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Short communication

Electrospray ionization mass spectral fragmentation study of amino acid derived oxovanadium Schiff base complexes and (oxo)-peroxovanadium Schiff base complexes

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Abstract

Amino acid derived oxovanadium Schiff base complexes and their in situ (oxo)-peroxovanadium Schiff base complexes were first studied with electrospray ionization tandem mass spectrometry (ESI-MS^n) with collision-induced dissociation (CID). Their fragmentation pathways are proposed on the base of the MS^n studies.

All of the molecular ions of the two group vanadium complexes easily lose a CO_2 molecule under ESI-MS condition. In the dissociation, H_2O, VO_2 will possibly be eliminated for oxovanadium Schiff base complexes, while (oxo)-peroxovanadium Schiff base complexes always yield the same ion at *m/z* 314 due to elimination of a molecule of aldehyde from amino acid residues. The dissociation rules may be extended to other metal Schiff base complexes and other peroxo-metal complexes.

Keywords: ESI-MS/MS; Oxovanadium complexes; (oxo)-Peroxovanadium complexes; Schiff base; Amino acids

1. Introduction

Oxovanadium complexes are used extensively in various oxidation reactions [1]. Some complexes can react with peroxide to yield (oxo)-peroxovanadium complexes. If appropriate chiral ligands were coordinated with oxovanadium complexes, catalytically asymmetric reactions occurred. Chiral amino acid derived oxovanadium Schiff base complexes were applied in enantioselective epoxidation of allyl alcohols [1], oxidative coupling of 2-naphthol [2] and sulfoxidation [3,4].

ESI mass spectral researches about oxovanadium complexes in gas phase are relatively scarce. Schröder and Schwarz investigated the fragmentation of alkoxo(catecholato)vanadium(V) complexes $[(C_6H_4O_2)V\ (OR_1)(OR_2)]^+$ in the gas phase, and interestingly they discovered that the CID spectra of all complexes show a signal which can be assigned to the complex $[(C_6H_4O_2)VO]^+$ [5]. Limbach studied ESI-MS of metalloporphyrins (including oxovanadium one) [6].

Vanadium-dependent haloperoxidases (VHPO) catalyze the oxidation of halide ion and organic sulfide by hydrogen peroxide [7]. In order to take insight into VHPO mechanism, Bortolini and Conte investigated the structure of peroxovanadium complexes mimicking VHPO by ESI-MS, which is particularly useful in the analysis of highly labile compounds [8–11]. In particular, they discovered the highly labile hypobromite-like vanadium intermediate as a vanadium-dependent bromoperoxidase (VBPO)-mimicking system [8].

Recently, Schulzke discovered that amino acid derived oxovanadium Schiff base complexes as a functional model coincided excellently with VBPO [12]. We recently discovered those complexes had much better stability than amino alcohol derived ones in sulfide oxidation, and much lower catalyst amount (less than 0.01 mol%) was required to completely, selectively transfer sulfide into sulfoxide due to antioxidation of amino acid derived those complexes to H_2O_2 (unpublished results). The phenomena were very similar to the high ratio of substrate and enzyme in oxidation of sulfides with VBPO [7]. So, those complexes will probably be valuable biomimetic catalysts.

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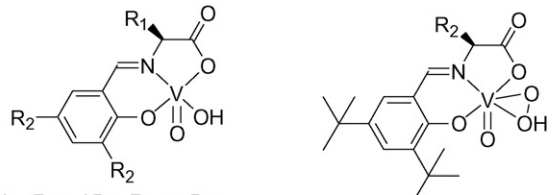


1a, R_1 = *i*-Bu, R_2 = *t*-Bu
1b, R_1 = *i*-Pr, R_2 = *t*-Bu
1c, R_1 = *t*-Bu, R_2 = *t*-Bu
1d, R_1 = CH(OH)Me, R_2= *t*-Bu
1e, R_1 = *t*-Bu, R_2 = *t*-Bu
1f, R_1 = *i*-Pr, R_2 = H

2a, R = *t*-Bu
2b, R = *i*-Pr
2c, R = Me

Scheme 1. Oxovanadium complexes **1** and (oxo)-peroxovanadium complexes **2**.

