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Note

Spectroscopic evidence on the interaction of prephenate, a shikimate pathway intermediate, with oxidovanadium(IV) species

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ABSTRACT

The interaction of the oxidovanadium(IV) cation with the sodium salt of prephenic acid was investigated by electron absorption and electronic paramagnetic resonance spectroscopies in aqueous solution at different pH values. The study allows to demonstrate once more the effectiveness of oxidovanadium(IV) to interact with carboxylate groups. The most probable binding modes of the solution complexes were determined by EPR method. Two main coordination environments around the metal center were established: one includes four-carboxylate moieties and the other the set probably involves alkoxide and hydroxide groups.

1. Introduction

Commonly known by its anionic form prephenate, prephenic acid (1-(2-carboxy-2-oxido-ethyl)-4-hydroxy-cyclohexa-2,5-diene-1-carboxylic acid) is an intermediate in the biosynthesis of aromatic aminoacids in plants, fungi, and bacteria [1–3]. This reaction involves the intramolecular rearrangement of chorismate(I) to prephenate(II). Chorismate mutase catalyzes the transformation in the shikimate pathway (Scheme1) that leads to the biosynthesis of phenylalanine and tyrosine [4].

Many hydroxyacids are important in plants metabolism and nutrition. They have been identified as exudated from living leaves and roots in agricultural weeds [5–10]. These phenolic compounds, which have several functionals available for binding of biometals, are widely recognized as antioxidants and they are involved in metal transport processes. There is a great interest on the study of the bioavailability of metals in plants, and on the inhibitory effects that the non-flavonoids compounds produce on deleterious oxidative processes (cancer and atherosclerosis) [11,12].

Vanadium is a biologically ultramicrotrace transition metal and its physiologically relevant oxidation states include mainly +4 (vanadyl cation VO^{2+}) and +5 (vanadate species). These specie can be classified as hard acids and can strongly interact with biochemical donor groups specially containing oxygen and nitrogen atoms. Vanadium is present in rocks (5–250 ppm) and soils (20–500 ppm) thus being more accessible to plants and animals [13,14], and it is proved by the presence of vanadium in plants, fungi and bacteria [15]. The uptake by higher plants has been confirmed by EPR measurements and it has also been shown that plant enzymes and root growth are vanadium-dependent [15]. In fungi, vanadium is accumulated in *Amanita muscaria* and it was demonstrated that amavadin [15] involves carboxylate groups in the coordination sphere of vanadium(IV) complex. In addition, some vanadium complexes containing hydroxy-carboxylate ligands have been reported to have potential pharmacological activities [16].

Taking into account that no previous reports exist about this system, the aim of this work is to study the interaction between vanadium and prephenate anion as ligand using EPR and UV–Vis spectroscopies.

2. Experimental

The barium salt of prephenic acid (Sigma) and $VOSO_4{\cdot}5H_2O$ (Merck) were used as reagents. The experiments were performed under nitrogen atmosphere to avoid oxidation phenomena. The electronic absorption spectra were measured with a Hewlett–Packard 8452 diode-array spectrophotometer using 10-mm quartz cells. Base line corrections, normalization, curve-fitting and calculations were carried out by means of Grams/32 (Galactic Industries Corporation, USA) software. The EPR spectra were obtained using a Bruker ESP300 spectrometer operating at X-band with standard Oxford low temperature devices (ESR900/ITC4). Anisotropic X-band EPR spectra of frozen solutions were recorded at 140 K, after

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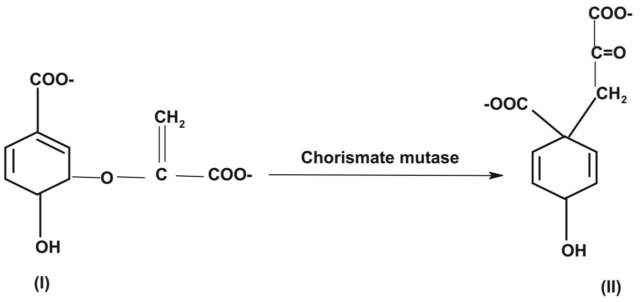

Scheme 1. Conversion of chorismate (**I**) to prephenate (**II**).

addition of 5% of DMSO to ensure good glass formation. All computer manipulations (simulation and difference) of the EPR spectra were performed using the program SimFonia (WINEPR SimFonia v1.25, Bruker Analytische Messtecnik GmbH, 1996).

3. Results and discussion

EPR spectra of the aqueous solution (1:1 and 2:1 L/M ratio) at 140 K were recorded at different pH values in order to assist in the identification of different vanadium specie and the corresponding geometries, particularly equatorial ligand donor set and the overall charges.

For the 2:1:prephenate/VO^{2+} system at pH 2.5 (Fig. 1), the EPR signal shows the characteristics line-wide trends for free $[VO(H_2O)_5]^{2+}$ ion denoting that no interaction occurs in high acidic medium. By adding NaOH 1 M aqueous solution, the increase of the pH value to 3.4 and 4.2 induces important variations on EPR features (Fig. 1) and a new resonance line appears together with the signal belonging to free vanadyl aquoion. In order to identify the specie, difference spectra were performed. The experimental and the simulated spectra at pH 4.2 are shown in Fig. 2. The simulation predicts that the new observed signal is originated by a V-chromophore with the spin Hamiltonian parameters of $g_z = 1.943$, $g_x = 1.977$, $g_y = 1.980$ and the hyperfine coupling constant of $A_z = 171 \times 10^{-4}$ cm^{-1}, $A_x = 60 \times 10^{-4}$ cm^{-1} and $A_y = 65 \times 10^{-4}$ cm^{-1} ($g_{iso} = 1.966$, $A_{iso} = 98.67 \times 10^{-4}$ cm^{-1}). Based on the calculated parameters, the experimental spectrum at pH 4.2 has been simulated and found fitting in good concordance with the experimental one (Fig. 3A).

