



Synthesis and characterization of fluoride-incorporated polyoxovanadates



Yuji Kikukawa, Taiga Yokoyama, Sanae Kashio, Yoshihito Hayashi*

Department of Chemistry, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan

ARTICLE INFO

Article history:

Received 27 October 2014
Received in revised form 17 February 2015
Accepted 18 February 2015
Available online 26 February 2015

Keywords:

Polyoxovanadate
Vanadium
Fluoride
Anion capture
Structure transformation

ABSTRACT

The speciation studies of oxovanadates are essential to clarify their biological activities. We surveyed the distribution of oxovanadate species in the presence of halide anions with various acid concentrations in an aqueous mixed-solvent system. The presence of chloride, bromide, and iodide anions has no effects on the appearance of polyoxovanadate species observed in ^{51}V NMR. Those are the precedent formation of metavanadate species and decavanadates. The presence of fluoride anion during the addition of acids exhibits strong intervention in the polyoxovanadate equilibria and we found the subsequent formation of two polyoxovanadate species by ^{51}V NMR observation. From the estimated experimental condition, we isolated fluoride-incorporated polyoxovanadates $[\text{Et}_4\text{N}]_4[\text{V}_7\text{O}_{19}\text{F}]$ and $[\text{Et}_4\text{N}]_4[\text{HV}_{11}\text{O}_{29}\text{F}_2]$, successfully. Polyanion $[\text{V}_7\text{O}_{19}\text{F}]^{4-}$ is the fluoride-incorporated all V(V) state polyoxovanadate which has two different coordination environments of tetrahedral and square pyramidal vanadium units within the one anionic structural integrity. The structural gap between tetrahedral-unit-based metavanadate and octahedral-unit-based decavanadate structures may be linked by this hybrid complex.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

Oxovanadates, VO_4^{3-} , in oxidation state (V) have long been recognized as an analogue of phosphate, PO_4^{3-} [1]. These oxo-anions show similar stepwise protonation and subsequent oligomerization. The structural similarity allows oxovanadates to interact with a biological system through phosphate-dependent metabolic processes [2–4]. Pharmacological properties of oxovanadates such as enzyme inhibitors and insulin-enhancing agents have been investigated [2–4]. An important difference between oxovanadates and phosphates is the preference of the coordination spheres. Oxovanadates readily form decavanadates, $[\text{V}_{10}\text{O}_{28}]^{6-}$, that is composed of VO_6 octahedral coordination spheres, while phosphates prefer tetrahedral PO_4 coordination sphere, exclusively. For oxovanadates, the solution system involves equilibria with mono-, di-, tri-, tetra-, penta-, and decavanadates [5]. One of the interesting utilizations of oxovanadates is developed by Crans' group. Once decavanadates are placed in micelles, it may interact with hydrophobic or hydrophilic sites, under the condition with a limited amount of water [6–9]. In such a confined-space, the chemical equilibrium may lead to a different distribution with a new species in-between metavanadates and decavanadates.

Oxovanadates can interact with some biological tissue and have the potential to play a role in the treatment of e.g. ulcers, cancer, and ischemic heart disease [10–14]. The biological reactivity of oxovanadates depends on which species is present in the solution [15]. Therefore, the speciation studies of oxovanadates are essential to clarify their

biological activities. Up to now, some reports on the speciation of oxovanadates under the biomimetic conditions, e.g. in the presence of chloride and phosphate anions, have been reported suggesting that the effects of simple anions are significant [16–18]. Although fluoride anions can be assimilated into the body through some kinds of tea, water, and toothpaste, the distribution of oxovanadates in the presence of fluoride anions remains largely unexplored.

We have studied the effects of halide anions for the polyoxovanadate syntheses in acetonitrile solution and found a few polyoxovanadate species such as $[\text{HV}_{11}\text{O}_{29}\text{F}_2]^{4-}$ and $[\text{HV}_{12}\text{O}_{32}(\text{Cl})]^{4-}$ [19]. In this study, we investigated acidification of metavanadates in the presence of fluoride anions in a mixed solvent of acetonitrile and water, which simulate the reaction in a limited amount of water with controlled proton concentration. This study leads to a discovery of rational syntheses of $[\text{V}_7\text{O}_{19}\text{F}]^{4-}$ and $[\text{HV}_{11}\text{O}_{29}\text{F}_2]^{4-}$. The successful isolation of the products allows the full characterization by X-ray crystallography, IR, ^{51}V and ^{19}F NMR, UV/visible (UV/Vis), and cyclic voltammetry.