To our best knowledge, there is no ESI-MS^n study on oxovanadium Schiff base complexes **1** and (oxo)-peroxovanadium Schiff base complexes **2** derived from amino acids (Scheme 1). Based on the value of the oxovanadium complexes and as the extension of our research [13,14], we investigated the ESI mass spectral fragmentation of the two kinds of complexes.

2. Experimental

2.1. Chemicals

Amino acids were purchased from GL Biochem (Shanghai, China). All of oxovanadium Schiff base complexes were prepared as follows. The mixture of 1 mmol amino acid, 1 mmol salicylaldehyde, and 4 mmol $NaOAc{\cdot}3H_2O$ were dissolved in a refluxing solution of 4 ml water, 8 ml THF and 8 ml alcohol to give a clear yellow Schiff base solution. Then 1 mmol $VO(acac)_2$ was added into the resulting solution in fluxing. After 2 h, the solvent was removed under reducing pressure. CH_2Cl_2 and water was added to the residue, and the mixture was stirred vigorously. At this time, oxovanadium(IV) Schiff base complex is facilely oxidized into purple oxovanadium(V) Schiff base complex, just as described by Fujita [2]. Then the purple organic layer was extracted and evaporated under reduced pressure to give a black solid, which is verified as oxovanadium(V) Schiff base complex by IR, ^{51}V NMR, ESI-MS and ESI-FTICRMS (**1a**, $C21H31NO5V^-$, calc.: 428.1647, observed: 428.1635; **1b**, $C20H29NO5V^-$, calc.: 414.1491, observed: 414.1498). A little dark solid was dissolved in 0.2 ml CH_2Cl_2, and then diluted with methanol. The resulting solution was divided into two sample tubes. One was for MS analysis of oxovanadium Schiff base complexes. 0.05 ml H_2O_2 was added to the other sample tube and then oxovanadium Schiff base complex was in situ turned into (oxo)-peroxovanadium Schiff base complex, which was directly analyzed by ESI-MS.

2.2. Mass spectrometry

The high-resolution mass spectra (HR-MS) of compounds **1b**, **1c** were obtained using a Bruker APEX II Fourier transform ion cyclotron resonance mass spectrometry (FTICRMS) (Bruker Daltonik, Bremen, Germany), equipped with an electrospray ionization (ESI) source. The other mass spectra were recorded on a Bruker Esquire 3000 ion trap spectrometer equipped with an electrospray ion source. The samples were dissolved first in CH_2Cl_2 and then diluted with methanol. They were introduced into the electrospray needle by mechanical infusion at a flow rate of 4 $\mu l\,min^{-1}$ with a Cole–Parmer Model 74900 syringe pump. The ESI source potentials were capillary 4.0 kV, lens 1 5.0 V, lens 2 60.0 V and capillary exit offset 75.9 V. The mass spectrometer was scanned at a rate of 300 mass units per second. Six scans were averaged to obtain each spectrum. Nitrogen was used as the nebulizer gas with a flow rate of 4 $l\,min^{-1}$ (nebulizer pressure 7 psi) at 300 °C. Tandem mass spectra were obtained by CID with helium as collision gas after isolation of the appropriate precursor ions. The fragmentation voltage amplitudes were maintained at 0.3–1.5 V to acquire better spectra.

