heterogenized **1b** (entry 11). The same tendency can be noticed for the oxidation of 3-methylhexane (entries 14–16). It is interesting that in the case of 2-methylhexane homogeneous catalyst **1a** oxidizes position C(6) more easily in comparison with position C(1), the normalized ratio C(1):C(6) being 1:1.13 (entry 10). An opposite situation [C(1):C(6) = 1:0.38] (entry 11) was found when heterogenized catalyst **1b** was used.



The oxidation of *cis*-1,2-dimethylcyclohexane using **1b** (entry 23) demonstrates that the reaction proceeds non-stereoselectively, as in the  $\text{H}_2\text{O}_2$ –vanadate anion–PCA reagent (entry 24), and this finding is in accord with the proposed heterogenized catalyst mechanism which involves participation of free hydroxyl radicals.

Table 1  
Selectivity parameters in oxidations of alkanes with H<sub>2</sub>O<sub>2</sub> catalyzed by various homogeneous and heterogeneous systems<sup>a</sup>

Entry	Alkane	System	Selectivity parameters
1	<i>n</i> -Hexane	<b>1a</b> -PCA	C(1):C(2):C(3) = 1:6.8:7.8
2		<b>1b</b> -PCA	C(1):C(2):C(3) = 1:8.1:8.8
3		<b>2a</b> -PCA	C(1):C(2):C(3) = 1:6.4:6.7
4		( <i>n</i> -Bu <sub>4</sub> N)VO <sub>3</sub> -PCA <sup>b</sup>	C(1):C(2):C(3) = 1:8.0:7.0
5		UV irradiation of H <sub>2</sub> O <sub>2</sub>	C(1):C(2):C(3) = 1:10.0:7.0
6	<i>n</i> -Octane	<b>1a</b> -PCA	C(1):C(2):C(3):C(4) = 1:6.1:6.8:5.2
7		<b>1b</b> -PCA	C(1):C(2):C(3):C(4) = 1:8.4:9.3:6.7
8		( <i>n</i> -Bu <sub>4</sub> N)VO <sub>3</sub> -PCA <sup>b</sup>	C(1):C(2):C(3):C(4) = 1:9.3:8.8:7.2
9		UV irradiation of H <sub>2</sub> O <sub>2</sub>	C(1):C(2):C(3):C(4) = 1:10.2:6.8:6.3
10	2-Methylhexane	<b>1a</b> -PCA	1°:2°:3° = 1:6.3:22; C(3):C(4):C(5) = 1:1.62:1.53; C(1):C(6) = 1:1.13
11		<b>1b</b> -PCA	1°:2°:3° = 1:3.5:14; C(3):C(4):C(5) = 1:1.20:1.25; C(1):C(6) = 1:0.38
12		( <i>n</i> -Bu <sub>4</sub> N)VO <sub>3</sub> -PCA <sup>b</sup>	1°:2°:3° = 1:8.7:37; C(3):C(4):C(5) = 1:1.32:1.37; C(1):C(6) = 1:1.50
13		UV irradiation of H <sub>2</sub> O <sub>2</sub>	1°:2°:3° = 1:6.0:34; C(3):C(4):C(5) = 1:1.00:0.60
14	3-Methylhexane	<b>1a</b> -PCA	1°:2°:3° = 1:6.7:27
15		<b>1b</b> -PCA	1°:2°:3° = 1:3.5:13
16		( <i>n</i> -Bu <sub>4</sub> N)VO <sub>3</sub> -PCA <sup>b</sup>	1°:2°:3° = 1:14:64
17	Isooctane <sup>c</sup>	<b>1a</b> -PCA	1°:2°:3° = 1:4.6:4.2
18		<b>1b</b> -PCA	1°:2°:3° = 1:2.8:5.6
19		( <i>n</i> -Bu <sub>4</sub> N)VO <sub>3</sub> -PCA <sup>b</sup>	1°:2°:3° = 1:3.0:12
20		UV irradiation of H <sub>2</sub> O <sub>2</sub>	1°:2°:3° = 1:4.0:20
21		UV irradiation of TBHP <sup>d</sup>	1°:2°:3° = 1:2.0:32
22		Cu(MeCN) <sub>4</sub> (BF <sub>4</sub> )-(TBHP instead of H <sub>2</sub> O <sub>2</sub> ) <sup>d</sup>	1°:2°:3° = 1:0:41
23	<i>cis</i> -1,2-DMCH	<b>1b</b> -PCA	<i>trans/cis</i> = 0.82
24		( <i>n</i> -Bu <sub>4</sub> N)VO <sub>3</sub> -PCA <sup>b</sup>	<i>trans/cis</i> = 0.75
25		UV irradiation of H <sub>2</sub> O <sub>2</sub>	<i>trans/cis</i> = 0.90

<sup>a</sup> All parameters were measured by the GC method after reduction of the reaction mixtures with triphenylphosphine and calculated based on the ratios of isomeric alcohols. Parameter C(1):C(2):C(3):C(4) is relative normalized (i.e., calculated taking into account the number of hydrogen atoms at each carbon) reactivities of hydrogen atoms at carbons 1, 2, 3 and 4 of the chain of unbranched alkanes. Parameter 1°:2°:3° is relative normalized reactivities of hydrogen atoms at primary, secondary and tertiary carbons of branched alkanes. Parameter *trans/cis* is the ratio of *trans*- and *cis*-isomers of *tert*-alcohols formed in the oxidation of *cis*-1,2-dimethylcyclohexane (*cis*-1,2-DMCH).

<sup>b</sup> For this system, which is believed to oxidize substrates via formation of hydroxyl radicals, see [2,4,6,7,10,12,19,38].

<sup>c</sup> 2,2,4-Trimethylpentane.

<sup>d</sup> For this system, see [46].

## 1. Experimental

For preparation and characterization of catalysts **1a** [34,35,49,50], **1b** [34,35], **2a** [34,35,49,50], **2b** [34,35], see the literature. Hydrogen peroxide solution (aqueous 35%, “Fluka”) was used as received. The experiments on the oxidations of benzene or cyclohexane were carried out in air in thermostated Pyrex cylindrical vessels (total volume 5 mL) with vigorous stirring. In a typical experiment, initially, a portion of the aqueous solution of H<sub>2</sub>O<sub>2</sub> was added to the solution of the substrate, catalyst and co-catalyst in acetonitrile. Concentration of phenol was determined by <sup>1</sup>H NMR (“Bruker AMX-400” instrument, 400 MHz) after addition of D<sub>2</sub>O or acetone-*d*<sub>6</sub> and dinitrobenzene as internal standard. In order to determine concentrations of cyclohexane oxidation products the samples of reaction solutions were analyzed twice (before and after their treatment with PPh<sub>3</sub> [4,7,12,36–39]) by GC (Chromatograph-3700, fused silica capillary column FFAP/OV-101 20/80 w/w, 30 m × 0.2 mm × 0.3 μm; helium as a carrier gas) measuring concentrations of cycloalkanol and cycloalkane. Oxidations of other hydrocarbons were carried out analogously. Authentic samples of all oxygenated products

were used to attribute the peaks in chromatograms (comparison of retention times was carried out for different regimes of GC-analysis).

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