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Synthesis and characterization of novel oxovanadium(IV) complexes with 4-acyl-5-pyrazolone donor ligands: Evaluation of their catalytic activity for the oxidation of styrene derivatives

Fabio Marchetti^{a,*}, Claudio Pettinari^a, Corrado Di Nicola^a, Riccardo Pettinari^a, Alessandra Crispini^b, Marcello Crucianelli^{c,**}, Andrea Di Giuseppe^c

^a Dipartimento di Scienze Chimiche, Università degli Studi di Camerino, Via S. Agostino 1, I-62032 Camerino, MC, Italy

^b Centro di Eccellenza CEMIF.CAL-LASCAMM, CR-INSTM (Unità della Calabria, Dipartimento di Chimica), Dipartimento di Scienze Farmaceutiche, Edificio Polifunzionale,

Università della Calabria, I-87030 Arcavacata di Rende, CS, Italy

^c Dipartimento di Chimica, Ingegneria Chimica e Materiali, Università dell'Aquila, via Vetoio, I-67100 Coppito, AQ, Italy

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ABSTRACT

Reaction of VOSO₄·5H₂O with a methanol solution of the HQ proligand (HQ=1-R¹-4-R²(C=O)pyrazol-5-one in general, in detail: HQ^{nPe}, R¹ = phenyl, R² = neopentyl; HQ^{Me,Me}, R¹ = R² = methyl; HQ^{Me,naph}, R¹ = methyl, R² = naphthalen-1-yl; HQ^{naph}, R¹ = phenyl, R² = naphthalen-1-yl; HQ^{Ph}, R¹ = R² = phenyl; HQ^{CF3}, R¹ = phenyl, R² = trifluoromethyl; HQ^{py,CF3}, R¹ = pyridin-2-yl, R² = trifluoromethyl) gave seven novel VO(Q)₂(H₂O) complexes which have been characterized by elemental analyses, IR, ESI-MS, electronic spectroscopy and magnetic susceptibility measurements and, in the case of derivative VO(Q^{CF3})₂, also by EPR spectroscopy. The X-ray diffraction study, carried out on derivative VO(Q^{nPe})₂(H₂O), evidenced a distorted octahedral environment with the two pyrazolonates in *anti* configuration and the vanadium atom 0.2914(7)Å away from the least-squares plane defined by the four equatorial oxygen atoms. The catalytic activity of these new oxovanadium(IV) complexes has been exhaustively tested for the oxidation of styrene, α -methylstyrene and *cis*- β -methylstyrene, in the presence of H₂O₂ as primary oxidant. The effects of oxidant to substrate molar ratio, catalyst amount, solvent and temperature have been studied. Overall, the vanadium complexes showed high activity and high to moderate selectivity toward the benzaldehyde (acetophenone) formation, depending from both the type of starting substrate and experimental reaction times.

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1. Introduction

The family of vanadium compounds is receiving increasing interest due to its rich applications in many fields [1–7]. In fact, it plays an important role in many enzymatic reactions such as halogenation of organic substrate and fixation of nitrogen [8–10]. Moreover, oxovanadium(IV) compounds with *O*,*O*-donor ligands are very effective insulin-like agents, as they show insulin-mimetic response which can simulate the uptake and metabolism of glucose through alternative signalling pathways [11–17]. In addition, a variety of enzymatic activities have been observed by vanadium complexes able to mimic, among others, the peroxidase and catalase activities [13], as showed in the case of different oxovanadium(IV) complexes in recently published papers [18,19]. One

* Corresponding author. Fax: +39 0737 637345.

** Corresponding author. Fax: +39 0862 433753.

E-mail addresses: fabio.marchetti@unicam.it (F. Marchetti), marcello.crucianelli@univaq.it (M. Crucianelli).

of the most important properties of the vanadium complexes, which considerable effort has been devoted to, is that they possess versatile oxidation states and unusual redox ability. Commonly, vanadium can exist in +3, +4 and +5 oxidation states. It has been documented that in +4 and +5 oxidation states vanadium has strong redox ability which can lead to some important reactions [20-22]. Currently, there is a growing interest in the study of catalytic applications of high-valent vanadium complexes, also due to the presence of vanadium in several metalloenzymes [23,24]. Soluble and supported vanadium complexes showed to efficiently catalyze various oxidative transformation of organic compounds as olefins and allylic alcohols, alkylaromatic compounds, alkanes, sulfides and alcohols, being able to activate environment friendly oxidants as dioxygen or hydrogen peroxide (see some reviews [25,26] and recent selected original papers [27-35]). H₂O₂ is an attractive oxidant not solely because it is more active than O_2 , but rather because it reacts affording H₂O as the only by-product. Moreover, in certain circumstances, it is better than dioxygen insofar as O₂/organic mixtures can sometimes spontaneously ignite.

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Oxo and peroxo derivatives of vanadium complexes play an important role in such catalytic oxidations, acting as oxotransfer agents [36,37]. Many different papers describing the synthesis, characterization and catalytic applications of peroxovanadium complexes, may be found in literature (for selected examples see [38–43]). A very interesting study devoted to elucidate the mechanism of oxidation with H_2O_2 , of either isopropanol or cyclohexane, promoted by oxovanadium(V) triethanolaminate/pyrazine-2-carboxylic acid system, has been recently published [44].

Herein we report the synthesis and full characterization of new oxovanadium(IV) acylpyrazolonate complexes, where acylpyrazolonate ligands are a new version of β -diketonates containing a pyrazole moiety fused to the chelating ring [45–49]. The catalytic properties of the new mononuclear complexes have also been thoroughly studied, in the hydrogen peroxide promoted oxidation of styrene derivatives, under homogeneous conditions. Interestingly, working with optimized experimental conditions, high to moderate selectivity toward benzaldehyde formation, has been observed, during oxidation of either styrene or *cis*- β -methylstyrene, irrespective from the nature of used catalyst. Benzaldehyde is an attractive target because of it is an important intermediate in the production of derivatives for perfumery, pharmaceutical, dyestuff and agrochemical industries.

