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Mixed crystals containing the dioxo complex $[{Ph_3SiO}_2VO_2]^$ and novel pentacoordinated oxoperoxo complex $[{Ph_3SiO}_2-VO(O_2)]^-$: X-ray crystal structure and assessment as oxidation catalysts

Maxence Vennat,*^a Jean-Marie Brégeault *^a and Patrick Herson^b

- ^a Laboratoire des Systèmes Interfaciaux à l'Echelle Nanométrique, Université Pierre et Marie Curie/CNRS, case 196, 4 place Jussieu, 75252 Paris cedex 05, France. E-mail: bregeaul@ccr.jussieu.fr; maxencevennat@yahoo.fr; Fax: +33 (0) 1 44 27 55 36
- ^b Chimie Inorganique et Matériaux Moléculaires, Université Pierre et Marie Curie/CNRS, case 42, 4 place Jussieu, 75252 Paris cedex 05, France. E-mail: herson@ccr.jussieu.fr

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 $[n-Bu_4N][\{Ph_3SiO\}_2VO_2]$ reacts with H_2O_2 to yield an oxoperoxo complex which crystallizes as a mixed-crystal compound, $[P(C_6H_5)_4][\{(C_6H_5)_3 SiO\}_2VO_2]_x[\{(C_6H_5)_3 SiO\}_2VO(O_2)]_{1-x}$, **1** (x = 0.57). It has been characterized by elemental analysis and spectroscopy (⁵¹V NMR, UV-visible and IR). The X-ray structure analysis reveals the presence of two interrelated anions: $[\{Ph_3SiO\}_2V^VO_2]^-$, **1a**, and $[\{Ph_3SiO\}_2V^VO(O_2)]^-$, **1b** with a cisoid geometry of the $\{VO(O_2)\}^+$ moiety. The two structures differ only slightly: anion **1a** exhibits unusual tetrahedral coordination around the vanadium centre found in the precursor, whereas the geometry at the metal ion in **1b** can be described as a trapezoidal pyramid. Steric constraints due to Ph_3SiO^- ligands and PPh_4^+ cations are responsible for this geometry. The reactivity of **1** in the C–C bond cleavage of 2-methylcyclohexanone under anaerobic conditions has been studied. The results suggest that peroxygen species are involved in the oxidative cleavage of C–C bonds of cycloalkanones.

Introduction

The catalytic oxidation of cyclohexanone and α -substituted cycloalkanones (2-hydroxycyclohexanone, 2-methylcyclohexanone, **2**, *etc.*) using dioxygen and vanadium (IV) or (V) precursors, to synthesize adipic acid or keto-acids, has been studied. Of these precursors, heteropolyacids H_{3+n}[PMo_{12-n}-V_nO₄₀]_{aq}, denoted HPA-n, give the highest activity ¹⁻⁶ (Scheme 1).



Monomeric pervanadyl species such as [{Ph₃SiO}₂VO₂] behave like the polyoxometalate but give lower yields of acids or keto-acids.¹ These oxidation reactions include vanadium v/IV redox steps which would appear to be the key steps in the formation of peroxidic vanadium; the acidity of HPA-n (n = 3, 4) favours enolization and strongly accelerates the overall reaction.¹⁻⁶ At the same time, the coordination chemistry of oxoperoxo vanadium (v) species has received considerable attention due to its relevance to the role of vanadium in biological systems (oxoperoxo vanadium complexes are good models for vanadium-containing biomolecules like vanadium haloperoxidases (VHPO)⁷⁻⁹) and in homogeneous catalysis.¹⁰⁻¹⁴ In this respect, it seemed that synthesis of mono-oxoperoxo species was relevant. A possible route is the reaction of the novel pervanadyl complex,¹ $Q^{+}[{Ph_3SiO}_2VO_2]^{-}$, (Q⁺ $[n-\mathrm{Bu}_4\mathrm{N}]^+$, PPh₄⁺, etc.) with hydrogen peroxide. In practice this leads to an unprecedented structure for a vanadium (v) oxoperoxo complex which is contained in a mixed crystal.