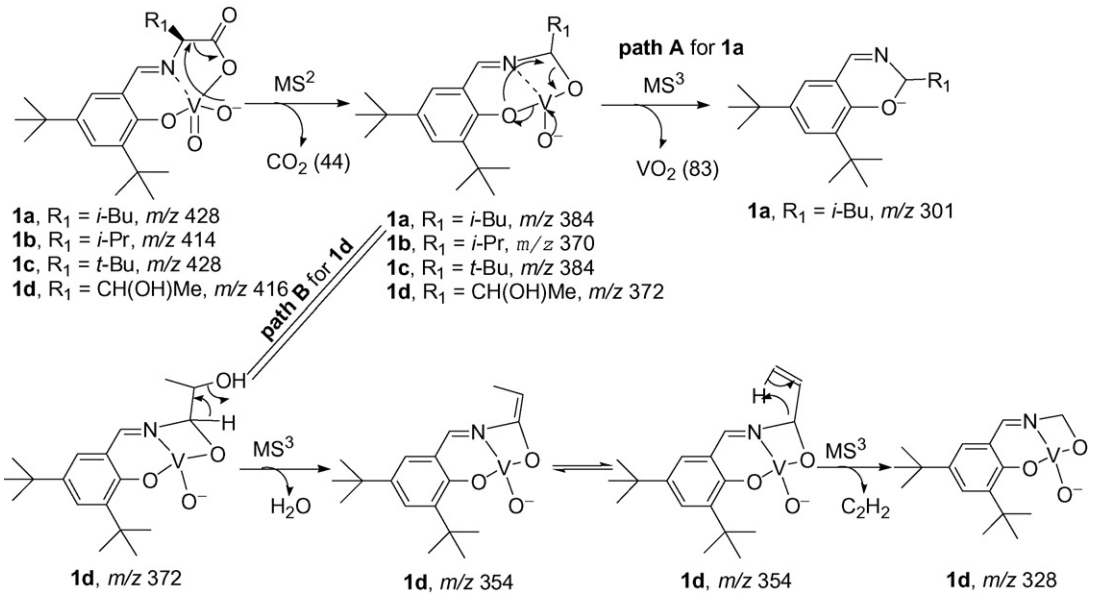
3. Results and discussion

The mass spectra of **1** were studied in detail and the data are given in Table 1. All of the molecular ions ($[M+H]^+$ or $[M–H]^-$) of oxovanadium Schiff base complexes **1a**–**1f** were detected under the ESI-MS condition. Those molecular ions as the precursor ionic species (P) eliminated a CO_2 molecule (Table 1, **1a**–**1f**), and lost a VO_2 (**1a** and **1e**). Loss of a molecule of H_2O from the protonated molecule ions was detected (**1e**,

Table 1
MS/MS and MS^3 fragment ions observed after CID of the precursor ions (P) of oxovanadium Schiff base complexes **1** with the relative abundance (%) in parentheses

Compound (mode)	P (*m*/*z*)	Fragment ions (*m*/*z*)					
		[P–44]	[P–18]	[P–83]	[P–18–26]	[P–18–44]	[P–18–83]
1a (−)	428(100)	384(65)					
	384(100)			301(68)			
1b (−)	414(37)	370(100)					
1c (−)	428(9)	384(100)					
1d (−)	416(100)	372(77)					
	372(100)		354(31)		328(20)		
1e (+)	318(89)		300(4)			256(42)	217(100)
1f (+)	304(100)	260(3)	286(34)				

18 Da, 44 Da, 83 Da, 26 Da correspond to H_2O, CO_2, VO_2, C_2H_2, respectively.



Scheme 2. Fragmentation pathway of negative **1a**–**1e** $[M–H]^-$.

1f). Bortolini and Conte discovered that peroxovanadium complexes, especially simple species, were available to coordinate several solvent molecules, such as H_2O, CH_3OH, C_2H_5OH [9,10]. But we could not observe the solvated ions, perhaps because the crowded sphere around center metal V in oxovanadium Schiff base complexes inhibits coordination of solvent molecule.

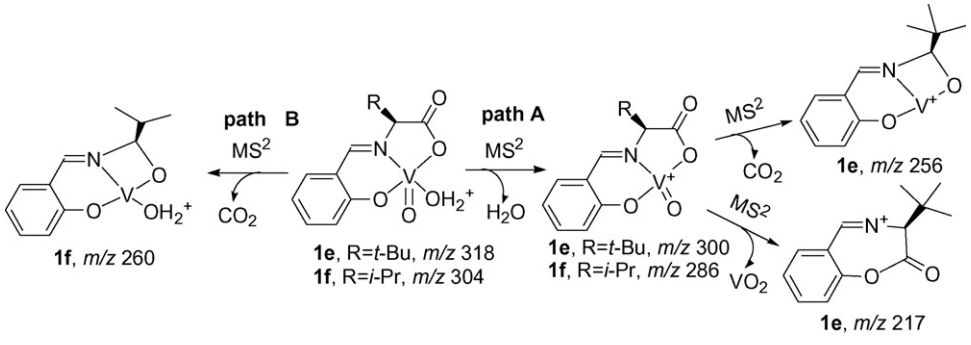
The fragmentation pathway of the negative **1a**–**1d** $[M–H]^-$ is shown in Scheme 2. The ESI-MS^3 of negative **1a** and the ESI-MS^2 of **1d** $[M–H]^-$ as typical samples are shown in Figs. 1 and 2, respectively.