2. Experimental section

2.1. Physical measurements

IR spectra were measured on Jasco FT/IR-4100 using KBr disks. NMR spectra were recorded with JEOL JNM-LA400. ^{51}V and ^{19}F NMR spectra were measured at 105.15 and 376.17 MHz, respectively. All spectra were obtained in the solvent indicated, at 25 °C unless otherwise noted. ^{19}F NMR spectra were referenced to neat CF_3COOH ($\delta = 0.00$). ^{51}V NMR spectra were referenced using a sample of 10 mM NaVO_3 in 2.0 M NaOH (−541.2 ppm). UV/Vis spectra were recorded using a

* Corresponding author. Fax: +81 76 264 5742.
E-mail address: hayashi@se.kanazawa-u.ac.jp (Y. Hayashi).

Hitachi U-3500 spectrophotometer. An ALS/CH Instruments electrochemical analyzer (Model 600A) was used for voltammetric experiments. The working electrode was glassy carbon, the counter electrode was Pt wire, and the reference electrode was Ag/Ag⁺. The voltage scan rate was set at 100 mV s⁻¹. The potentials in all voltammetric experiments were converted using data derived from the oxidation of Fc (Fc/Fc⁺, Fc = ferrocene) as an external reference. Elemental analyses of C, H, and N were performed by the Research Institute for Instrumental Analysis at Kanazawa University. Elemental analysis of F was performed by the Center for Organic Elemental Microanalysis Laboratory at Kyoto University.

2.2. NMR studies for the effect of the presence of halide anions on the distribution of oxovanadate species

{Et₄N}₄[V₄O₁₂]·2H₂O (238 mg, 0.25 mmol) and {*n*-Bu₄N}X (0.20 mmol, X = F⁻, Cl⁻, Br⁻, or I⁻) were dissolved in a mixed solvent of CD₃CN and D₂O (2 mL, 3:1, v/v). Then, the required amounts of 2.0 M *p*-toluenesulfonic acid (TsOH) CD₃CN/D₂O solution (3:1, v/v) were added. The dissolved species was monitored by ⁵¹V NMR.

2.3. Synthesis

2.3.1. Materials

The chemicals and reagents were purchased from various commercial sources and were used without further purification unless otherwise stated. {Et₄N}₄[V₄O₁₂]·2H₂O was synthesized according to the reported procedure [20].

2.3.2. Synthesis of {Et₄N}₄[V₇O₁₉F]

To an acetonitrile solution of {Et₄N}₄[V₄O₁₂] (0.25 mmol, 2 mL), {*n*-Bu₄N}F·3H₂O (45 mg, 0.14 mmol) and TsOH·H₂O (108 mg, 0.57 mmol) were added. The solution was filtered and the filtrate was kept for several hours at 5 °C, giving orange crystals suitable for X-ray crystallographic analysis (91 mg, 53% yield based on V). Anal. Calcd. for {Et₄N}₄[V₇O₁₉F]: C, 32.01; H, 6.72; N, 4.67; F, 1.58; found: C, 31.93; H, 6.84; N, 4.55; F, 1.62. IR (KBr pellet; 4000–400 cm⁻¹): 3419, 2984, 2950, 1636, 1486, 1456, 1441, 1394, 1369, 1305, 1174, 1122, 1069, 1057, 1005, 955, 930, 931, 788, 622, 562, and 448 cm⁻¹. ⁵¹V NMR (105.15 MHz, propylene carbonate/CD₂Cl₂, 1:1, v/v, 25 °C): δ = 453, -541, and -605 ppm. ¹⁹F NMR (376.17 MHz, propylene carbonate/CD₂Cl₂, 1:1, v/v, 25 °C): δ = 71 ppm.

2.3.3. Synthesis of {Et₄N}₄[HV₁₁O₂₉F₂]

To an acetonitrile solution of {Et₄N}₄[V₄O₁₂] (0.25 mmol, 2 mL), {*n*-Bu₄N}F·3H₂O (57 mg, 0.18 mmol) and TsOH·H₂O (156 mg, 0.82 mmol) were added. The solution was filtered and the filtrate was kept for several hours, giving red crystals (91 mg, 63% yield based on V). Anal. Calcd. for {Et₄N}₄[HV₁₁O₂₉F₂]: C, 24.26; H, 5.15; N, 3.54; found: C, 24.76; H, 5.33; N, 3.59. IR (KBr pellet; 4000–400 cm⁻¹): 3446, 2981, 2951, 1635, 1484, 1458, 1391, 1374, 1308, 1184, 1118, 1080, 1056, 1010, 987, 965, 853, 792, 732, 651, and 486 cm⁻¹. ⁵¹V NMR (105.15 MHz, propylene carbonate/CD₂Cl₂, 1:1, v/v, 25 °C): δ = 466, -470, -488, -502, -527, and -536 ppm. ¹⁹F NMR (376.17 MHz, propylene carbonate/CD₂Cl₂, 1:1, v/v, 25 °C): δ = 67 ppm (d, J_{F,F} = 50 ± 20 Hz) and -72 ppm (d, J_{F,F} = 50 ± 20 Hz).

