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Review article

Vanadium (V) peroxocomplexes: Structure, chemistry and biological implications

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Abstract

A short account on the identification in solution of diverse type of vanadium peroxocomplexes is offered. The methodology used is a combination of several techniques, i.e., multinuclear NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS) and theoretical calculation. The analysis has been carried out in aqueous alcoholic solutions, and in some case also in the presence of appropriate ligands, in order to model some of the natural conditions where vanadium-dependent haloperoxidase enzymes (VHPO) work. With the results obtained, it has been possible to shed light on important aspects of the catalytic cycle of VHPO. Furthermore, a number of synthetic aspects of the reactivity of the various vanadium peroxocomplexes is reviewed.

Keywords: Vanadium; Peroxo complexes; Haloperoxidases; Oxidation processes; Mass spectrometry; Ab initio calculations

1. Introduction

The relevance of peroxo transition metal compounds either in oxidation chemistry [1] or in biochemical systems [2] is well established. Vanadium peroxides, in particular, are effective oxidants of different organic and inorganic substrates like thioethers, alkenes, alcohols, aromatic and aliphatic hydrocarbons, halides and sulphur dioxide, as summarized in the rosette of Scheme 1. These processes either stoichiometric or catalytic, where the oxidant can be hydrogen peroxide or an alkylhydroperoxide, are usually carried out in mild conditions and are associated to good product yield and selectivity. The enantioselective version of some of these processes has been reported [1].

Vanadium and vanadium peroxides generate a number of biological and biochemical responses [3] and have a potential as insulin-mimetic agents in the treatment of human diabetes [4]. In addition vanadium, as vanadate, is an essential prosthetic group of some haloperoxidase enzymes [5–8].

Hydrogen peroxide readily associates with V(V) forming a number of peroxo vanadates whose nature depends on pH and relative concentrations of the reagents. We have shown that a detailed speciation of the V(V)–H_2O_2–(H^+) system may be obtained by the association of electrospray ionization mass spectrometry (ESI-MS) with ^{51}V NMR spectroscopy and theoretical calculations [9,10]. The identification of the vanadium complexes, for a given condition, is fundamental in order to understand the mechanisms and products distribution of reactions in which vanadium complexes are involved.

In this short report, we will focus our attention on speciation, reactivity and biological implications of

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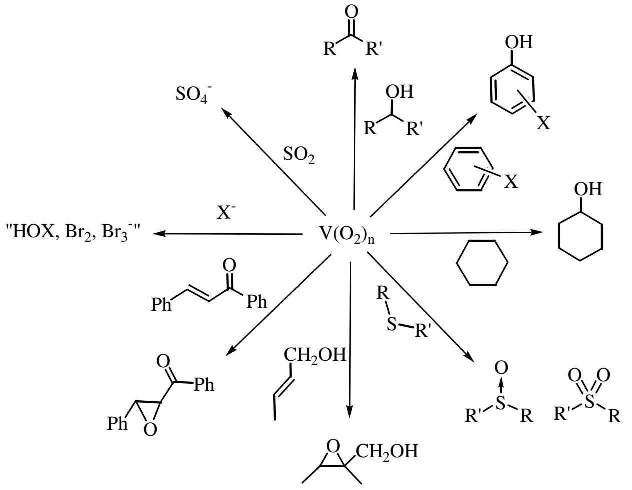


Scheme 1. Reactivity of vanadium peroxides with organic and inorganic substrates.

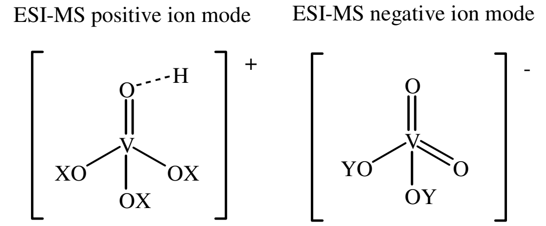
vanadium mono-, di- and triperoxo derivatives, with emphasis to the relationship between these species and vanadium-dependent haloperoxidases enzymes (VHPO).