Experimental

Reagent and apparatus

The solvents were purified by standard procedures and distilled under nitrogen.¹⁵ Commercial stabilized 30% aqueous solutions of hydrogen peroxide were acidic (pH ~ 1.5; phosphate concentration lower than 1.6 mM, or without phosphates in order to avoid the formation of phosphato-oxoperoxo vanadate species; supplied by Aldrich). tert-Butylhydroperoxide (TBHP; 5.0-6.0 M in decane) was used as received with 4% water. [n-Bu₄N][{Ph₃SiO}₂VO₂], HPA-3 and HPA-4 were prepared as previously described.¹ 2-Methylcyclohexanone, 2, better than 99% pure by GC and NMR analysis, was used without further purification. IR spectra (resolution: 2 cm⁻¹) were recorded on KBr pellets or Nujol suspensions using a Fourier transform apparatus (Bruker Vector 22). UV-visible diffuse reflectance spectra were measured on a Varian Cary 5E spectrophotometer equipped with an integration sphere and coupled to a microcomputer (BaSO₄ used as standard). ⁵¹V NMR spectra were recorded on a Bruker AC300 spectrometer operating at 78.9 MHz, in the Fourier transform mode, using a 10° pulse width of 2 µs without relaxation delay. Neat VOCl₃ was used as an external reference for chemical shifts ($\delta = 0$ ppm). Acquisition time: 45 ms; 10⁴ transients were accumulated. The solutions were obtained by dissolving 0.25 mmol of the compounds in 0.5 mL of CH₃CN and 0.1 mL of the deuterated solvent. Elemental analyses were carried out at the Service Central d'Analyses (CNRS, Lyon). Catalysis tests were performed in an all-glass reactor vessel (40 mL), which was attached to a vacuum line with a manometer and a gas inlet. It was charged with the catalyst (equivalent to 0.076 mmol of vanadium), the solvent (5 mL) and the substrate (7.6 mmol). The mixture was stirred magnetically for 8-24 h at 40, 50, or 60 °C. Under anaerobic conditions (dinitrogen), H₂O₂ or TBHP (15 mmol) was added. Under aerobic conditions, dioxygen uptake was monitored by means of a gas burette system. In both cases, the mixture was cooled and analysed by GC (OV 1701). An aliquot portion (usually 1 mL) including a standard (methyl heptanoate or naphthalene) was esterified by the addition of an ethereal solution of diazomethane to the crude mixture or after removing vanadium complexes on active charcoal. Products were identified by GC-MS analysis performed on a Trace GC 2000 gas chromatograph (50 m capillary column) interfaced to a (RTX-MS) mass selective detector. ¹H and ¹³C NMR spectra as well as MS (70 eV) or MS (CI, NH₃) data correspond to our previous identification ⁴ or to literature data.

$\label{eq:constraint} \begin{array}{l} \mbox{Preparation of } [P(C_6H_5)_4][\{(C_6H_5)_3\,SiO\}_2VO_2]_x-\\ [\{(C_6H_5)_3SiO\}_2VO(O_2)]_{1-x}, 1\ (x=0.57) \end{array}$

 $[n-Bu_4N]$ {Ph₃SiO}₂VO₂]¹ (0.5 g, 0.6 mmol) was dissolved with stirring in acetonitrile (5 mL). This solution was cooled in an ice bath and a 30% m/v aqueous solution of H₂O₂ (0.125 mL, 1.2 mmol) was added gradually. To the violet solution formed, an acetonitrile solution (2 mL) of PPh₄⁺Cl⁻ (0.42 g, 1.2 mmol) was added, leading to the precipitation of a greyish violet powder. This powder was filtered off, washed with diethyl ether and dried over P_4O_{10} to give 60% of 1. The product was recrystallized twice in acetonitrile/H₂O₂ mixtures at 10 °C to give blackish violet crystals used for X-ray measurements. The peroxygen content was determined by potentiometry (Ce3+/ Ce^{4+} titration with 0.1 M aqueous $[Ce(NH_4)_4(SO_4)_4]\cdot 2H_2O;$ oxidation with Ce(IV) involves peroxo groups only, showing the presence of nearly one O_2^{2-} for two vanadium centres, whereas iodine titration involves the reduction of the peroxo group and of V(v) to V(Iv)). The proportion of the mononuclear units in the mixed crystal was estimated from the final refinements (vide infra). It was in good agreement with ⁵¹V NMR measurements.