2. Experimental

2.1. Instruments and reagents

All reagents and solvents were purchased from Alfa (Karlsruhe) and Aldrich (Milwaukee) in the highest purity grade available and were used as such. A 35% aqueous solution of hydrogen peroxide was used as primary oxidant. The acylpyrazolone proligands HQ, namely HQ^{nPe} (1-phenyl-3-methyl-4-tert-butylacetyl-5-HO^{Me,Me} (1,3-dimethyl-4acetyl-5-pyrazolone), pyrazolone), HQnaph [1-phenyl-3-methyl-4-(1-naphthoyl)-5-pyrazolone], HQ^{Me,naph} [1,3-dimethyl-4-(1-naphthoyl)-5-pyrazolone], HQ^{Ph} HQ^{CF3} (1-phenyl-3-methyl-4-benzoyl-5-pyrazolone), (1 -

phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone), and HQ^{py,CF3} [1-(2-pyridyl)-3-methyl-4-trifluoroacetyl-5-pyrazolone], were synthesized as previously reported [46-49]. The samples for microanalyses were dried in vacuo to constant weight (20°C, ca. 0.1 Torr). Elemental analyses (C, H, N, S) were performed in-house with a Fisons Instruments 1108 CHNS-O Elemental Analyzer. IR spectra were recorded from 4000 to 600 cm⁻¹ with a Perkin Elmer Spectrum 100 FT-IR instrument. ¹H and ¹⁹F NMR spectra of proligands HQ were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ¹H and 282.2 MHz for ¹⁹F). The electrical conductances of the acetonitrile solutions were measured with a Crison CDTM 522 conductimeter at room temperature. The magnetic susceptibilities were measured at room temperature (20 °C) by the Gouy method, with a Sherwood Scientific Magnetic Balance MSB-Auto, using HgCo(NCS)₄ as calibrant and correcting for diamagnetism with the appropriate Pascal constants. The magnetic moments (in BM) were calculated from the equation $\mu_{\text{eff}} = 2.8428 (\chi_m^{corr} T)^{-1/2} (\chi_m^{corr}$ is the molar susceptibility corrected for diamagnetism and T is the temperature in kelvin degrees). The electronic spectra of the ligands HQ^{nPe} and HQ^{CF3} and of the corresponding derivatives I and VI (see onward Scheme 1) were recorded in ethanol (or acetonitrile) solution with a HP 8452A Diode Array spectrophotometer. The positive and negative electrospray mass spectra were obtained with a Series 1100 MSI detector HP spectrometer, using an acetonitrile or methanol or ethanol mobile phase. Solutions (3 mg/mL) for electrospray ionization mass spectrometry (ESI-MS) were prepared using reagent grade acetonitrile or methanol or ethanol. For the ESI-MS data, mass and intensities were compared to those calculated using IsoPro Isotopic Abundance Simulator, version 2.1 [50]. Peaks containing vanadyl(IV) and vanadium(III) ions were identified as the highest peak of an isotopic cluster. TGA-DTA spectra were obtained with a STA 6000 Simultaneous Thermal Analyzer Perkin-Elmer. The 9.5 GHz EPR X-band spectrometer was a conventional assembly of Bruker units (Bruker Spectrospin, Milano, Italy), namely: a magnet B-M8, a resonant cavity 4108 TMH/9101, and a microwave bridge ER040XR, equipped with the field controller BH15. Gas chromatography-mass spectrometry (GC-MS) analyses of the



Scheme 1. General procedure for the preparation of oxovanadium(IV) complexes I-VII.

Table 1

Yields and elemental analyses obtained	for the novel oxovanadium(IV) compl	exes I–VII.
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Compound	Yield (%)	Formula	Calculated (found)		
			%C	%Н	%N
VO(Q ^{nPe}) ₂ (H ₂ O) I	78	C ₃₂ H ₄₀ N ₄ O ₆ V	61.24 (61.56)	6.42 (6.60)	8.93 (9.31)
VO(Q ^{Me,Me}) ₂ (H ₂ O) II	88	$C_{14}H_{20}N_4O_6V$	42.98 (43.34)	5.15 (4.93)	14.32 (14.39)
VO(Q ^{Me,naph}) ₂ (H ₂ O) III	84	C ₃₂ H ₂₈ N ₄ O ₆ V	62.44 (62.06)	4.59 (4.57)	9.10 (8.89)
$VO(Q^{naph})_2(H_2O)$ IV	86	$C_{42}H_{32}N_4O_6V$	68.20 (67.83)	4.36 (4.31)	7.57 (7.37)
$VO(Q^{Ph})_2 V$	80	$C_{34}H_{26}N_4O_5V$	65.70 (66.02)	4.22 (4.30)	9.01 (9.21)
$VO(Q^{CF3})_2$ VI	83	$C_{24}H_{16}F_6N_4O_5V$	45.75 (45.49)	2.43 (2.54)	8.63 (8.84)
$VO(Q^{py,CF3})_2$ VII	77	$C_{22}H_{14}F_6 N_6O_5V$	44.50 (43.51)	2.25 (2.32)	13.55 (13.84)

oxidative reaction products were performed by means of a Varian 2000 GC-MAS instrument, using a 30 m × 0.32 mm × 0.25 μ m film thickness (crosslinked 5% phenylmethylsiloxane) column and chromatography grade helium, as carrier gas. In GC calculations, all peaks amounting to at least 0.5% of the total products were taken into account. When necessary, ¹H and ¹³C NMR analyses of products were performed after flash-chromatographic purification on columns packed with silica gel (230–400 mesh), and compared with authentical sample. Mass spectra were recorded with an electron beam of 70 eV.

2.2. Catalysts preparation

2.2.1. General procedure for the preparation of $VO(Q^{nPe})_2(H_2O)$ (I)

A water solution (10 mL) of VOSO₄·5H₂O (0.253 g, 1.0 mmol) was added to a methanol solution (20 mL) containing the proligand HQ^{nPe} (0.544 g, 2 mmol) and NaOCH₃ (0.108 g, 2 mmol), and the reaction mixture was refluxed by stirring for 4 h. A pale green precipitate slowly afforded which was filtered off, washed with methanol (10 mL) and dried under vacuum. It is soluble in acetone, acetonitrile, dimethylsulfoxide (DMSO) and chlorinated solvents. Compounds **II–VII** were prepared following the same procedure as that reported for **I**, by using VOSO₄·5H₂O, the corresponding proligands (*i.e.* HQ^{Me,Me} for **II**, HQ^{Me,naph} for **III**, HQ^{naph} for **IV**, HQ^{Ph} for **V**, HQ^{CF3} for **VI**, HQ^{Py,CF3} for **VII**, respectively) and NaOCH₃.

2.3. Catalyst characterization

Yields and elemental analyses obtained for oxovanadium(IV) complexes **I–VII**, are shown in Table 1.