All of the negative molecular ions **1a**–**1d** $[M–H]^-$ as the precursor ions in the MS/MS typically lose a CO_2 molecule $[M–H–CO_2]^-$ (Table 1). Their fragmentation mechanism probably is that $V–O^-$ attacks to the partially positive charge α-carbon of carboxyl, and then loss of a CO_2 molecule gives $[M–H–CO_2]^-$ of **1a**, **1b**, **1c**, **1d** at *m/z* 384, 370, 384, 372, respectively (Scheme 2).

For **1a**, further dissociation takes place according to **path A** in the MS^3 (Scheme 2). Its fragmentation mechanism probably is that transfer of the negative charge of $V–O^-$ to Ar–O through V atom, and then the latter $Ar–O^-$ attacks to the partially positive charge of the α-carbon of amino group, loss of a VO_2 segment gives a negative ion $[M–H–CO_2–VO_2]^-$ at *m/z* 301.

Threonine derived oxovanadium Schiff base complex **1d** shows different fragmentation mechanism in the MS^3 (Scheme 2). Its negative-ion mode tandem mass spectra of $[M–H]^-$ is shown in Fig. 2. Further fragmentation occurs according to **path B** in MS^3 due to threonine residue containing a hydroxyl group. Its dissociation mechanism is that elimination of a H_2O molecule yields an alkenyl-containing negative ion $[M–H–H_2O]^-$ at *m/z* 354, which interconverts with terminal alkene; and then the H-rearrangement of the terminal alkenyl group results in loss of an acetylene molecule from the complex and a new negative ion $[M–H–H_2O–C_2H_2]^-$ at *m/z* 328 is obtained.

Contrary to 3,5-di-*tert*-butylsalicylaldehyde derived oxovanadium complexes **1a**–**1d**, simple salicylaldehyde derived ones **1e**–**1f** yield protonated molecule ion $[M+H]^+$ at *m/z* 318 and *m/z* 304 (and no peak detected in negative mode) (Scheme 3). The fact that 3,5-di-*tert*-butylsalicylaldehyde derived oxovanadium complexes **1a**–**1d** are only formed as anions in the ESI-MS condition, while simple salicylaldehyde derived ones **1e**–**1f** are



Scheme 3. Fragmentation pathway of **1e** cation $[M+H]^+$.