$$\label{eq:c6H5} \begin{split} & [P(C_6H_5)_4][\{(C_6H_5)_3SiO\}_2VO_2]_x[\{(C_6H_5)_3SiO\}_2VO(O_2)]_{1-x}, \quad 1 \\ & (x=0.57): \ C_{60}H_{50}O_{4.43}PSi_2V \end{split}$$

Anal. calc.: C, 73.53; H, 5.14; P, 3.16; Si, 5.73; V, 5.20; found: C, 73.40; H, 5.05; P, 3.07; Si, 5.30; V 5.10.

Single-crystal X-ray diffraction analysis

X-ray data for complex 1 were collected at room temperature using a Enraf-Nonius CAD-4 four-circle diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71069$ Å) by the $\omega - 2\theta$ method. The data were corrected for Lorentz and polarization effects and for absorption (ψ scan). The structure was solved by direct methods using the SHELX-86 program,¹⁶ subsequent Fourier difference techniques, and refined anisotropically for all non-hydrogen atoms. All hydrogen atoms were found on difference Fourier maps; their positions were not refined and they were given one overall isotropic parameter: $U_{\rm iso} = 0.113(3)$. Final refinements with CRYSTALS¹⁷ resulted in R = 0.051 and $R_w = 0.064$. Other refinement details and crystal data are summarized in Table 1. Bond lengths and angles are given in Table 2. The atomic scattering factors were taken from International Tables for Crystallography.¹⁸ (x = 0.50 corresponds to high values of U_{iso} for O(2) and O(3), an optimum would be $x = 0.57 \pm 0.03$).

CCDC reference number 222221.

See http://www.rsc.org/suppdata/dt/b4/b400657g/ for crystallographic data in CIF or other electronic format.

Results and discussion

CAMERON representations¹⁹ are shown in Figs. 1, 2 and 3.

The structure of $[P(C_6H_5)_4][\{(C_6H_5)_3SiO\}_2VO_2]_x$ - $[\{(C_6H_5)_3SiO\}_2VO(O_2)]_{1-x}, 1 (x = 0.57)$

The volume V of the unit cell (5085(4) Å³) is higher than previously found for pure $[P(C_6H_5)_4][\{(C_6H_5)_3SiO\}_2VO_2]$

Table 1 Crystal data and structure refinement of **1** $[P(C_6H_5)_4]-[\{(C_6H_5)_3 \text{ SiO}\}_2 \text{VO}_2]_x[\{(C_6H_5)_3 \text{ SiO}\}_2 \text{VO}(O_2)]_{1-x} (x = 0.57)$

Chemical formula	$C_{60}H_{50}O_{4.43}PSi_2V$			
Formula weight <i>M</i> /g mol ⁻¹	980.02			
Crystal system	Monoclinic			
Space group	$P2_1/n$ (no.14)			
aĺÅ	22.362 (8)			
b/Å	11.270 (6)			
c/Å	23.069 (6)			
βl°	119.00 (2)			
V/Å ³	5085 (4)			
Ζ	4			
μ/cm^{-1}	3.22			
Reflections: total	9714			
Used $(F_0)^2 > 3\sigma(F_0)^2$	5459			
Final R	0.0512			
Final $R_w^a I > 3\sigma(I)$	0.0636			
Goodness of fit (on F^2)	1.105			

^{*a*} Weighting scheme of the form $w = w'[1 - (||F| - |F_c|])/6\sigma(F_o)^2]^2$ with $w' = 1/\Sigma_r A_r T_r(X)$ for a Chebyshev series for which $X = F_c/F_c(\max)$ with coefficients for 1: 11.0, 3.5 and 8.99.

