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Heterolytic Dissociation of Water Demonstrated by Crystal-to-Crystal Core Interconversion from (μ-Oxo)divanadium to Bis(μ-hydroxo)divanadium Substituted Polyoxometalates

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Supporting Information

ABSTRACT: The heterolytic dissociation of water with the previously unknown four-coordinated syn-linear (μ-oxo)-divanadium core to form the five-coordinated bis(μ-hydroxo)-divanadium core was confirmed by a crystal-to-crystal transformation.

The adsorption and dissociation or activation of water on metals or metal oxides are very important and have been enthusiastically investigated for a quarter of a century.[1−3] The homolytic and heterolytic dissociation of water is quite difficult under uncatalyzed gaseous conditions, because the respective energies are estimated to be ca. 0.4934 and 1.635 MJ mol^{-1}. The bond dissociation of water has been reported to proceed through (i) oxidative addition to the low-valent transition metal center-(s),[4] (ii) photocatalytic and electronic activation on the metal oxide surface,[1b,5] (iii) adsorption (coordination) followed by the disproportionation of two water molecules into H_3O^+ and OH^- (water bilayer model),[1b,6] or (iv) dissociative adsorption on the oxygen vacancy or the structural defects such as the step and the kink.[1b,7] Whereas much effort has been made to elucidate the mechanism of dissociation of water with computational methods, the details have not yet been disclosed due to the lack of experimental and analytical procedures at the atomic or molecular level.

From a coordination chemistry point of view, there is no experimental evidence for the reactivity of the five- or six-coordinated (μ-oxo)dimetal complexes with water to produce a bis-(μ-hydroxo)dimetal complex, which could be regarded as the heterolytic dissociation of water. However, the reaction of the five-coordinated (μ-oxo)diiron core with water to form the corresponding six-coordinated bis(μ-hydroxo)diiron core has been proposed by spectroscopy[8] and is considered to be an important step in the proposed mechanism for methane monooxygenase.[2] In addition, the four-coordinated (μ-oxo)divanadium(V) site on TiO_2 has recently been proposed to be an active site for the reaction by DFT calculations,[9] while divanadium complexes with five- or six-coordinated anti-linear,[10] anti-angular,[11] twist-linear,[12] twist-angular,[13] and syn-angular[14] $(OV)_2(\mu\text{-O})$ cores have been reported. We report the heterolytic dissociation of water on a metal oxide cluster with the previously unknown four-coordinated syn-linear (μ-oxo)divanadium core, $(TBA)_4[\gamma\text{-SiV}_2W_{10}O_{39}]$ (**1**; TBA = tetra-*n*-butylammonium), by using a crystal-to-crystal transformation.[15,16]

A dark red single crystal of **1** suitable for X-ray crystallographic analysis was obtained by the treatment of $(TBA)_4[\gamma\text{-H}_2SiV_2W_{10}O_{40}]$ with excess phenyl isocyanate (PhNCO) in 1,2-dichloroethane under argon and standing at room temperature for 2 days (58% yield). The solid-state ^{51}V MAS NMR spectrum of **1** showed a signal at −585.8 ppm (Figure S8A). X-ray crystallography of **1** revealed the formation of $(TBA)_4[\gamma\text{-SiV}_2W_{10}O_{39}]$ with a (μ-oxo)-divanadium(V) core (Figure 1A; Tables S1 and S2). The two vanadium centers have a tetrahedral geometry with longer $V\cdots O(-Si)$ bonds (2.759 and 2.707 Å). The V(101)−O(113) and V(102)−O(113) distances are 1.738(11) and 1.768(11) Å, respectively, indicating the partial double bond nature of V−O bonds. The bond valence sum (BVS) values of vanadium (5.18, 5.29), tungsten (5.95−6.18), silicon (3.89), and oxygen (1.88−2.29) indicate that the respective valences in **1** are +5, +6, +4, and −2 (Table S3).[17] The V(101)−O(113)−V(102) angle and the dihedral angle O(101)−V(101)−V(102)−O-(102) are 178.0(7) and 0.00°, respectively, showing a previously unknown syn-linear conformation of the $(OV)_2(\mu\text{-O})$ core.

In order to confirm the nature of the syn-linear $(OV)_2(\mu\text{-O})$ core in **1**, DFT calculations (6-31G*/LanL2DZ hybrid basis sets with B3LYP level of theory) were carried out by using the conductor-like polarizable continuum model (IEFPCM) with the parameters of the United Atom Topological Model (UAKS) (Figure 1B).[18,19] The orbital of the $(VO)_2(\mu\text{-O})$ core (HOMO-4) mainly consisted of 44% of the p_y and 21% of the p_z orbitals of terminal oxo ligands, 70% of the p_z orbital of the bridging oxo ligand, and 5% of the d_{z^2} and 4% of the d_{yz} orbitals of two vanadium centers, showing the weak $d\pi-p\pi-d\pi$ conjugation of the syn-linear $(VO)_2(\mu\text{-O})$ core.[20] The negative charges of the bridging and terminal oxo ligands were calculated to be −0.809 (−0.702) and −0.509 (−0.485), respectively, by a Mulliken charge (natural bond population) analysis. These results suggest that the bridging oxo ligand of the $(VO)_2(\mu\text{-O})$ core can act as a nucleophile.