2.4. X-ray crystallographic analysis

Single crystal structure analysis was performed at -150 °C by using a Rigaku/MSC Mercury diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å) and with 0.5° ω-scans at 0° and 90° in φ. The crystal data is summarized in Table S1. Data were collected and processed by using the CrystalClear program [21]. Numerical absorption corrections were applied by using CrystalClear and corrections for Lorenz and polarization effects were performed. The structure

analysis was performed using CrystalStructure [22]. All structures were solved by SHELXS-97 (direct methods) and refined by SHELXL-2013 [23,24]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms are positioned geometrically and refined using a riding model.

3. Results and discussion

3.1. Distribution studies in the presence of halide anions

The vanadium speciation in aqueous solution has been well established. In the neutral pH, mono-, di-, tetra- and pentavanadate species are distributed in equilibrium, and in acidic condition, decavanadates are preferably formed [16–18,25]. The vanadium chemistry in an organic solution is quite different from that in an aqueous solution. In an organic solution, various polyoxovanadate species such as [V₅O₁₄]³⁻, [PdV₆O₁₈]⁴⁻, [Cu₂V₈O₂₄]⁴⁻, [Mn₂(V₅O₁₅)₂]⁶⁻, [Co₂(OH)₂V₁₀O₃₀]⁶⁻, [HTeV₉O₂₈]⁴⁻, and [V₁₂O₃₂Cl]⁵⁻, which could not be obtained in an aqueous solution, have been synthesized by using [V₄O₁₂]⁴⁻ as a precursor [26–29]. Recent studies in our laboratory have focused on the exploration of a mixed solvent system with water, which mimic the confinement environment surrounded by organic compounds and water at the same space in a biological system.

To survey the effect of halide anions on the distribution of oxovanadate species, proton concentration was varied by the addition of 0 to 3.4 equivalents of *p*-toluenesulfonic acid (TsOH) with fluoride, chloride, bromide, or iodide anions. As a control experiment, the same experiment without halide anions was carried out. {Et₄N}₄[V₄O₁₂] was dissolved in a mixed solvent of acetonitrile and water (3:1, v/v). ⁵¹V NMR spectrum showed two signals at -585 and -596 ppm due to [V₄O₁₂]⁴⁻ and [V₅O₁₅]⁵⁻, respectively (Fig. 1). By the addition of 1.1 equivalents of TsOH, signals at -423, -500, and -519 ppm due to a decavanadate were observed. By the addition of 1.7 equivalents of TsOH, intensity ratio of the signals due to a decavanadate increased. Signals at -601 and -608 ppm were assigned as the signals from [V₁₂O₃₂(CH₃CN)]⁴⁻ [30]. Further addition of TsOH (2.4 equivalents) yielded the yellow precipitate of {Et₄N}₃[H₃V₁₀O₂₈], which was estimated by IR spectrum (Fig. S1). These distributions of vanadium species depending on the acid concentration closely resembled the distribution in water, without the formation of dodecavanadate [25].

To the {Et₄N}₄[V₄O₁₂] solution in the presence of 0.8 equivalents of {*n*-Bu₄N}Cl, {*n*-Bu₄N}Br, or {*n*-Bu₄N}I, the addition of 1.7 equivalents of TsOH gave almost the same spectra as that of the control experiment, showing that Cl⁻, Br⁻, and I⁻ have no effect on the vanadium speciation (Fig. S2). On the other hand, in the presence of 0.8 equivalents of {*n*-Bu₄N}F, the acidified solution gave novel three signals at -460, -547, and -611 ppm without those due to decavanadates (Fig. 2).

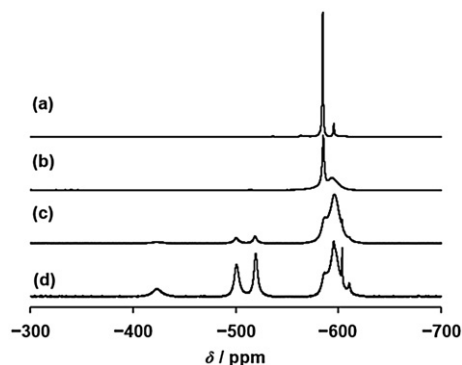


Fig. 1. ⁵¹V NMR spectra in a mixed solvent of CD₃CN and D₂O (3:1, v/v) after the addition of (a) 0, (b) 0.57, (c) 1.1, and (d) 1.7 equivalents of TsOH with respect to {Et₄N}₄[V₄O₁₂]. Signals around -585 and -596 ppm were due to [V₄O₁₂]⁴⁻ and [V₅O₁₅]⁵⁻, respectively. Signals at -423, -500, and -519 ppm were due to a decavanadate. Signals at -601 and -608 ppm were assigned to [V₁₂O₃₂(CH₃CN)]⁴⁻.

Download English Version:

<https://daneshyari.com/en/article/1315893>

Download Persian Version:

<https://daneshyari.com/article/1315893>

[Daneshyari.com](https://daneshyari.com)