Table 2 Selected bond lengths (Å) and angles (°) for 1

Bond lengths		Bond angles	
V(1)–O(1)	1.619 (3)	O(1)–V(1)–O(4)	111.2 (4)
V(1)–O(4)	1.624 (9)	O(1)–V(1)–O(11)	111.7 (2)
V(1)–O(11)	1.820(2)	O(4)–V(1)–O(11)	110.6 (4)
V(1)–O(12)	1.829 (2)	O(1)-V(1)-O(12)	107.7 (2)
V(1)–O(2)	1.846 (8)	O(4) - V(1) - O(12)	111.7 (3)
V(1)–O(3)	1.787 (15)	O(11)–V(1)–O(12)	103.7 (1)
Si(1)–O(11)	1.612(2)	O(2)-V(1)-O(3)	47.6 (3)
Si(2)–O(12)	1.615(2)	O(1)-V(1)-O(3)	102.7 (5)
O(2)–O(3)	1.467 (8)	O(1)-V(1)-O(2)	104.7 (3)
Si(1)–C(101)	1.883 (4)	O(12)-V(1)-O(2)	89.0 (3)
Si(1)–C(107)	1.880 (4)	O(11)–V(1)–O(3)	98.0 (5)
Si(1)–C(113)	1.873 (4)	O(11)-V(1)-O(2)	135.0 (3)
Si(2)–C(221)	1.876 (4)	O(12)–V(1)–O(3)	132.3 (4)
Si(2)-C(227)	1.874 (4)		
Si(2)-C(233)	1.876 (4)		



Fig. 1 CAMERON view of the anion $[{Ph_3SiO}_2V^VO_2]^-$, 1a, of the mixed-crystal compound, 1.

 $(4976(2)Å^3)$.¹ Mononuclear oxoperoxo pentacoordinated d⁰ metal complexes are rare;^{10,20} only a chloroperoxidase isolated from *Curvularia inaequalis*, recently characterized by X-ray both in its native and its peroxo forms, is a pentacoordinated species.^{21,22} We have now been able to isolate a compound **1** which contains two interrelated anions: $[{Ph_3SiO}_2V^VO_2]^-$, **1a**, and $[{Ph_3SiO}_2V^VO(O_2)]^-$, **1b**, together in a mixed compound. In the crystal, the anions **1a** and **1b** are located at the same zones in the unit cell; *only the coordination numbers of the vanadium centres are different*.

Thus, the structures of **1a** and **1b** differ only slightly; in **1a** the vanadium atom has unusual tetrahedral coordination found in the parent *mononuclear complex* (Fig. 1), with the oxygen atoms



the mixed-crystal compound, 1.

C225



Fig. 3 CAMERON view of the coordination of the metal centre in $[{Ph_3SiO}_2V^VO(O_2)]^-$, **1b**, of the mixed-crystal compound, **1**.

of the Ph₃SiO ligands occupying two sites, and two terminal oxygen atoms occupying the remaining sites. The characteristic bond lengths in 1a are similar to those found in the previously studied mononuclear complex,¹ [PPh₄][{Ph₃SiO}₂VO₂]; the VO bond lengths to the terminal oxygens are 1.618(3) and 1.622(9) Å to O(1) and O(4), respectively. This suggests a bond order approaching two for the V=O linkages in the VO₂ group with a π component arising from electron transfer from O (p π) to V $(d\pi)$ orbitals.

The average V–O (Si) bond distance is 1.825(2) Å. The Si–O bond distances, 1.612(2) and 1.615(2) Å are comparable to those found in the parent siloxane rings.²³⁻²⁶

The Si(1)O(11)V(1)O(12)Si(2) moiety of 1a is almost planar, the largest deviation from the least-squares plane being 0.17 Å for V(1). The angle between the O(1)V(1)O(4) and Si(1)V(1)Si(2) planes is 90°. To the best of our knowledge, the first monomeric tetrahedral vanadium (V) species containing two silanolato ligands has been observed recently in the solid state;¹ only distorted square pyramidal, trigonal bipyramidal and octahedral geometries have been characterized with cis-dioxo groups²⁷⁻²⁹ but tetrahedral species exist in chains of purely inorganic vanadates.