VO(**Q**^{nPe})₂(**H**₂**O**) (**I**): μ_{eff}: 1.82 BM. IR (nujol, cm⁻¹): 3325br ν(O–H), 3070w ν(C_{arom}–H), 1658sh ν(O–H), 1600m, 1592s ν(C... O), 1575vs, 1532m ν(C...N+C...C), 977vs ν(V=O), 506sh, 494vs, 471s ν(V–O_Q). UV–vis (CH₃CN): 255 nm very broad (*n*–π^{*} and π–π^{*}), 580 nm very broad, 660 nm broad (*d*–*d*). UV–vis of the proligand HQ^{nPe} (CH₃CN): 233 nm (*n*–π^{*}), 268 nm (π–π^{*}). ESI-MS (MeCN) (+): *m/z* (%)=610 (35) [{VO(Q^{nPe})₂}H]⁺, 632 (45) [{VO(Q^{nPe})₂}Na]⁺, 648 (100) [{VO(Q^{nPe})₂}K]⁺. TGA-DTA (mg% vs.°C): heating from 35 to 500°C with a speed of 7°C/min; from 98 to 120°C loss of one water molecule (weight loss found 2.15%, calcd 2.86%; Δ*H* = 14.90 kJ/mol); an onset fusion at 238°C (Δ*H*_{fusion} = 16.87 kJ/mol). **VO(Q^{Me,Me})₂(H₂O) (II)**: scarcely soluble in all common solvents.

VO(**Q**^{Me,Me})₂(**H**₂**O**) (**II**): scarcely soluble in all common solvents. μ_{eff} : 1.95 BM. IR (nujol, cm⁻¹): 3300br ν (O–H), 1665sh δ (O–H), 1595vs ν (C... O), 1535s, 1503vs ν (C... N+C... C), 890vs ν (V... O). ESI-MS (MeCN) (+): m/z (%)=374 (100) [{VO(**Q**^{Me,Me})₂}H]⁺, 412 (80) [{VO(**Q**^{Me,Me})₂}K]⁺, 437 (40) [{VO(**Q**^{Me,Me})₂(MeCN)}Na]⁺, 769 (75) [{VO(**Q**^{Me,Me})₂}Na]⁺. TGA-DTA (mg% vs. °C): heating from 35 to 500 °C with a speed of 7 °C/min; from 110 to 130 °C loss of one water molecule (weight loss found 4.50%, calcd 4.60%, ΔH = 39.56 kJ/mol); from 280 to 350 °C sublimation, confirmed by the IR spectrum of the sublimed powder ($\Delta H_{sublimation}$ = 134.04 kJ/mol). **VO**(**Q**^{Me,naph})₂(**H**₂**O**)(**III**): soluble in acetone, acetonitrile, DMSO and chlorinated solvents. μ_{eff} : 1.85 BM. IR (nujol, cm⁻¹): 3350br ν (O–H), 3054w ν (C_{arom}–H), 1660sh δ (O–H), 1580vs, 1570vs, 1506m ν (C... O+C... N+C... C), 967vs ν (V... O). ESI-MS (MeOH) (+): *m/z* (%) = 289 (30) [(HQ^{Me,naph})Na]⁺, 598 (30) [{VO(Q^{Me,naph})₂}H]⁺, 620 (20) [{VO(Q^{Me,naph})₂}Na]⁺, 1196 (10) [{VO(Q^{Me,naph})₂}2H]⁺, 1218 (100)[{VO(Q^{Me,naph})₂}2Na]⁺, 1234 (10)[{VO(Q^{Me,naph})₂}2K]⁺. TGA-DTA (mg% vs.°C): heating from 35 to 600°C with a speed of 7°C/min; from 60 to 110°C loss of one water molecule (weight loss found 3.12%, calcd 2.92%); from 230 to 600°C progressive decomposition, with a final black residual of 50% weight.

VO(**Q**^{naph})₂(**H**₂**O**) (**IV**): soluble in DMSO and slightly soluble in acetonitrile. μ_{eff} : 1.80 BM. IR (nujol, cm⁻¹): 3390br ν (O–H), 3053w ν (C_{arom}–H), 1665sh δ (O–H), 1600s ν (C... O), 1563vs, 1528m ν (C... N+C... C), 971s ν (V... O). ESI-MS (MeCN) (+): m/z (%)=351 (100) [(HQ^{naph})Na]⁺, 367 (50) [(HQ^{naph})K]⁺, 722 (10) [{VO(Q^{naph})₂}H]⁺, 744 (20) [{VO(Q^{naph})₂}Na]⁺, 760 (25) [{VO(Q^{naph})₂}K]⁺. TGA-DTA (mg% vs. °C): heating from 35 to 600 °C with a speed of 7 °C/min; from 140 to 200 °C loss of one water molecule (weight loss found 2.62%, calcd 2.43%); from 230 to 600 °C progressive decomposition, with a final black residual of 55% weight.

VO(**Q**^{Ph})₂ (**V**): soluble in acetone, acetonitrile, DMSO and chlorinated solvents. μ_{eff} : 1.85 BM. IR (nujol, cm⁻¹): 3051w ν (C_{arom}-H), 1601s, 1591s ν (C... O), 1567vs, 1536m ν (C... N+C... C), 900vs ν (V... O). ESI-MS (MeCN) (+): m/z (%)=644 (60) [{VO(Q^{Ph})₂}Na]⁺, 660 (95) [{VO(Q^{Ph})₂}K]⁺, 1265 (100) [{VO(Q^{Ph})₂}2Na]⁺. TGA-DTA (mg% vs.°C): heating from 35 to 700 °C with a speed of 7 °C/min; at 325 °C an onset fusion (ΔH_{fusion} = 51.15 kJ/mol); from 327 to 700 °C progressive decomposition, with a final black residual of 44% weight.

VO(**Q**^{CF3})₂ (**VI**): soluble in acetone, acetonitrile, DMSO and chlorinated solvents. μ_{eff} : 1.76 BM. IR (nujol, cm⁻¹): 3067w ν (C_{arom}-H), 1618sbr ν (C... O), 1587sbr, 1543m ν (C... C + C... N), 896vs ν (V=O), 519s, 480s, 400s ν (V–O_Q). UV–vis (CH₃CN): 242 nm (n– π *), 296 nm (π – π *), 627 nm broad, 745 nm very broad (d–d). UV–vis of the proligand HQ^{CF3} (CH₃CN): 231 nm (n– π *), 271 nm (π – π *). ESI-MS (CH₃CN) (+): m/z (%)=293 (95) [(HQ^{CF3})Na]⁺, 606 (35) [$VO(Q^{CF3})_2$]H]⁺, 628 (100) [$VO(Q^{CF3})_2$]Na]⁺. ESI-MS (EtOH) (+): m/z (%)=293 (82) [(HQ^{CF3})Na]⁺, 428 (100) [$VO(Q^{CF3})_2$ [HOH)₂]]⁺, 606 (70) [$VO(Q^{CF3})_2$]H]⁺, 628 (38) [$VO(Q^{CF3})_2$]Na]⁺, 652 (25) [$VO(Q^{CF3})_2$ (EtOH)]H]⁺, 674 (15) [$VO(Q^{CF3})_2$ (EtOH)]Na]⁺, ESI-MS (EtOH) (–): m/z (%)=269 (80) [(Q^{CF3})]⁻, 561 (100) [$Na(Q^{CF3})_2$]⁻, 650 (40) [$VO(Q^{CF3})_2$ (EtO)]⁻, 718 (17) [$VO(Q^{CF3})_2$ (EtO)₂Na]⁻, 874 (20) [$VO(Q^{CF3})_3$]⁻, 1227 (15) [$VO(Q^{CF3})_2$]OH]⁻. TGA-DTA (mg% vs. °C): heating from 35 to 600 °C with a speed of 7 °C/min; from 250 to 355 °C sublimation, confirmed by the IR spectrum of the sublimed powder ($\Delta H_{sublimation}$ =33.42 kJ/mol).

