

Synthesis and Characterization of Niobium Complexes Employed as Homogeneous Oxidation Catalysts by ^{31}P and ^{93}Nb Nuclear Magnetic Resonance

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Abstract: Peroxonio niobium species complexed with tributylphosphine oxide, picolinic acid and 8-hidroxiquinoline were synthesized and characterized by ^{31}P and ^{93}Nb solution NMR.

Resumo: Espécies peroxonióbio complexadas com o óxido de tributilfosfina, ácido picolínico e 8-hidroxiquinolina foram sintetizados e caracterizados por RMN de ^{31}P e ^{93}Nb em solução.

Introduction

The epoxidation of alkenes with manganese, molybdenum, rhenium, titanium, tungsten, vanadium catalysts with organic hydroperoxides is well-established in the literature.¹⁻³ For this oxidation reaction, hydrogen peroxide is a useful reagent, as it is cheap and does not cause effluent problems.⁴ The development of effective catalysts for the oxidation of alcohols and olefins using environmentally benign and inexpensive oxidants is an important challenge.⁵

Niobium catalysts have attracted interest, and efforts have been made to develop new applications for chemical processes.⁶ Several tetraperoxoniobate⁷, carboxylate (peroxo) compounds⁸, fluorperoxo complexes⁹, schiff base peroxo complexes¹⁰ and water-soluble peroxo[poliaminocarboxilato] of niobium (V)¹¹ have already been described in the literature. Niobium peroxo complexes of some tri and tetradentate ligands act as active catalysts in presence of t-butylhydroperoxide (TBHP),

resulting in oxidation products.¹⁰ Sodium tetraperoxo niobate $\text{Na}_3[\text{Nb}(\text{O}_2)_4] \cdot 13\text{H}_2\text{O}$ was tested for the epoxidation of cyclohexene and oxidation of alcohols with hydrogen peroxide as a homogeneous catalyst. The $[\text{Nb}(\text{O}_2)_4]^{3-}$ anion was found to catalyze the epoxidation of cyclohexene with 30% aqueous H_2O_2 in homogeneous solution giving cyclohexene oxide with a 73% selectivity and 7% cyclohexene conversion at 45°C. It also showed some catalytic activity for the homogeneous oxidation of alcohols (ethanol, isopropanol, 1- and 2- butanol) with H_2O_2 .⁷

The ^{93}Nb nucleus has natural abundance of 100%, a spin $I = 9/2$, and an electric quadrupole moment of $-0,22 \times 10^{-28} \text{ cm}^2$, the lowest of the first row transition metals, with the result that excessive linewidth would not be a problem in solution ^{93}Nb spectroscopy. The relative intensity is 0.482 compared with equal number of protons, and is the third among all the elements in terms of receptivity.¹² The study of vanadium and manganese chemical shifts has shown that the metal oxidation state

is a primary determinant of metal atom shielding. Niobium (V) is the only oxidation state for which ^{93}Nb NMR data have been obtained. As a result, the range of chemical shifts observed is rather narrower than that found for comparable metals.

Although new peroxo complexes of niobium (V) have been prepared and characterized by ^{13}C ,^{11,13} few reports about characterization of niobium compounds by ^{93}Nb NMR have been described in the literature.¹⁴⁻¹⁶ Continuing our interest in the oxidation of alcohols and olefins by peroxoniobium species^{15,17,18}, we are studying systems comprising peroxoniobium (V) species complexed with tributylphosphine oxide, picolinic acid and 8-hydroxiquinoline which were synthesized and characterized by ^{93}Nb NMR. The signal was compared with those niobium tetraphenyl porphyrin and potassium tetraperoxoniobate. The complexes were checked for the catalytic oxidation of cinnamic alcohol and cyclohexene by hydrogen peroxide. A complex of vanadium with picolinic acid was prepared and tested in the cinnamic alcohol oxidation.

Experimental

Acetonitrile, cinnamic alcohol, chloroform and cyclohexene were purified by distillation before use.¹⁹ Picolinic acid, tributylphosphine oxide, tetraphenylphosphonium bromide, and 8-hydroxiquinoline were commercially available high-purity products (Aldrich) and were used as received. Hydrogen peroxide solution [30% (w/w%)] was purchased from Peróxidos do Brasil S/A and potassium niobate ($\text{K}_4\text{Nb}_6\text{O}_{17} \cdot 3 \text{H}_2\text{O}$) from Companhia Brasileira de Metalurgia e Mineração (CBMM). K_3NbO_8 (A)²⁰, $\text{P}\text{O}_4[\text{Nb}(\text{O}_2)_2\text{Pic}_2]3\text{H}_2\text{O}$ (B),²¹ niobium