In most monomeric oxoperoxo complexes the geometry is pentagonal bipyramidal.¹⁰ The only two cases of a pentagonal pyramidal geometry are for oxodiperoxovanadium complexes;30-31 for the other complexes with pentagonal monopyramids, the oxygen atom of another molecule or even of another metal centre may well serve as the seventh ligand with a long axial bond.32,33

Complex 1b is the first pentacoordinate structure for a monooxoperoxo anion for which the coordination environment of the vanadium atom is severely distorted and is close to a trapezoidal pyramid, with the oxo group occupying the apical position; the base is the peroxo group and the oxygen atoms of the triphenylsilanolato ligands (Figs. 2 and 3). It is derived from the tetrahedral structure of **1a** by replacing one of the two oxo ligands by a peroxo group.

The structure analysis is good enough ($R \simeq 5\%$) for unambiguous characterization of this novel arrangement which is consistent with the peroxygen content, IR and UV-visible spectra (vide infra). Crystallizations with other cations did not succeed in separating anions 1a and 1b. We think that there is an equilibrium between the two vanadium (v) species with decomposition of 1b and of excess H₂O₂ during the slow crystallization process. It is well known that aqueous (and nonaqueous) solutions of peroxovanadates are not as stable as their analogues with peroxotungstates. They decompose rapidly with the formation of $V_2O_5 \cdot nH_2O$ gels rather than stable oxoperoxo compounds. The isolation of the mixed salt corresponds to the equilibrium between 1a and 1b with the optimum concentrations for precipitation of 1 with PPh₄⁺Cl⁻. The peroxo group O(2)-O(3) with O(11) and O(12) defines a trapezium (Fig. 3) with vanadium and O(1) atoms 0.547 and 2.161 Å, respectively, from the rms plane corresponding to a V=O bond length of 1.619(3) Å, in accordance with the vanadium complexes.¹⁰ The vanadium to oxygen bond lengths of the η^2 -peroxo group are 1.846(8) and 1.787(15), in line with what is found in the complexes considered above, 10,13,32,33 as is the O(2)– O(3) length of 1.467(8) Å; usually the O–O separation in peroxo groups is in the range 1.379-1.451 Å. The Si-O and Si-C bond distances are comparable to those found in siloxane rings and metallasiloxanes.23-26

$$[\{(C_6H_5)_3SiO\}_2VO_2]^- + H_2O_2 \rightleftharpoons$$
1a
$$[\{(C_6H_5)_3SiO\}_2V(O)(O_2)]^- + H_2O$$
1b

UV-visible spectroscopy

1.2

The instability of solutions of the oxoperoxo species, even in the presence of H₂O₂, led us to study solid samples. The UV-visible spectra of 1 exhibit three maxima, at 288, 356 and 559 nm (Fig. 4). The first one, nearly identical to one band of the free ligand, is probably due to an intraligand $\pi \rightarrow \pi^*$ transition,²⁸ whereas the second one can be attributed to a LMCT band originating from the high π -donating power of the oxo group. In the dioxo complex of vanadium (v), $[PPh_4]$ -[{Ph₃SiO}₂VO₂],¹ these two bands also appear but they are shifted to lower values (281 and 349 nm, respectively). The third maximum is mainly due to the presence of the peroxo ligand, which induces strong charge transfer to the metal centre. It is noteworthy that this band is located in the 510-560 nm region

355.9 1,0 0.8 ရှိ 0,6 [PPh4][(Ph3SiO)2VO2]x [(Ph₃SiO)₂VO(O₂)]_{1-x}, 1 0,4 0,2 0,0 200 400 600 800 λ (nm)

Fig. 4 UV-visible spectra of [PPh₄][(Ph₃SiO)₂VO₂]_v[(Ph₃SiO)₂- $VO(O_2)_{1-x}$, 1, (x = 0.57) and [PPh₄][(Ph₃SiO)₂VO₂] (solid samples).



Fig. 5 IR spectra of 1 and of [n-Bu₄N][{Ph₃SiO}₂VO₂] (solid samples).

characteristic for peroxo complexes of vanadium (v).³⁴ (The mono-oxoperoxo vanadium cation forms a deep red solution with $\lambda_{max} = 462$ nm.) As vanadium (v) complexes are d⁰ systems, d–d bands are not expected in these complexes.