VO(**Q**^{**py**,**CF3**})_{**2**} (**VII**): soluble in acetone, acetonitrile, DMSO and chlorinated solvents. μ_{eff} : 1.85 BM. IR (nujol, cm⁻¹): 3148w ν (C_{arom}-H), 1675s ν (C... O), 1611m, 1581s, 1558s, 1538m ν (C... C+C... N), 919vs ν (V=O), 518s, 475s, 436s ν (V–N_Q). ESI-MS (MeCN) (+): m/z (%)=294 (100) [(HQ^{py,CF3})Na]⁺, 608 (50) [{VO(Q^{py,CF3})₂}H]⁺, 629.8 (100) [{VO(Q^{py,CF3})₂}Na]⁺. TGA-DTA (mg% vs.°C): heating from 35 to 700 °C with a speed of 7 °C/min;

Table 2

Crystal data and structure refinement for complex I.

Compound	I
Empirical formula Formula weight Temperature (K) Wavelength (Å) Crystal system Space group	C ₃₂ H ₄₀ N ₄ O ₆ V 627.62 293(2) 0.71073 Triclinic <i>P</i> -1
Unit cell dimensions a (Å) b (Å) c (Å) α (°) β (°) γ (°) Z D_{calc} (g/cm ³) Absorption coefficient (mm ⁻¹)	9.5785(6) 13.3511(8) 13.7135(8) 68.560(2) 76.160(3) 77.988(3) 2 1.327 0.365
Index ranges	$-11 \le h \le 11$ $-16 \le k \le 16$ $-17 \le l \le 17$
Reflections collected Independent reflections $[R_{int}]$ Data/restraints/parameters Goodness-of-fit on F^2 Final $R^{a,b}$ indices $[I > 2\sigma(I)]$ R indices (all data) Largest diff. HLR ³ and hole (eÅ ⁻³)	28056 6278 [0.0420] 6278/3/395 1.073 R1 = 0.0686, wR2 = 0.2099 R1 = 0.0828, wR2 = 0.2209 1.082 and -0.357

^a $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|.$

^b wR2 = $[\Sigma w (F_o^2 - F_c^2)^2 \Sigma w (F_o^2)^2]^{1/2}$.

from 300 to 700 °C progressive decomposition, with a final black residual of 32% weight.

2.3.1. X-ray crystallography

X-ray data for complex **I** were collected at room temperature on a Bruker-Nonius X8 Apex CCD area detector equipped with graphite monochromator and Mo K α radiation ($\lambda = 0.71073$ Å). Data were processed through the SAINT [51] reduction and SADABS [52] absorption software. The structure was solved by standard Patterson methods through the SHELXTL-NT [53] structure determination package and refined by full-matrix least-squares based on F^2 . All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as idealized atoms riding on the respective carbon atoms with C–H bond lengths appropriate to the carbon atom hybridization. Water hydrogen atoms were included in the refinement with fixed bond lengths. Details of the crystal data collection are listed in Table 2.

2.3.2. EPR experiments

Under typical conditions, the spectrometer operated at a central magnetic field of 355 mT (3550 G), scan range 110 mT (1100 G), sweep time 165 s, time constant 100 ms, modulation frequency 100 kHz, modulation amplitude 0.1 mT (1 G), at room temperature. The effective 28 mW microwave power on the samples was generated by a 280 mW microwave power source (10 dB attenuation). The analyzed samples were prepared by dissolving 1.0 mg of **VI** in 1.0 mL of acetonitrile, and spectra were recorded at room temperature (298 K). After addition of single drop portions of a 35% aqueous solution of H_2O_2 to the previous solution, the successive EPR spectra were recorded, at the same temperature, after 5 min.

2.4. Catalytic tests

Catalytic experiments were carried out in a 5.0 mL two-necked glass flask, fitted with a water condenser. In a typical experiment, a 0.5 mol% of catalyst (0.0019 mmol) were dissolved in 1.5 mL of

acetonitrile. Then, 1.140 mmol of H_2O_2 (3.0 equiv.) solution were added followed, after 2 min, by 0.380 mmol of selected olefin. The mixture was allowed to stir at chosen temperature, for selected times. The reaction products were monitored at periodic time intervals using GC–MS analyses. At the end of reaction, mixture was quenched with 5.0 mg of MnO₂, and after 15 min, filtered and evaporated under reduced pressure. The oxidation products were identified by comparison of their GC retention times with those of authentic samples.

3. Results and discussion

3.1. Synthesis and characterization of oxovanadium(IV) complexes

The vanadyl(IV) derivatives here reported, having the general composition $VO(Q)_2(H_2O)$ (**I–IV**) and $VO(Q)_2$ (**V–VII**) respectively, have been synthesized by a general procedure based on the mixing of an aqueous solution of $VOSO_4$ ·5H₂O with a methanol solution of the HQ proligand and of sodium methoxide as base, in a 1:2:2 molar ratio, and isolation of final precipitate by filtration (Scheme 1). They are all stable to air and moisture, without any kind of decomposition also after several months, however derivatives **V–VII** absorb water when left in a moist environment for a prolonged time, thus assuming a final $VO(Q)_2(H_2O)$ composition, as for derivatives **I–IV**. All derivatives are insoluble in water, but quite soluble in chlorinated solvents, alcohols, acetonitrile and DMSO. Acetonitrile solutions of complexes **VI** and **VII** showed to be stable at least for 72 h, at r.t., as confirmed by UV–vis and EPR analyses.