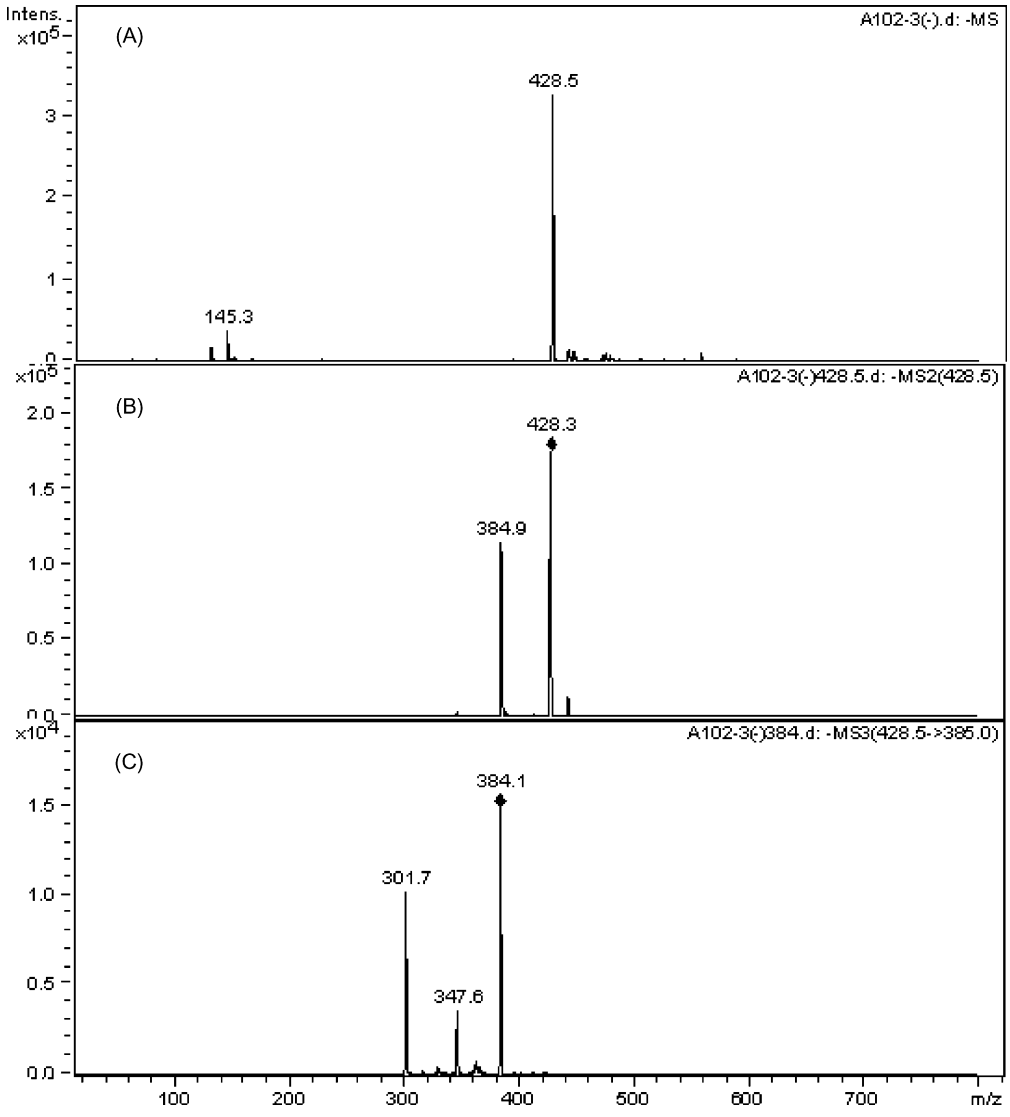


Fig. 1. Negative-ion mode tandem mass spectra of $[M–H]^-$ of compound **1a**: (A) the source spectrum, (B) daughter ions from *m/z* 428, (C) daughter ions from *m/z* 384.

only formed as positive ions is strange, and we cannot explain it now. The facile loss of a H_2O molecule according to **path A** affords a daughter ion $[M+H–H_2O]^+$ at *m/z* 300 and *m/z* 286 for **1e** and **1f**, respectively. In successive CID of the precursor ion $[M+H–H_2O]^+$, a CO_2 molecule or a VO_2 segment are dissociated and produce positive ions $[M+H–H_2O–CO_2]^+$ at *m/z* 256 and $[M+H–H_2O–VO_2]^+$ at *m/z* 217 (Scheme 3, Fig. 3). However, a CO_2 molecule is released directly from the protonated molecule ion $[M+H]^+$ in **path B** of **1f** (Scheme 3).

MS/MS and MS^3 fragment ions of (oxo)-peroxovanadium Schiff base complexes **2** is listed in Table 2. All of (oxo)-peroxovanadium Schiff base complexes **2** are only formed as anions due to the easy removal of a proton from its structure as shown in Scheme 1. Interestingly, Bortolini and Conte observed that monoperoxo-vanadium complexes were facile to take a proton and form protonated molecular ions $[M+H]^+$ [9] while bisperoxovanadium compounds and triperoxo vanadium complexes often lost protons and gave negative molecular ions $[M–H]^-$ under the ESI-MS conditions [10,11].