IR spectroscopy

As 1 is a mixed-crystal, its IR spectra (Fig. 5) exhibit several bands, due to the presence of both anions: $[{Ph_3SiO}_2V^VO_2]^-$, 1a, and $[{Ph_3SiO}_2V^VO(O_2)]^-$, 1b. Fig. 5 clearly shows the main differences between 1 and the precursor. All characteristic bands appear in the regions expected for oxoperoxo complexes of vanadium (v).35 A sharp band at 872 cm⁻¹ is associated with the peroxo moiety of the anion 1b, as described in the literature.^{10,36} Two maxima at 625 and 756 cm⁻¹ are tentatively assigned to the symmetrical and antisymmetrical vibrations of the vanadium peroxo unit, $V(O_2)$ in 1b, based on previous comparisons with the mono-oxoperoxo complexes and with Ph₃SiOH and PPh₄⁺ salts.³⁶⁻³⁸ These bands confirm the η^2 -coordination of the peroxo group. A band at 975 cm⁻¹ is attributed to the $\tilde{v}(V=O)$ mode of the mono-oxo group of anion 1b. Indeed, all the mono-oxo complexes display one sharp band in the 950–980 cm⁻¹ region, while the dioxo compounds usually show two bands corresponding to \tilde{v}_{sym} (O=V=O) and $\tilde{v}_{antisym}$ (O=V=O). In our case, 1 presents only one band at 938 cm⁻ due to the pervanadyl species, VO_2^+ , with a shoulder at 917 cm⁻¹. This band is located at 939 cm⁻¹ with a shoulder at 919 cm⁻¹ in the IR spectra of [PPh₄][{Ph₃SiO}₂VO₂].¹ In addition, some bands can be assigned to the [Ph₃SiO]⁻ ligands. Thus, a sharp ligand band in the 1580-1600 cm⁻¹ region is associated with the $\tilde{\nu}(C-C)$ of the phenyl ring ^{36,38} and a very sharp band at 1109 cm⁻¹ corresponds to an in-plane deformation of the phenyl ring δ (C–H), with some \tilde{v} (Si–C) character. The IR data are in agreement with the structure found by X-ray analysis. The Raman spectra for solid and MeCN solutions suggest that the overall structures of 1a and 1b are conserved at room temperature during a short time, as would be expected for a compound originally prepared in acetonitrile.

⁵¹V NMR spectra of dioxo-species and of 1 in a mixture of CH₃CN/CD₃CN

At 297 K, the resonances have line-widths at half-height of approximately 80–100 Hz which is still considered as narrow in ⁵¹V NMR spectroscopy. The dioxovanadium (v) complex, $[n-Bu_4N][\{Ph_3SiO\}_2VO_2]$, exhibits one strong resonance at ca. -593.3 ppm while the dinuclear complex $[n-Bu_4N]_2[\{Ph_2-SiO_2VO_2\}]_2$ displays one band at -576.3 ppm. We never observed a peak around $\delta = -545$ ppm due to the free $[VO_2]^+$ cation of the HPA-*n* solutions (n = 3, 6) which suggests that the overall structure of the two pervanadyl complexes are conserved in CH₂CN/CD₂CN at room temperature as they were in methanol.¹ The spectrum of the solution obtained just after dissolution of 1 exhibits two sharp, not completely resolved peaks at -595.3 and -596.8 ppm which are assigned to the dioxo and oxoperoxo anions. Deconvolution of the spectra leads to the relative ratio 55/45 in agreement with X-ray and chemical analysis determinations. The two peaks progressively broaden while one and two bumps appear at around -592.6 ppm. The origin of these new peaks is not clear. There is no evidence of [VO(O₂)]⁺ characterized at -539.0 ppm. The ⁵¹V NMR spectrum of the solution progressively changes with time (more than 5 peaks after 4 weeks at room temperature). Recent work shows that mono-oxoperoxo complexes display resonance around -590 ppm;³⁹ thus 1 with two sharp peaks (-595.3 and -596.8 ppm) can be considered as a mixed compound. These spectra are not run with strict exclusion of air, and we know that some redox chemistry and dioxygen activation can take place between the vanadium peroxo complexes and dissolved dioxygen.