3.2. IR spectral studies

The IR spectra of I–VII show strong absorption bands between 1500 and 1675 cm⁻¹, due to the stretching modes ν (C=O), ν (C=C) and ν (C=N) of the acylpyrazolonate ligands [45]. In particular, in the spectra of **I–VI**, the higher frequency band due to ν (C=O) is shifted to lower frequency upon coordination. In the IR spectrum of derivative **VII** the highest ν (C=O) band falls at 1673 cm⁻¹, a value analogous to that found in the previously reported silver complex [Ag(Q^{py,CF3})₂(Meim)] (Meim = 1-methylimidazole) containing a N,N-chelating Q^{py,CF3} ligand, as confirmed by X-ray crystal data [46-49]. On this basis we have hypothesized for derivative VII the structure depicted in Scheme 1. However, we cannot exclude the existence of weak intermolecular interactions involving the C-O arms of the ligands, as previously observed either in the polynuclear $[Ag_2(Q^{py,CF3})_2(MeCN]_{\infty}$ or in the same $[Ag(Q^{py,CF3})_2(Meim)]$ complexes [46-49]. An additional information from IR spectra arises from the strong band observed in the range $880-1000 \text{ cm}^{-1}$, assignable to v(V=0) fragment [21]. For example, such stretching band was found at 996 cm^{-1} in the IR of $[VO(acac)_2]$ [54]. The hydrate derivatives I-IV exhibit this band at frequencies higher than 960 cm⁻¹, whereas in the IR spectra of the anhydrous **V–VII** this band falls in the range 890–920 cm⁻¹. The lowering of the v(V=O) value may arise from the presence of a bridging vanadyl group [46–49] which coordinates the vanadium atom of a neighbour molecule. Finally, IR spectra of derivatives I-IV show a broad band in the region 3100–3300 cm⁻¹, due to the –OH group of the coordinated H₂O molecule in the complex, whereas this band is absent in the IR spectra of V-VII.

3.3. Magnetic and EPR measurements

The room-temperature magnetic susceptibility data for I-VII show paramagnetic behaviour due to the d^1 system. The effective magnetic moments obtained for the oxovanadium(IV) complexes



Fig. 1. EPR spectrum of oxovanadium complex VI in acetonitrile at 298 K.

(1.76-1.95 BM) are within the normal range for the spin only contribution of a d^1 system when the orbital contribution is completely quenched [55].

In order to confirm, by X band EPR analyses, the fast oxidation of metal from +4 to +5 oxidation state, a well known process occurring for the oxovanadium(IV) complexes after H₂O₂ addition, we focused our attention on complex VI being it the most soluble in acetonitrile. As expected, EPR spectrum of VI in acetonitrile, at 298 K, exhibited a hyperfine structure (HFS) derived from the interaction of free electron $(3d^1)$ with the magnetic nuclear moment of 51 V (I=7/2, 99.76% of natural abundance), so confirming the presence of isolated V^{IV} species as pertain to a mononuclear complex. In this case, the EPR signal splits into eight-fold lines of all anisotropic components (Fig. 1) with values of g_{iso} = 1.98 and A_{iso} = 109 G. This values could correspond to vanadyl ions (VO²⁺) in octahedral distorted symmetry [56]. Moreover, the g-value lies in the 1.9-1.99 range and agrees with the fact that when the *d*-shell is less than half filled, the spin-orbit effect reduces the g-value in comparison with that of a free electron (2.0023) [57]. The same measurements were carried out on the same sample after dropwise titration with a 35% aqueous solution of H₂O₂, in order to mimic catalytic reaction medium. The new EPR spectra showed the disappearance of previous well defined HFS, as expected when the oxidation to oxovanadium(V) complex derivatives, occurred.

3.4. Electronic spectral studies

The electronic spectra of I and VI and the corresponding proligands HQ^{nPe} and HQ^{CF3} have also been performed in ethanol. For the ligands two main bands have been observed below 300 nm, in particular at 233 and 268 nm for HQnPe and at 231 and 271 nm for HQ^{CF3}, those at lower frequency being due to the π - π * transition of the phenyl group while the others at higher frequency are assigned to the $n-\pi^*$ transition of the carbonyl group in the acyl fragment. Upon coordination these absorption bands are red shifted to form a broad and unresolved band at 255 nm (derivative I) and to 242 and 296 (derivative VI), respectively, indicating the involvement of the carbonyl group in the complex formation with the metal ion, a behaviour similar to that of a series of oxovanadium(IV) 4-acyl-5pyrazolone complexes, previously reported [58]. Moreover, in the region 500-900 nm there are overlapping absorptions corresponding to d-d transitions of these d^1 complexes. Oxovanadium(IV) compounds usually show five and six coordination numbers giving tetragonal pyramidal and distorted octahedral structures respecTable 3

Selected bond distances (Å) and angles ($^\circ$) for complex I.

V-O(1)	2.025(3)	O(1)-V-O(5)	98.2(2)
V-O(2)	1.992(2)	O(1)-V-O(6)	81.1(1)
V-O(3)	1.989(2)	O(2)-V-O(3)	163.3(1)
V-0(4)	2.013(3)	O(3)-V-O(4)	88.4(1)
V-O(5)	1.584(3)	O(3)-V-O(5)	99.3(1)
V-0(6)	2.262(3)	O(3)-V-O(6)	81.4(1)
O(1)-V-O(2)	89.1(1)	O(4)-V-O(5)	98.7(2)
O(1)-V-O(3)	87.9(1)	O(4)-V-O(6)	82.1(1)
O(1)-V-O(4)	163.2(1)	O(5)-V-O(6)	179.0(1)

tively [46–49,59]. Because of the presence of a strong axial field, the energy levels associated with these two structures do not differ considerably [60]. Moreover, in ethanol solution it is not unlikely the coordination of an EtOH molecule in the sixth coordination site *trans* to the oxygen of V=O fragment in derivative **VI**, to give a tetragonally distorted octahedral complex as for **I** [61–63]. A distortion from the square pyramidal geometry removes the degeneracy between the d_{xz} and d_{yz} orbitals. The *e* level will then split into two, $b_1(d_{xz})$ and $b_2(d_{yz})$, and accordingly four transitions are expected in the case of a complex with a distorted square pyramidal or a tetragonally distorted octahedral geometry [46–49,64–66]. In the electronic spectra of our complexes we were not able to precisely assign such transitions due to broadness of the bands, that however exhibit a general pattern similar to that observed for vanadyl(IV) β -diketonate derivatives [46–49,67].