There exist two dissociation pathways of (oxo)-peroxovanadium Schiff base complexes **2a** (Scheme 4). Its ESI-MS^n is shown in Fig. 4. In **path A**, loss of a CO_2 molecule due to the attack of oxygen atom of peroxyvanadium VO_2 to the α-carbon of carboxyl group gives a negative fragment ion $[M–H–CO_2]^-$ at *m/z* 400. The facile break of peroxy O–O and the following rearrangement results

Table 2
MS/MS and MS^3 fragment ions observed after CID of the precursor ionic species (P) of (oxo)-peroxovanadium Schiff base complexes **2** with the relative abundance (%) in parentheses

Compound	P (*m/z*)	Fragment ions (*m/z*)		
		$[P–CO_2]^-$	$[P–RCHO]^-$	$[P–O]^-$
2a	444(8) 314(100)	400(3) 287(6)	314(100)	428(1)
2b	430(20)	386(5)	314(100)	414(6)
2c	402(100)	358(11)	314(3)	

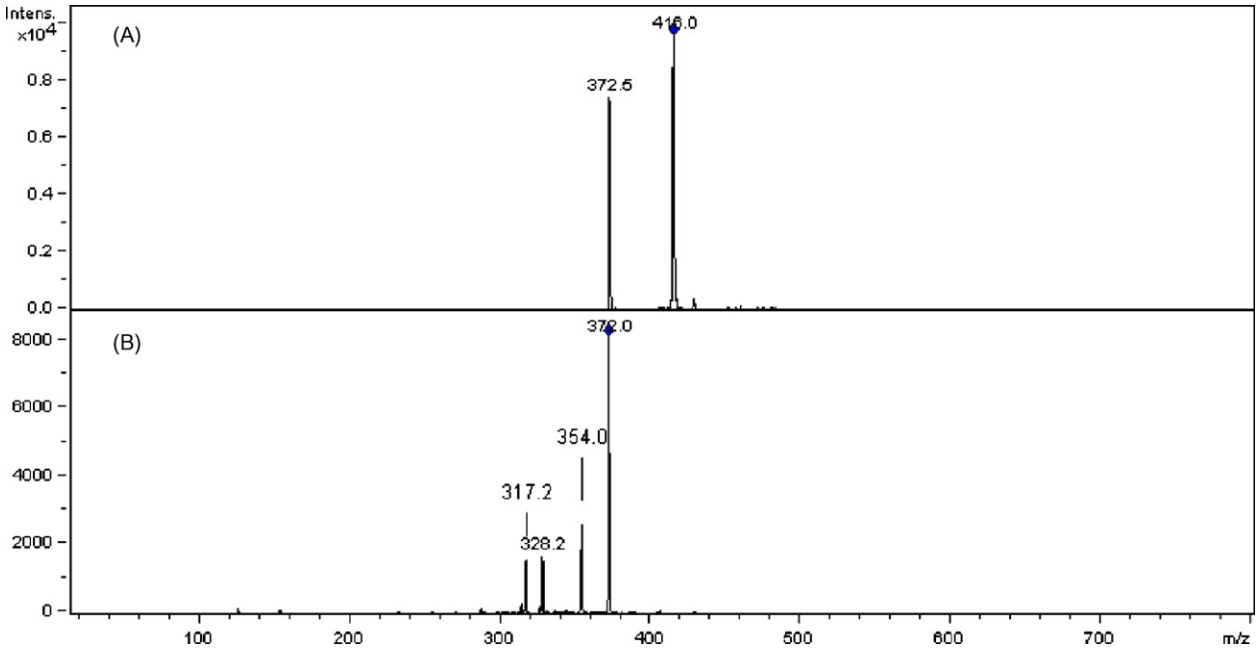


Fig. 2. Negative-ion mode tandem mass spectra of $[M–H]^-$ of compound **1d**: (A) daughter ions from *m/z* 416 and (B) daughter ions from *m/z* 372.