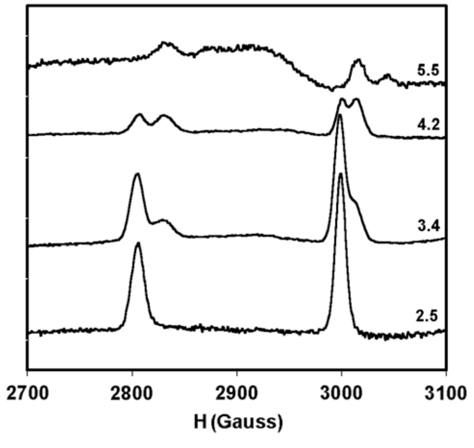

Fig. 1. X-band anisotropic EPR spectra (A_{II} region, Low Field) of the 2:1 prephenate–oxidovanadium(IV) system in frozen solutions (140 K) at differents pH values. Total concentration VO^{2+}: 2.5 mM, prephenate: 5 mM.

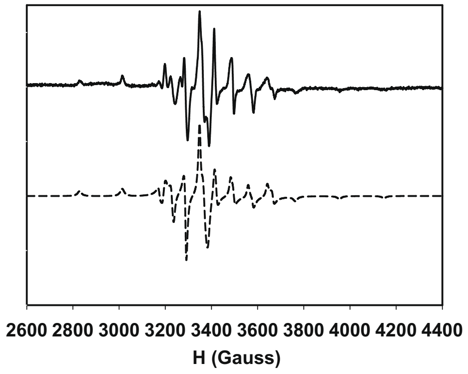

Fig. 2. X-band anisotropic EPR spectra. Solid line represents difference spectrum for the 2:1 prephenate–oxidovanadium(IV) frozen solutions (140 K) at pH 4.2 minus the $VO(H_2O)_5^{2+}$ contribution. Dash line, simulation. Total concentration VO^{2+}: 2.5 mM, prephenate: 5 mM.

Significant changes on the spectra are detected when the pH of the solution is modified. The highest possible value for pH is 5.5 because precipitation (probably $VO(OH)_2$) takes place. In this condition (Fig. 3B) two distinct specie are possible to be observed once more: the specie detected at pH 4.2 and a new one. For the new signal, the calculated EPR parameters are $g_z = 1.951$, $g_x = 1.977$, $g_y = 1.982$ and the hyperfine coupling constant of $A_z = 156 \times 10^{-4}$ cm^{-1}, $A_x = 60 \times 10^{-4}$ cm^{-1} and $A_y = 65 \times 10^{-4}$ cm^{-1} ($g_{iso} = 1.970$, $A_{iso} = 93.7 \times 10^{-4}$ cm^{-1}) suggesting both the formation of a new complex with some modification of the equatorial coordinated groups. Calculated EPR spectrum at pH 5.5 is in good concordance with the experimental one (Fig. 3B). Upon increasing the pH of the solution, the relative intensity of the signals decreases (not shown), precipitation takes place and probably oligonuclear specie start to be predominant, leading to extinction of the signal [17].

For the 1:1 prephenate/VO^{2+} system the same species have been detected. It is known that parallel component of the hyperfine coupling constant is sensitive to the type of donor atoms on the equatorial positions of the coordination sphere. The following empirical relationship is frequently used in order to determine the identity of the equatorial ligands in V(IV) complexes: $A_z = \sum n_i A_{z,i}$, (n_i: number of equatorial ligands of type I, $A_{z,i}$: contribution to the parallel hyperfine coupling from each of them) [18–20]. Considering the contributions to the parallel hyperfine coupling constant of the different coordination modes of the ligand ($COO^- = 42.72$ [17–19], $ArO^- = 38.6$ and $OH^- = 38.7 \times 10^{-4}$ cm^{-1} [20], respectively) and using the additivity rule for the detected species at pH 4.2, the empirical parameter was calculated. Very close to the $A_z = 171$ cm^{-1} obtained from the simulated EPR spectrum, the obtained value of $A_z = 170.9$ cm^{-1} is consistent with the species which could be interpreted assuming an equatorial ligand interaction via four $-COO^-$ moieties with O atoms in the planar donor set as schematically shown in Fig. 4 [21]. Comparable values are predicted considering other complexes with similar donor sets, and the calculated parameters fit well in the corresponding g_{II} versus A_{II} diagram [22]. The reduction of A_z with increasing pH (A_z calc $= 155 \times 10^{-4}$ cm^{-1}) is attributed to changes in the coordination sphere of the vanadyl moiety, probably including the dissociation and coordination of the alkoxide group of the ligand and the incorporation of OH^- to the coordination sphere [18,23,24]. At this pH value, species containing one OH^- around the oxidovanadium(IV) cation were usually identified [25]. The calculated A_z value matched well with two possibilities (A_z (2 ArO^- + 2 OH^-) = 154.6 and A_z (1 ArO^- + 3 OH^-) = 154.7) which were consistent with the hypothesis of the presence of the hydrolytic complex. Considering that undetectable precipitation began, the oxidovanadium(IV) concentration