3.5. ESI-mass spectrometry analyses

The ESI-MS studies of I-VII have been carried in acetonitrile, apart for derivative III that is almost insoluble in this solvent, and for which a methanol solution was used. The positive spectra always show at least a peak due to the $[VO(Q)_2E]^+$ species (where E = H, Na or K), together with absorptions due to $[(HQ)Na]^+$ species in the spectra of III, IV, VI and VII and to $[VO(Q^{nPe})_2(MeCN)Na]^+$ in the spectrum of I. Additionally, in the spectra of derivatives II, III and $\hat{\mathbf{V}}$, some dinuclear charged species of the type $[\{VO(Q)_2\}_2E]^+$ (E=H, Na or K) have been identified, which further confirms the ability of V=O systems to self-aggregate. The negative spectrum of derivative **VI** exhibits peaks attributable to (Q^{CF3})⁻, [(Q^{CF3})₂Na]⁻, $[VO(Q^{CF3})_2(OEt)]^-$, $[VO(Q^{CF3})_3]^-$ and also to a dinuclear species of composition $[{VO(Q^{CF3})_2}_2(OH)]^-$. Finally, the positive and negative ESI-MS spectra of VI in ethanol have been recorded for comparative purposes. It is worth to note that two new peaks at 652 and 675 m/z have been found, which could be assigned to $[{VO(Q^{CF3})_2(EtOH)}H]^+$ and $[{VO(Q^{CF3})_2(EtOH)}Na]^+$, respectively, thus confirming the coordination of solvent molecules to vanadium in ethanol solution, as previously hypothesized.

3.6. Thermogravimetric analyses

Thermal studies have been performed for all derivatives **I–VII**. The data indicate that they are stable to decomposition up to 250-300 °C. Moreover, derivatives **I–IV** loose the coordinated water within the range 60-200 °C, as expected [68]. During the thermal run of derivatives **II** and **VI**, we have observed the sublimation of their anhydrous form [VO(Q)₂] without any decomposition in the range 280-350 °C.

3.7. X-ray structure determination of $[VO(Q^{nPe})_2(H_2O)](I)$

Crystals of complex I suitable for X-ray analysis were obtained from acetonitrile. A view of the structure of I is shown in Fig. 2. Table 3 lists relevant bond lengths and angles. The two *O*,*O*chelating acylpyrazolonates occupy the equatorial plane of the



Fig. 2. Perspective view of complex I with atomic numbering scheme (ellipsoids at the 40% level).

oxovanadium(IV) complex in an *anti* configuration to each other and the distorted octahedral environment is reached through the coordination to V centre of a water molecule *trans* to the oxo group. The geometry of the equatorial coordinating donor atoms is slightly pyramidal, with the vanadium atom 0.2914(7)Å away from the least-squares plane defined by the four equatorial oxygen atoms.

As reported in Table 3, the V-O bond distances of the two chelated acylpyrazolonates are in the range 1.99-2.02 Å; the V=O distance of 1.584(3)Å as well as the average "bite" angles of $89.1(1)^{\circ}$ and $88.4(1)^{\circ}$, are comparable with those found searching the CSD (Cambridge Structural Database, Version 5.30) for oxovanadium(IV) compounds with 0,0-donor ligands. The rotationally free phenyl rings of the two acylpyrazolonate ligands show different values of the tilt angle around the N_{py} -C bond, of 24.1° and 5.7°, respectively, indicating the different intermolecular environment experienced by the two moieties. Indeed, only the less tilted phenyl ring is involved in both an intermolecular hydrogen bond of the $C-H \cdots O$ type with the oxygen atom of the oxo group of a symmetrically related molecule $[C(28)\cdots O(5)^i 3.184(5) \text{ Å}, H(28)\cdots O(5)$ 2.56 Å, C(28)–H(28)···O(5) 125(3)°, i = -x+2, -y+2, -z+1 and an associated $\pi - \pi$ stacking contact of 3.6 Å (measured stacking interplanar distance) (Fig. 3a).

Moreover, each molecule of complex I is involved in the formation of four intermolecular hydrogen bonds of the O_{water} -H···N_{py} type, working at the same time as acceptor, with both nitrogen atoms N(1) and N(3) of the acylpyrazolonates and donor, with the coordinated water molecule, in the formation of a tight supramolecular aggregation $[O(6) \cdots N(1)^{i} 2.908(4) \text{ Å}, H(6w) \cdots N(1) 2.06 \text{ Å}, O(6)-H(6w) \cdots N(1) 176(3)^{\circ}, i=-x+2, -y+1, -z+2; O(6) \cdots N(3)^{ii} 2.948(4) \text{ Å}, H(7w) \cdots N(3) 2.12 \text{ Å}, O(6)-H(7w) \cdots N(3) 167(3)^{\circ}, ii=-x+2, -y+2, -z+1]$ (Fig. 3b).



Scheme 2. Main products observed during the catalytic oxidation of styrene derivatives 1–3.



Fig. 4. Effect of H_2O_2 concentration on styrene oxidation with catalyst **VI**. *Reaction conditions*: styrene (0.3 mmol), catalyst (0.5 mol%), acetonitrile (1.5 mL), r.t.

3.8. Catalytic activity studies

In order to screen and evaluate the catalytic oxidative activity of the synthesized complexes, several of them (**I**, **II**, **IV–VII**) were applied in the oxidation of styrene **1** and of its derivatives namely α -methylstyrene **2** and *cis*- β -methylstyrene **3**, with H₂O₂ as primary oxidant. The formation of different products is outlined in Scheme 2. In the absence of the catalyst, conversion of substrates lower than 2% was observed.

In search of suitable reaction conditions to achieve the best results in terms of both maximum conversion of reagents and products selectivity, the effect of oxidant concentration (moles of H_2O_2 per moles of olefins), catalyst ratio (referred as mol% per mole of olefin), nature of solvent and temperature of the reaction, were studied. The effect of oxidant concentration on the oxidation of substrate **1**, is illustrated in Fig. 4. Different H_2O_2 /styrene molar ratios (1:1, 3:1 and 5:1) were evaluated, while keeping the fixed amount of styrene (0.3 mmol) and catalyst (**VI**, 0.5 mol%) in 1.5 mL of ace-



Fig. 3. Packing diagram showing the formation of intermolecular hydrogen bonds of (a) C-H···O and (b) O_{water}-H···N_{py} type (view down the *b* axis) in complex I.



Fig. 5. Effect of catalyst amount on styrene oxidation with catalyst VI. *Reaction conditions*: styrene (0.3 mmol), H₂O₂ (1:1), acetonitrile (1.5 mL), r.t.

tonitrile, at r.t., running for 18 h. The progress of the reaction was regularly monitored at different intervals of time, by GC–MS analysis. Increasing the H_2O_2 /styrene ratio from 1:1 to 5:1 increases the conversion until about 98%, even if larger conversion values are not accompanied by a corresponding increase in the yield of product having more added value as epoxide (**1c–3c**, Scheme 2). For this reason and with the aim to reduce the oxidant consumption, we decided to work with a 3:1 excess of oxidant. As can be observed in Fig. 4, the best conversion values were reached after only one-third of the overall running reaction time (18 h). The reaction comes to almost steady state within 6 h, and then after only minor changes in the percent conversion were observed.