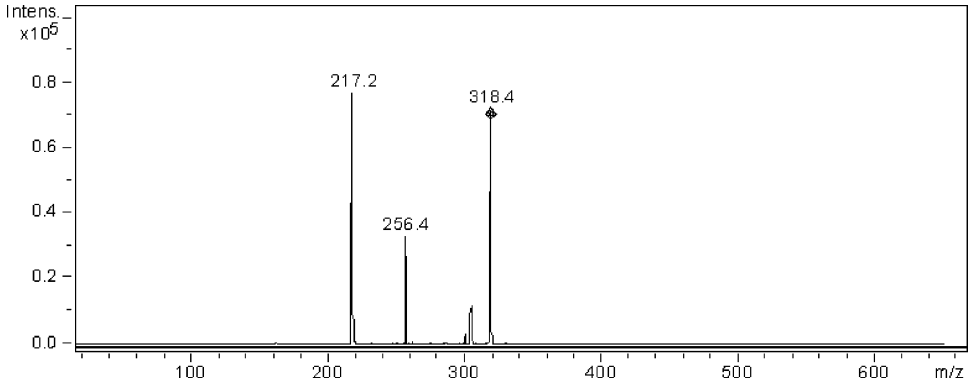
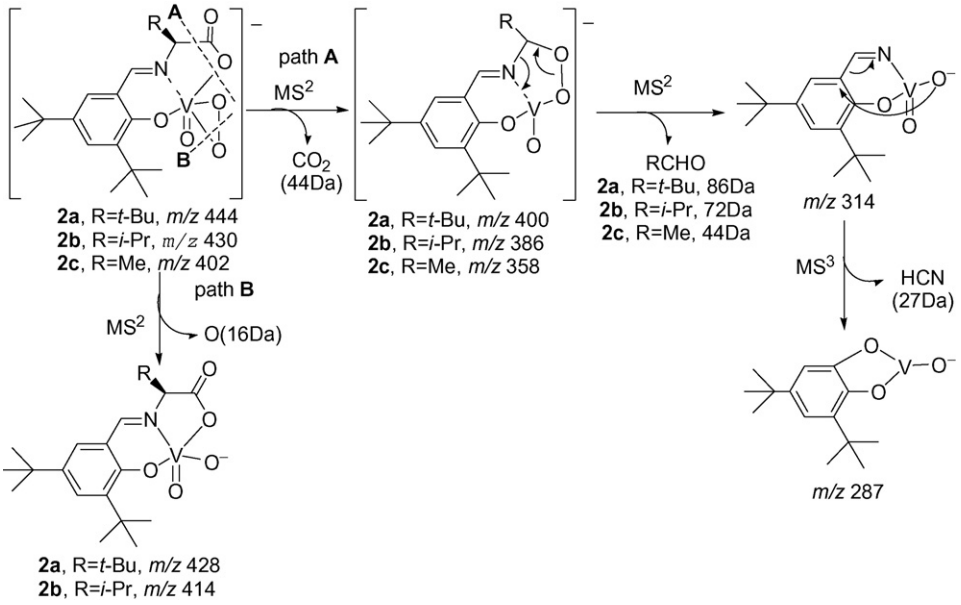


Fig. 3. Positive-ion mode tandem mass spectra of $[M–H]^+$ of compound **1e**: daughter ions from *m/z* 318.



Scheme 4. Fragmentation pathway of negative **2a**.