tetraphenyl porphyrin (E)¹⁸ and $\text{P}\text{O}_4[\text{VO}(\text{O}_2)\text{Pic}_2] \cdot 3\text{H}_2\text{O}$ (F)²¹ were prepared as described in the literature. Complexes $\text{P}\text{O}_4[\text{Nb}(\text{O}_2)_2\text{Q}_2]3\text{H}_2\text{O}$ (C) and $\text{NbOH}(\text{O}_2)_2(\text{OPBu}_3)_2$ (D) are new, not previously prepared or characterized. Complex (C) was prepared dissolving potassium niobate (960 mg, 5mmol) in 30% hydrogen peroxide (10mL). A solution of 8-quinolinol (1.46g, 10mmol) and of tetraphenylphosphonium bromide in ethanol were added. Addition of ethanol (6 mL) and storage at 0°C gave an orange solid, which was filtered off, washed with ethanol and air-dried. The yield of C was 69%. Anal. calc. (%) C 60.0, N 3.3, H 4.5; found C 59.1, N 3.6, H 4.5. Complex (D) was synthesized from a solution of Nb_2O_5 (4mmol) in hydrogen peroxide. Subsequently, 1mL of HNO_3 and the solution of tributylphosphine oxide (7 mmol) in methanol was added with constant stirring and cooling, simultaneously, in an ice bath. The solid complex obtained was filtered off, washed with methanol and dried. Anal. calc.(%): C 47.27, Nb 15.10 and O 10.16; found C 47.41, Nb 15.12 and P 10.11, yield 14%.

Elemental analysis (C, H, N) was performed using a Perkin Elmer 2400 elemental analyzer. IR spectra were recorded in KBr discs on a Nicolet FTIR spectrometer. $^{31}\text{P}\{^1\text{H}\}$ and ^{93}Nb NMR spectra were obtained at room temperature on a DRX300 Bruker spectrometer (7.05 Tesla) operating at 121.5 MHz (^{31}P) and 73.35 MHz (^{93}Nb). Solutions in D_2O , CDCl_3 and DMSO-d_6 were examined in 5 mm o.d. tubes. Chemical shifts in ppm are referred to the residual signal of the solvent (^1H , ^{13}C), to 85% H_3PO_4 (^{31}P) and to an external CD_3CN solution of $\text{NbCl}_6\text{N}(\text{Et})_4^+$ (^{93}Nb), synthesized from NbCl_5 . Negative δ

values correspond to resonances at low frequency in relation to the reference.

The variations of substrate and product contents were followed using a VARIAN model 3800 gas-chromatograph equipped with a hydrogen flame ionization detector (FID) system and capillary column VA-5, 30 m, 0.32 mm ID, 1 μ m df. Temperature was programmed from 80°C to 280°C at 20°C/min, with H₂ as carrier gas at 2mL/min.

The identification of the products was carried out by gas-chromatography mass spectrometry analysis (CG-MS) on a HP 6890, utilizing a DB-5 (30m) fused silica column under the same temperature conditions and with He as carrier gas.

Results and Discussion

The results of elemental analysis obtained for the two new peroxy niobium complexes (C and D), which were not previously reported in the literature, were in close agreement with the calculated values based on molecular structure. Each of the diperoxy-niobium (V) complexes exhibited a characteristic spectral pattern in the infrared region (Table 1). Significant features are absorptions near 825, 600 and 560 cm⁻¹ assigned to ν (O-O), ν_s Nb(O)₂ and ν_{as} Nb(O)₂, respectively.

Table 1. Infrared data of Nb peroxy complexes

Complex	Infrared Data (cm ⁻¹)	
	ν (O-O)	ν (Nb-O)
K ₃ NbO ₈ (A)	815	595, 543
PØ ₄ [Nb(O ₂) ₂ PiC ₂]3H ₂ O (B)	873, 857	528, 572
PØ ₄ [Nb(O ₂) ₂ Q ₂]3H ₂ O (C)	825, 847, 859	525
[NbOH(O ₂) ₂ (OPBu ₃) ₂](D)	883	584, 571, 603