Reactivity

Preliminary catalysis tests (oxidation of 2-methylcyclohexanone, 2) were made under anaerobic and aerobic conditions. The results are summarized in Table 3. We used peroxo and alkylperoxocomplexes of vanadium (v)⁴⁰ and heteropolyacids, $H_{3+n}[PMo_{12-n}V_nO_{40}]_{ag}$ with n = 3 and 4 as reference catalysts. Regioselective cleavage of 2 gives 6-oxoheptanoic acid, 3, in the form of its methyl ester as the main product, the best results being obtained with HPA-n and dioxygen. Reactions carried out with H₂O₂ or TBHP are less selective and more by-products are obtained because of several competing homolytic processes; among the by-products acetic acid and cyclopentanone were detected. It is noteworthy that reactions involving H₂O₂ or TBHP can be carried out at room temperature; however, the rate rises significantly on going to 40-50 °C with a decrease in selectivity. Moreover, hydroxylation of C₆H₅ groups was observed as a minor reaction with V/H₂O₂ systems related to the formation of HO' radicals. Nevertheless, it is reasonable to assume that peroxo derivatives can act as intermediates in the oxidative cleavage of C-C bonds.¹ The results with H_2O_2 are not surprising since it was found a long time ago that V₂O₅/ H₂O₂-H₂O/MeOH/cyclohexanone mixtures give adipic acid and 6-oxohexanoic acid (adipaldehyde).41

The peroxo complexes of vanadium have not, compared to the other elements (Ti(Iv), Mo(vI) and W(vI)) been used extensively. The ease of the redox step, V(v)–V(Iv), introduces a mixture of two-electron and one-electron character into vanadium-peroxo chemistry, which in many cases leads to side-reactions of substrate and products. With H_2O_2 , vanadium

ble 3	Oxidation of 2-methylcyclohexanone, 2, to 6-oxoheptanoic acid, 3						
	Ru	un	Catalyst precursor	Oxidant	Conv. (%) ^{<i>e</i>}	Yield (%) ^e	
	1^{a} 2^{b} 3^{c} 4^{d}	1 	1 [VO(OO- <i>t</i> -Bu)(dipic)(H ₂ O] HPA-4 (V ^{IV} /V ^V) HPA-3	$\begin{array}{c} H_2O_2\\ TBHP\\O_2\\O_2\end{array}$	80 92 100 99	55 67 90 97	

.... Ta

^a Reaction conditions: precursor, 0.076 mmol; 2, 7.6 mmol; H₂O₂, 15 mmol; MeCN, 5 mL; temperature, 40 °C; reaction time, 24 h. ^b Reaction conditions: precursor, 0.76 mmol; 2, 7.6 mmol; TBHP in decane, 15 mmol; decane, 5 mL; temperature, 50 °C, reaction time, 24 h. e Reaction conditions: precursor, equivalent to 0.076 mmol of vanadium; 2, 7.6 mmol; methanol, 5 mL; dioxygen pressure, 0.1 Mpa; temperature, 60 °C; reaction time, 24 h. d Reaction in water (5 mL) for 8 h; see (c) for the other parameters. Conversions (% of substrate consumed) and yield ([mmol of product per mmol of substrate] × 100) were determined by GC analysis (OV 1701) after addition of an ethereal solution of diazomethane.

exhibits some one-electron (V(v)-(IV)) redox chemistry, introducing free-radical character into its reactions.

A final practical note is that, owing to the one-electron chemistry, much more decomposition of excess H₂O₂ is caused by vanadium systems than with W, Mo and Re. Our work is devoted to the development of catalysts for C-C bond cleavage by dioxygen, hydrogen peroxide and alkyl hydroperoxide with purely inorganic precursors (without any oxidizable ligand) easy to prepare and to apply. These precursors or catalysts are a trump card for homogeneous, two- or even three-phase systems. Here, the ligand Ph₃Si-O is sensitive to "oxidative degradation" and we cannot consider a thorough study on this system as a priority.