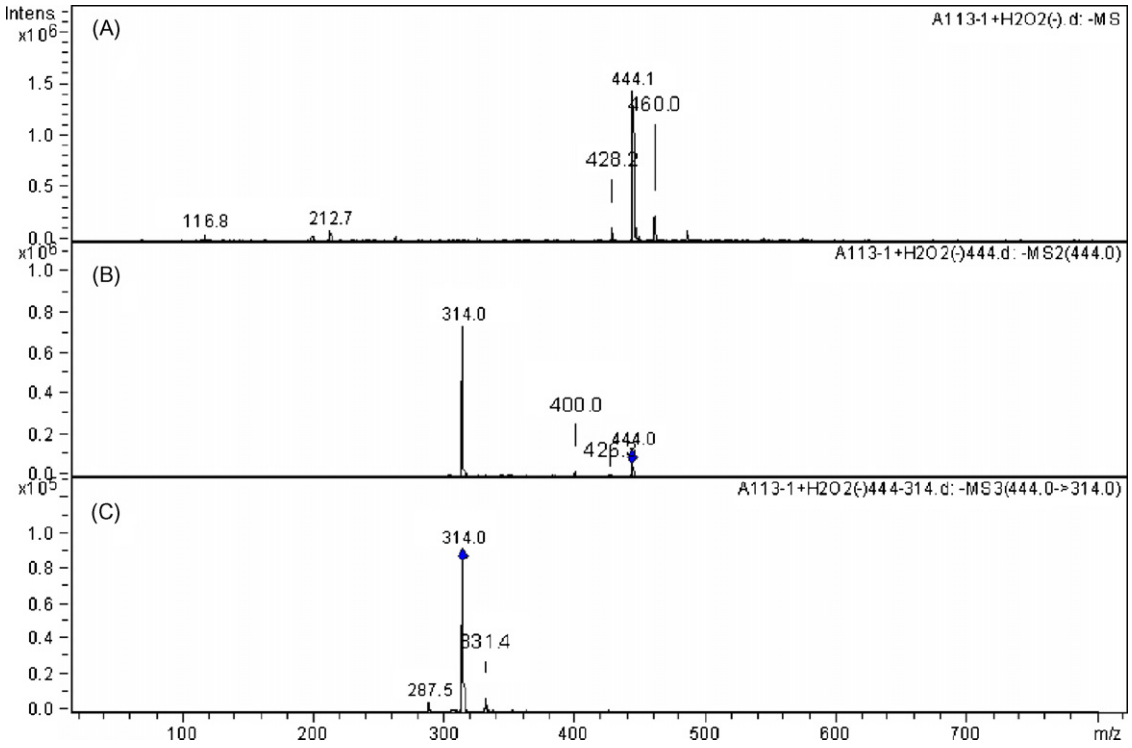


Fig. 4. Negative-ion mode tandem mass spectra of $[M–H]^-$ of compound **2a**: (A) the source spectrum, (B) daughter ions from *m/z* 444, (C) daughter ions from *m/z* 318.

in the elimination of *t*-BuCHO (86 Da) and a vanadium-containing ion $[M–H–CO_2–Bu^tCHO]^-$ is obtained at *m/z* 314, which is especially typical ion for (oxo)-peroxovanadium Schiff base complexes **2**. In the MS^3 of the precursor ion $[M–H–CO_2–Bu^tCHO]^-$ *m/z* 314, elimination of a HCN molecule due to the attack of $V–O^-$ to phenyl cycle affords vanadium-containing negative ion at *m/z* 287. Complexes **2b** and **2c** take a similar dissociation to **2a** according to **path A**. Due to difference of amino acid residues, complex **2b** releases an *i*-PrCHO molecule (72 Da) and complex **2c** eliminates a CH_3CHO molecule (44 Da) during the CID courses.

Oxygen atoms are directly released from negative molecular ions $[M–H]^-$ **2a** and **2b** according to **path B** due to the facile break of peroxy O–O bond, and negative ions of corresponding oxovanadium Schiff base complex $[M–H–O]^-$ appear at *m/z* 428 and at *m/z* 414, respectively.

4. Conclusion

Oxovanadium Schiff base complexes derived from amino acids were synthesized. They and their in situ (oxo)-peroxovanadium Schiff base complexes were studied by ESI-MS^n. Their fragmentation pathways are proposed on the base of the MS^n studies.

Oxovanadium Schiff base complexes generally lose a CO_2 molecule, dissociate a H_2O molecule for positive-ion mode, and sometimes followed by the elimination of VO_2 segment from positive- or negative-ions. Threonine derived oxovanadium complex takes different dissociation pathway due to the presence of a hydroxyl group in threonine residue.

Interestingly, (oxo)-peroxovanadium Schiff base complexes always lose a CO_2 molecule and finally yield the same ion at *m/z* 314 due to elimination of a molecule of aldehyde from amino acid residue; the ESI-MS^3 of the precursor ion at *m/z* 314 release a HCN molecule.

The dissociation rules may be extended to other metal Schiff base complexes and other peroxo-metal complexes.

Acknowledgements

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