A deep evaluation devoted to select the best solvent for our catalytic reactions, has been effected by comparing the results obtained working in 1.5 mL of four different solvents as dichloromethane, acetonitrile, THF and ethanol, while keeping fixed the amount of olefins (1-3, 0.3 mmol) and catalysts (V or VI, 0.5 mol%), at r.t., running for 18 h. While dichloromethane acted as the worst solvent showing very low conversion values, also when used in 1:1 mixtures with acetonitrile, THF on the contrary afforded complex mixtures of products most of them attributable to solvent oxidation. Ethanol worked well as did acetonitrile, in terms of conversion of substrate but, differently from the latter, showed to interact widely with the formed oxidation products affording, as an example in the case of styrene 1 oxidation, ethyl benzoate and 2-ethoxy-2-phenylethanol (derived from the nucleophilic styrene epoxide opening), in mixture with other products. So, in order to reduce solvent interactions and better evaluate the selectivity during catalytic oxidations, we decided to use acetonitrile as reaction solvent.

Similarly, four different amounts of catalyst *i.e.* 0.5, 1.0, 1.5 and 2.0 mol% with respect to substrate, were considered to evaluate the effect of catalyst amount on the rate of the reaction, while keeping fixed the amount of styrene (0.3 mmol) and H_2O_2 (1:1), at r.t., running for 18 h. As shown in Fig. 5, an increase in the amount of catalyst had adverse effects and conversion values regularly decreased, the large differences being observed between 0.5 and 1.0 mol%. The decrement in the substrate conversion at higher catalyst concentrations may be due to the faster decomposition of H_2O_2 , in the presence of a larger number of available metal active catalytic sites, even at r.t.

This trend, *i.e.* the importance to prevent the negative effect on the substrate conversion due to the fast decomposition of hydro-



Fig. 6. Effect of temperature on styrene oxidation with catalyst VI. *Reaction conditions*: styrene (0.3 mmol), catalyst (0.5 mol%), H₂O₂ (1:1), acetonitrile (1.5 mL).

gen peroxide, has also been observed during the evaluation of the role exerted by the temperature. As can be seen in Fig. 6, a lower temperature (r.t.) is necessary even if working with a stoichiometric amount of oxidant (1:1), in order to optimize substrate conversions.

We then selected the best experimental conditions to carry out further oxidative catalytic studies with the remaining oxovanadium(IV) complexes, as **I–II**, **IV–V** and **VII**, as follows: substrate (0.38 mmol), catalyst (0.5 mol%), H_2O_2 (3:1), acetonitrile (1.5 mL), r.t., 18 h. The results we have obtained in the oxidation of styrene derivatives **1–3**, are described in Table 4, which provides details on conversion values, turnover numbers (TON), selectivities and yields for the various products obtained. Firstly, it can be observed that the selectivity toward the formation of the most commercially valuable product, the epoxide, is generally low (13–30%) being this product detectable only in the oxidation of *cis*- β -methylstyrene **3** (Table 4, product **3c**). A similar trend was previously observed by some of us, during the hydrogen peroxide promoted oxidation of styrene derivatives by means of methyltrioxorhenium based catalysts [69].

Probably, after its initial formation the epoxide is transformed into other products. Moreover, the selectivity toward the formation of benzaldehyde 1a (or the corresponding acetophenone 2a) is generally higher for olefin 1 (or 2), than for $cis-\beta$ -methylstyrene 3. The hypothesis that benzaldehyde formation (during oxidation of olefin 1) could be due to the nucleophilic attack of H_2O_2 on the less substituted carbon of the initially formed epoxide ring, followed by cleavage of the intermediate hydroxyl-hydroperoxystyrene, cannot be excluded [70]. In the case of substrate 3 the opening of epoxide ring should be less favourable due to the steric hindrance exerted by the presence of a methyl group as substituent in the β -carbon of vinyl residue, so the formation of a discrete amount of epoxide 3c, is favoured. In addition, benzaldehyde (1a or 3a, Scheme 2) or acetophenone (2a, Scheme 2) formation could also be facilitated by direct oxidative cleavage of the vinyl double bond, via a radical mechanism [70-72]. The formation of benzoic acid (1b or **3b**, Scheme 2) in consequence of benzaldehyde oxidation is quite likely. A plausible mechanism involving the hydrolysis of epoxide by water present in H₂O₂ solution to the corresponding diol derivatives (1d or 2d, Scheme 2), may be rationally invoked. Fig. 7 shows a typical plot of benzaldehyde 1a, benzoic acid 1b, epoxystyrene **1c** and diol **1d** formation vs. time during styrene **1** oxidation by oxovanadium(IV) complex VI, in acetonitrile (Table 4, entry 13).

218	
Table	4

Ovidation	of olefins 1	-3 in CH	CN with H	one and	catalysts I_II	IV_VII ^a

Entry	Olefin ^b	Catalyst	Conv. (%)	TON ^c	Products ^d (% selectivity) [% yield] ^e
1	1	I	88	176	1a (62) [55], 1b (23) [20], 1d (15) [13]
2	2	I	82	164	2a (83) [68], 2d (17) [14]
3	3	I	89	178	3a (63) [56], 3b (11) [10], 3c (26) [23]
$4^{\rm f}$	1	П	48	96	1a (86) [41] , 1b (4) [2] , 1c (6) [3] , 1d (4) [2]
5 ^f	2	П	76	152	2a (100) [76]
6 ^f	3	II	64	128	3a (70) [45] , 3c (30) [19]
7 ^f	1	IV	35	70	1a (100) [35]
8 ^f	2	IV	46	92	2a (100) [46]
9 ^f	3	IV	32	64	3a (72) [23], 3c (28) [9]
10	1	v	84	168	1a (70) [59], 1b (19) [16], 1d (11) [9]
11	2	v	81	162	2a (80) [65], 2d (20) [16]
12	3	v	86	172	3a (63) [54], 3b (13) [11], 3c (24) [21]
13	1	VI	90	180	1a (67) [60] , 1b (21) [19] , 1d (12) [11]
14	2	VI	98	196	2a (78) [77], 2d (22) [21]
15	3	VI	94	188	3a (73) [69], 3b (12) [11], 3c (15) [14]
16	1	VII	85	170	1a (71) [60] , 1b (23) [20] , 1d (6) [5]
17	2	VII	94	188	2a (88) [83], 2d (12) [11]
18	3	VII	84	168	3a (74) [62], 3b (13) [11], 3c (13) [11]

^a The reactions were performed in CH_3CN , with 3 equiv. of H_2O_2 , 0.5 mol% of catalyst, at r.t., running for 18 h.

^b Olefins: **1** = styrene; **2** = α -methylstyrene; **3** = *cis*- β -methylstyrene.

^c TON: (turnover number) moles of substrate converted per mole of catalyst.