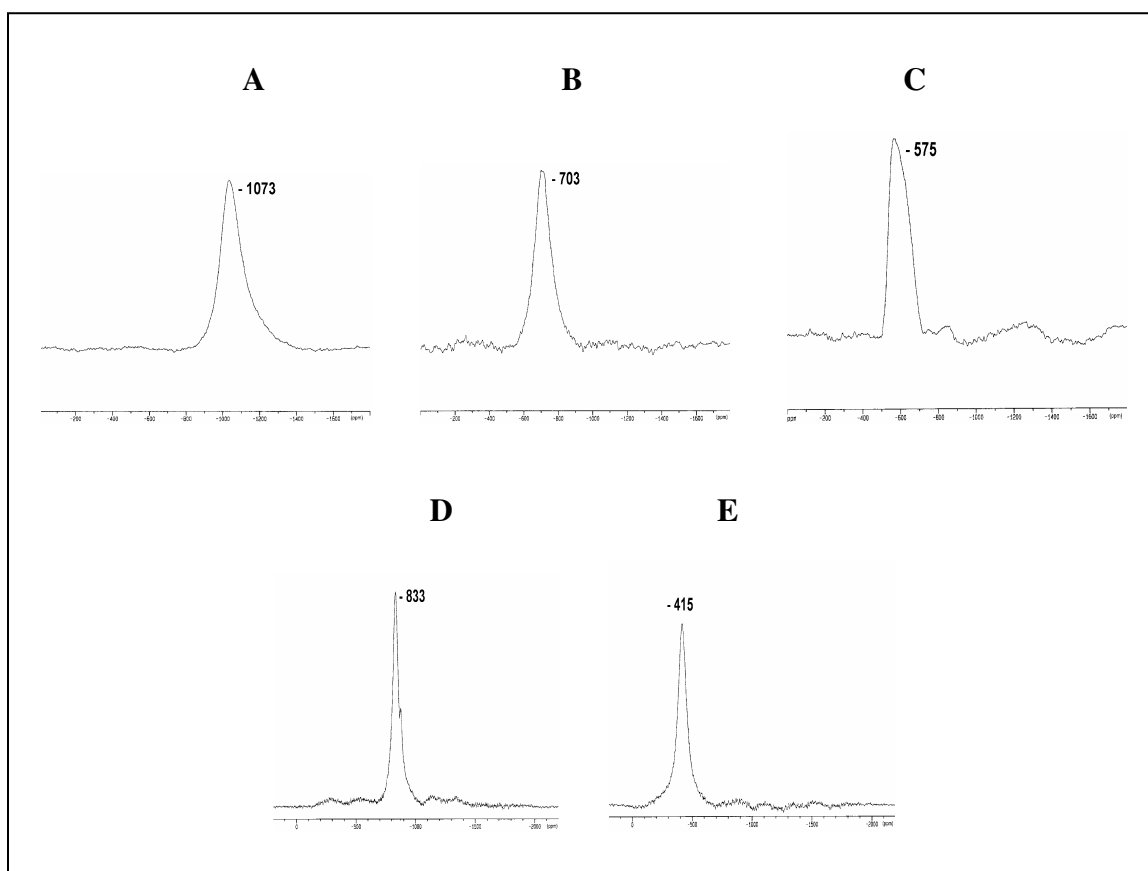
These results are in accordance with those reported for carboxylate peroxy complexes of niobium.⁹ Niobium peroxy complexes were also investigated with ⁹³Nb NMR spectroscopy (Figure 1). The solubility of the salts in DMSO and CHCl₃ allowed measurement of ³¹P and ⁹³Nb NMR spectra (Table 2).

A continuous decrease of ⁹³Nb NMR, chemical shift is observed with increasing the basicity of the oxygen of the ligands. This finding allowed us to establish a correlation

between increases in electron donating properties of the ligands, as expected. Comparison of the chemical shifts values of species A, B and C indicated that the substitution of the peroxy group with an anionic ligand causes a decrease of 370 ppm for picolinate and 498 ppm for quinolate, indicating a decrease of magnetic shielding.

Table 2. Solution $^{31}\text{P}\{\text{H}\}$ and ^{93}Nb NMR chemical shifts obtained for Nb complexes

Complex	$^{31}\text{P}\{\text{H}\}$, δ ppm	^{93}Nb , δ ppm
K_3NbO_8 (A)	-	-1073 ^a
$\text{NbOH}(\text{O}_2)_2(\text{OPBu}_3)_2$ (D)	73.8	-833 ^c
$\text{P}\emptyset_4[\text{Nb}(\text{O}_2)_2(\text{Pic})_2] 3\text{H}_2\text{O}$ (B)	23.5	-703 ^b
$\text{P}\emptyset_4[\text{Nb}(\text{O}_2)_2(\text{Q})_2] 3\text{H}_2\text{O}$ (C)	23.6	-575 ^c
$[\text{Nb}(\text{TPP})_2]\text{O}_3$ (E)	-	-415 ^c

(a) D_2O as solvent, (b) DMSO-d_6 as solvent, (c) CDCl_3 as solvent**Figure 1.** Solution ^{93}Nb NMR spectra for complexes K_3NbO_8 (A, -1073ppm), $\text{P}\emptyset_4[\text{Nb}(\text{O}_2)_2\text{Pic}_2]3\text{H}_2\text{O}$ (B, -703 ppm), $\text{P}\emptyset_4[\text{Nb}(\text{O}_2)_2\text{Q}_2]3\text{H}_2\text{O}$ (C, -575 ppm), $\text{NbOH}(\text{O}_2)_2(\text{OPBu}_3)_2$ (D, -833 ppm) and $[\text{Nb}(\text{TPP})_2]\text{O}_3$ (E, -415 ppm).