2. Results and discussion

2.1. Monoperoxo compounds

In the absence of hydrogen peroxide, vanadium (V) is present in aqueous solution as vanadate or vanadate derivatives depending on pH and reduction potential [3]. The ESI-MS analysis both in positive [11] and negative-ion mode [12], that may be considered as an analogous of acid and basic medium conditions [13],[1] conducted in mixed water–alcohol solvent, revealed the presence of monomeric and dimeric species, with different coordination spheres. An overview of the mononuclear complexes is given in Scheme 2.

cis-VO_2^+ is reported to be the major species in aqueous vanadate solutions at pH 1 [14,15]. This ion, centered at *m*/*z* 83, is observed in the ESI mass spectrum, although in very low relative abundance if compared with the other ions listed above. The concomitant presence in the ESI droplets, where a precise definition of the pH value is not possible, of the alcoxy derivatives, however, suggests **1** as the most likely structure in place of solvated $[VO_2(H_2O)_n]^+$ species. From neutral to alkaline medium, V(V) exists primarily as monomeric oxyanion



1 **2**

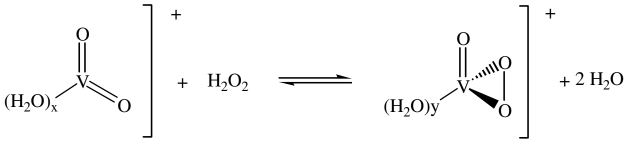
X=H,H,H	m/z 119	Y=H,H	m/z 117
X=H,H,Me	m/z 133	Y=H,Pr^i	m/z 159
X=H,Me,Me	m/z 147	Y=Pr^i,Pr^i	m/z 201
X=Me,Me,Me	m/z 161		

Scheme 2. Mononuclear non-peroxo vanadium derivatives identified by ESI-MS.

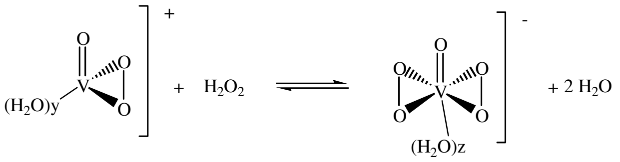
(VO_4^{3-}, HVO_4^{2-}, $H_2VO_4^-$) [16] in agreement with ESI-MS findings [12]. Vanadium ions have many structural roles in living organisms that reflect the analogy with phosphorous. The presence and the chemistry of this element in the biosphere, in insulin mimics [4] and in most biological systems has been recently reviewed [3].

The addition of H_2O_2 to the vanadate solutions produces significant changes in the ESI mass spectra [11]. The positive-ion mode mass spectrum of a solution containing equimolar amounts of V(V) and H_2O_2, pH of the water–methanol infusion solution ca. 1, is shown in Fig. 1.

Most of the peaks correspond to vanadium monoperoxo compounds $[OV(O_2)(H_2O)_m(MeOH)_n]^+$ with different coordination sphere composition (*m*, *n* = 0–4) i.e., $[OV(O)_2]^+$ *m*/*z* 99, $[OV(O)_2(H_2O)]^+$ *m*/*z* 117, $[OV(O)_2(MeOH)]^+$ *m*/*z* 131, $[OV(O)_2(H_2O)_2]^+$ *m*/*z* 135, $[OV(O)_2(H_2O)(MeOH)]^+$ *m*/*z* 147. Worthy of note is the presence in the mass spectrum of the ionic species at *m*/*z* 83, identified as VO_2^+. This experimental evidence may suggest an equilibrium between the non-peroxidic **1**-like type species listed above and the mentioned ion, with VO_2^+ acting as precursor for the formation of peroxo derivatives, according to Eq. (1).



(1)



(2)

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[1] The ESI process of aqueous or mixed alcohol–water solutions of various analytes has been reported to produce a marked pH change in the nebulized droplets with respect to the bulk. Droplets formed under ESI positive-ion mode may undergo considerable pH decrease, whereas droplets produced in negative-ion mode show a significant pH increase.