^d Products: **1a** = **3a** = benzaldehyde; **1b** = **3b** = benzoic acid; **1c** = epoxide; **1d** = glycol; **2a** = acetophenone; **2d** = glycol; **3c** = epoxide.

^e Yields are calculated on substrate conversion.

^f Running time = 4 h.

The epoxide **1c** was mainly formed at the beginning of the reaction, but progressively disappeared with time, at the expense of the oxidative cleavage compounds. A similar behaviour has been previously observed in the oxidation of 2-methyl-2-pentene with the vanadium(V) peroxo complex $[VO(O_2)(Pic) \cdot H_2O]$ [43].

Shorter reaction times afforded higher selectivities as observed in the oxidation of olefins 1-2 with catalysts II and IV (Table 4, entries 5, 7–8), even if with lower conversion values. This confirms that the increasing conversion of starting materials is accompanied by a further reactivity of initially formed oxidation products (*i.e.* benzaldehyde to benzoic acid, and epoxide to diol), and consequently by a decreasing of selectivity.

For what concerns a comparison in terms of activity and selectivity showed by the different oxovanadium(IV) complexes on catalytic oxidations of styrene derivatives **1–3**, we have focused our attention on complexes **I**, **V–VII**, because of their larger solubility in acetonitrile. The results in terms of catalyst activities and



Fig. 7. Oxidation of styrene 1 by complex VI. Reaction conditions: styrene (0.3 mmol), catalyst (0.5 mol%), H_2O_2 (3:1), acetonitrile (1.5 mL), r.t.

catalyst selectivities are shown in Figs. 8 and 9, respectively. In general, the catalytic activity of complexes **I**, **V–VII** showed to be mutually comparable (Fig. 8), with TON values within the range of 162–196, according with others oxovanadium complexes previously described in literature [27,73], being the complex $VO(Q^{CF3})_2$ (**VI**) the most active one. In terms of selectivity observed for oxidation of styrene, undoubtedly the highest selectivity (in the range 62–100%) was observed for the formation of benzaldehyde, irrespective to the nature of the complex used as catalytic system (Fig. 9).

This result confirms the accepted hypothesis that, under these experimental conditions, an oxovanadium(V)monoperoxo complex (α) or, more likely, an oxovanadium(V)bisperoxo anionic complex (β) (the latter lacking of any potential ligand contribution to the reaction outcome) can be invoked as the real active catalytic species (Fig. 10). On the other hand, the formation of the anionic complex (β) prone to participate in oxidation reactions, by transfering one of its oxygens to substrate, in the H₂O₂ promoted oxidations of various olefins, has been already largely demonstrated [36–44]. Moreover, the relevant occurrence of oxidation products deriving from an oxidative cleavage mechanism (Scheme 2, products **a**–**b**)



Fig. 8. Comparison between the activities showed by the oxovanadium(IV) complexes **I**, **V–VII**, in the oxidation of olefines **1–3**. *Reaction conditions*: substrate (0.3 mmol), catalyst (0.5 mol%), H_2O_2 (3:1), acetonitrile (1.5 mL), r.t., 18 h.



Fig. 9. Comparison between the selectivities showed by oxovanadium(IV) complexes **I**, **V–VII**, in the oxidation of styrene. *Reaction conditions*: styrene (0.3 mmol), catalyst (0.5 mol%), H_2O_2 (3:1), acetonitrile (1.5 mL), r.t., 18 h.

implies that, in this study, an alternative but otherwise important role for catalytically active radical complex species, cannot be ruled out.

3.9. The fate of complex **VI** in the presence of H_2O_2

In order to evaluate intermediate species formed during catalytic oxidation, the acetonitrile solution of neat complex **VI** was treated with a 35% aqueous solution of H₂O₂, and the reaction was monitored by UV-vis spectroscopy (Fig. 11). The results showed that the successive additions of 2.0 μ L of a 0.05 M H₂O₂ aqueous solution to 10 mL of acetonitrile solution of **VI** (1.0 mg), resulted in the reduction of the intensity of $n-\pi^*$ transition band at 296 nm. At the same time this band marginally shifts toward higher wavelengths along with broadening, while in the region 500-900 nm the overlapping absorptions corresponding to d-d transitions (not shown) slowly become weaker and finally disappears. These results are in accord with the above suggested hypothesis of formation of peroxovanadium(V) species [73,74]. It should be noted that the UV-vis spectra of titrated solution of complex **VI**, remained unchanged after 24 h.



Fig. 10. Probable oxoperoxovanadium(V) complex derivatives, formed during H₂O₂ oxidation.



Fig. 11. Electronic spectra of HQ^{CF3} and VO(Q^{CF3})₂ (**VI**). The reactivity of **VI** with H₂O₂, is also showed. Spectra were recorded after the successive addition $(2.0 \,\mu\text{L})$ of 0.05 M H₂O₂ aqueous solution to 10 mL of acetonitrile solution of **VI** (1.0 mg).

4. Conclusions

A series of new oxovanadium(IV) complexes containing variously substituted 4-acyl-5-pyrazolone donor ligands have been synthesized and fully characterized. In the case of complex I, namely $VO(Q^{nPe})_2(H_2O)$, its crystal and molecular structures have been resolved by single crystal X-rays diffraction, showing a distorted octahedral environment reached through the coordination of two 0,0-chelating acylpyrazolonate ligands occupying the equatorial plane in anti configuration to each other, and a water molecule trans to the oxo group. The oxovanadium(IV) complexes I-II, IV-VII have been used as catalysts for oxidation of aromatic olefins like styrene 1 and its derivatives 2-3, with H₂O₂ as primary oxidant. Various parameters as solvent, temperature, catalyst amount and oxidant concentration have been tested in order to optimize both activity and selectivity of the oxidative process. Under optimized conditions, high values of conversion of substrates within the range 98-81% have been observed, with TON values ranging from 196 to 162. Generally, shorter reaction times (4h) afforded higher selectivity, even if with lower conversion values ranging from 32% to 76% (TON from 64 to 152). Among the different oxidized products formed from aromatic olefins 1-3, the selectivity for benzaldehyde is highest, regardless the type of catalyst employed. The best selectivity toward epoxide formation has been solely observed during oxidation of $cis-\beta$ -methylstyrene 3. The catalytic activity of selected oxovanadium complexes I, V-VII in the oxidation of olefins 1-3 showed to be reciprocally comparable, being the complex VI the most active one. Further studies devoted to gain more mechanistic details on the mechanism active with this family of catalysts or with similar derivatives (including the effects, if any, exerted by molecular dioxygen) and to extend their applicability toward catalytic synthetic oxidations, will be planned in our laboratories.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2010.02.022.

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