The signal of the new complex D, a neutral complex, was compared with that of niobium tetraphenyl porphyrin (E). The chemical shift values (Table 2) obtained in the solution $^{31}\text{P}\{\text{H}\}$ and ^{93}Nb NMR spectra show a larger

shielding effect on Nb sites for complexes D and A, compared with the chemical shifts of ^{93}Nb observed for compound E. Cyclohexene oxidation reactions were run in biphasic media formed by chloroform and aqueous H_2O_2 . Due

to the low oxidizing power of the hydrogen peroxide, the non-catalytic reaction was unproductive (Table 3). The results showed that the yields of the products increased

significantly with complex C, whereas complexes D and B showed moderate catalytic activity.

Table 3. Oxidation of cyclohexene by hydrogen peroxide in the presence of niobium complexes^a

Entry	Catalytic System	T °C	Time/h	Conversion (%)	Epoxide ^b (%)	Diol ^b (%)
1	6eq. H ₂ O ₂ ^c	50	24	0.5	-	-
2	6eq.H ₂ O ₂ +0.03eq. A	50	24	<1%	-	-
3	6eq.H ₂ O ₂ + 0.03 eq. D	50	6	5.3	27.2	72.8
		50	24	8.5	21.5	78.5
4	6eq.H ₂ O ₂ .+ 0.03 eq. C	50	24	27.4	34.0	66.0
		50	72	33.0	24.0	76.0
5	6eq.H ₂ O ₂ + 0.1 eq. B	50	24	4.5	34.0	66.0
6	10eqH ₂ O ₂ +0.02eq.cat ^d	45	20	7	73	-
7	10eq. H ₂ O ₂ + E ^b	40	72	80	47.4	52.6

a- Reaction conditions: 0.03 mmol of catalyst, 30ml of chloroform, 6 mmol of H₂O₂, 3 mmol of cyclohexene, 50°C with stirring; b- By ¹H NMR, ref. 18 ; c- without catalyst; d-ref.7 .

The oxidation reactions of cinnamyl alcohol were carried out under homogeneous conditions where the solvent was acetonitrile, or in biphasic conditions where the solvent was

chloroform and the oxidant was an aqueous solution of hydrogen peroxide (Table 4). The two niobium complexes (B and C) yielded more cinnamaldehyde than epoxide.

Table 4. Oxidation of cinnamyl alcohol by hydrogen peroxide in the presence of niobium and vanadium complexes^a

Entry	Catalytic System	Time(h)	Conversion (%)	Distribution of Products (%)		
				1	2	3
1	6 eq. H ₂ O ₂ ^b	24	No reaction	-	-	-
2	6eq.H ₂ O ₂ +0.03 eq.A ^b	24	No reaction	-	-	-
3	6eq.H ₂ O ₂ + 0.03eq.C ^b	7	27.5	17	41.3	41.7
4	6eq H ₂ O ₂ + 0.03 B ^c	1	32	20.1	49,5	30.4
		8	47.6	23.1	44.1	32.8
5	6eq.H ₂ O ₂ +0.03 eq.F ^c	1	96	9.3	8.3	82.4

a- Reaction conditions: 0.03 mmol of the catalyst, 30ml of chloroform or acetonitrile, 6 mmol of H₂O₂, 3 mmol of cinnamyl alcohol, 50°C with stirring;

b- Analysis by NMR; reaction in chloroform;

c- Analysis by CG, reaction in acetonitrile.1-epoxide, 2-cinnamaldehyde, 3-benzaldehyde.

Complex F (a vanadium complex) appears to be the most reactive catalyst, but shows poor selectivity towards epoxide formation. These results are in agreement with previous reports.²² Complex B shows higher activity than C, but the selectivity in both cases was similar towards benzaldehyde, cinnamaldehyde and epoxide formation. Further work is underway to assess the correlation between the activity of those niobium-based catalysts with spectroscopic properties, as shown by ³¹P and ⁹³Nb NMR.

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