With the discovery that solvents, acidity function, counterions and experimental conditions (for the addition of dioxygen or H₂O₂) have a major effect on rates and selectivity of reactions (involving HPA-n and dioxygen or peroxovanadates and H_2O_2) there is a need for thorough studies on the reaction of vanadium- and tungsten-based systems with H2O2 as a means of preparing adipic acid from cyclohexene as well as from cyclohexane and dioxygen; they are under study in our group.5,42,43

Conclusion

As part of a general programme concerned with modelling heteropolyacid catalysts, $H_{3+n}[PMo_{12-n}V_nO_{40}]_{aq}$ (where n = 1-9), we investigated the synthesis, characterization and reactivity of complexes containing the pervanadyl, $[VO_2]^+$, and $[VO(O_2)]^+$ cores with ligands derived from weak¹ and very strong acids⁴³ (e.g. Ph₃SiOH, Ph₂Si(OH)₂, etc. and Me-C₆H₄SO₃H, CF₃SO₃H, etc.). The preparation and characterization of a mixed crystal, $[P(C_6H_5)_4][\{(C_6H_5)_3SiO\}_2VO_2]_x[\{(C_6H_5)_3SiO\}_2VO(O_2)]_{1-x},$ (x = 0.57), with an oxoperoxoheterosiloxane vanadium (v) anionic moiety and a novel type of structure, have been described, demonstrating that vanadium (v) in a peroxo compound can be five-coordinated. Complex 1b with the $[VO(O_2)]^+$ core provides a coordination number and even an arrangement around vanadium which is the closest to that found in Vchloroperoxidase in Curvularia inaequalis (peroxygen form).^{21,22} In the native chloroperoxidases, vanadium is also in a fivecoordinated trigonal bipyramidal geometry.²¹ Addition of hydrogen peroxide converts the arrangement to tetragonal pyramidal;²¹ the double-bonded oxygen is in the apical position while the peroxo ligand is bound to the vanadium in an η^2 fashion and is in the basal plane, as are a hydroxyl ligand and nitrogen from histidine. To the best of our knowledge, the first models of VHPOs have pentagonal bipyramidal structures with axial carboxylate oxygen and terminal oxo ligand.⁴⁶ In 1b, two oxygen atoms of the Ph₃SiO⁻ ligands replace O and N from the hydroxyl and histidine, respectively. Steric constraints of the Ph₃SiO⁻ ligands and PPh₄⁺ are certainly responsible for this structure. This anion also stabilizes novel structural types (e.g. pentagonal monopyramidal arrangement in mono- and dianionic species, [Ph₃SiO{MO(O₂)₂}]⁻ and [(Ph₂SiO{MO- $(O_2)_2$ }_2O]^{2-} with M = Mo or W).³⁷ [PPh₄]⁺[Ph₃SiO{WO(O_2)_2}]⁻ is one of the rare examples of "six-fold phenyl embrace" (6PE) between a $-SiPh_3$ group and a PPh_4^+ cation with Si \cdots P = 6.61 Å, O-Si \cdots P-C colinearity = 175.4°.⁴⁴ 1 gives another example of multiple phenyl interactions (Si \cdots P = 6.03–6.75 Å and O–Si \cdots P–C colinearity = 172.0°). Peroxo complex 1 and the alkylperoxo complex [VO(OO-t-Bu)(dipic)(H₂O)],⁴⁰ catalyse oxidative C-C bond cleavage in 2-methylcyclohexanone, 2, and a number of compounds under study. Oxoperoxo derivatives are also probably intermediates in the reactions which involve HPA-*n* catalysts, $[VO_2]^+$, cycloalkanone and dioxygen giving peroxygen species which decompose by homolytic fission of O-O bonds, with simultaneous or concerted C-C bond cleavage, as proposed recently.1 Rates and selectivity of oxidation of varied substrates by HPA-n or oxoperoxo complexes are significantly affected by several parameters;42,45-46 their impact will be further investigated with the study of novel catalysis systems.

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