When a dark red crystal of **1** was placed under a humid atmosphere, its color gradually changed to pale yellow (Figure 2; Figure S10). Upon exposure of **1** to $H_2{}^{16}O$ vapor for 2 min, the molecular structure of **2** was successfully determined by X-ray crystallography (Figure 1C). Four TBA cations per anion were found in **2**. The $V\cdots V$ distance in **2** is 3.253 Å, in good

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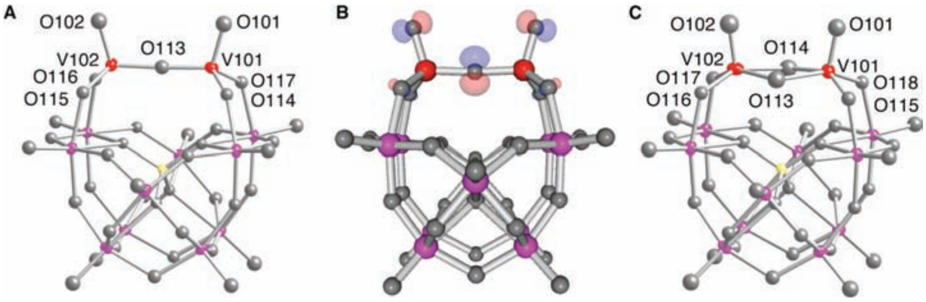

Figure 1. Molecular structures of **1** and **2**: (A) molecular structure of (TBA)$_4$[γ-SiV$_2$W$_{10}$O$_{39}$], drawn at the 50% probability level; (B) HOMO-4 orbital of (TBA)$_4$[γ-SiV$_2$W$_{10}$O$_{39}$], drawn with an isosurface value of 0.100; (C) molecular structure of (TBA)$_4$[γ-H$_2$SiV$_2$W$_{10}$O$_{40}$], drawn at the 50% probability level. Selected bond distances (Å) and angles (deg) of **1**: V101−O101, 1.609(12); V102−O102, 1.591(13); V101−O113, 1.737(11); V102−O113, 1.768(11); V101−O113−V102, 178.1(7); V···V, 3.505; O101−V101−V102−O102, 0.00. Selected bond distances (Å) and angles (deg) of **2**: V101−O101, 1.594(16); V102−O102, 1.585(15); V101−O113, 2.019(15), V101−O114, 2.060(15); V102−O113, 1.993(14); V102−O114, 2.008(15); V···V, 3.253; O101−V101−V102−O102, 0.514.

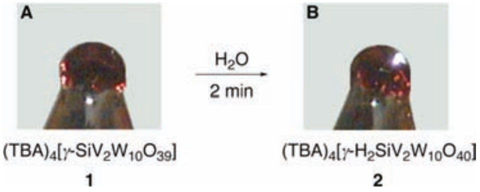

Figure 2. Crystal-to-crystal transformation from **1** to **2**: (A) (TBA)$_4$-[γ-SiV$_2$W$_{10}$O$_{39}$] as synthesized; (B) (TBA)$_4$[γ-SiV$_2$W$_{10}$O$_{39}$] upon exposure to H$_2$O for 2 min.

agreement with the value 3.200 Å calculated for [γ-H$_2$SiV$_2$-W$_{10}$O$_{40}$]$^{4-}$ and larger than the value 3.096 Å in the starting (TBA)$_4$[γ-H$_2$SiV$_2$W$_{10}$O$_{40}$]. The BVS values of O(113) and O(114) are 1.14 and 1.09, respectively, suggesting that these oxygen atoms are assignable to the hydroxo ligands (Table S4). The BVS values of vanadium (5.01, 5.13), tungsten (5.90−6.18), silicon (3.88), and the other oxygen (1.84−2.06) indicate that the respective valences in **2** are +5, +6, +4, and −2. These data reveal the formation of the bis(μ-hydroxo)divanadium substituted polyoxometalate (TBA)$_4$[γ-H$_2$SiV$_2$W$_{10}$O$_{40}$] by a crystal-to-crystal transformation.[19,20]

When the contact time with the water vapor was prolonged beyond 2 min, the crystallinity was lowered and the molecular structure could not be determined by X-ray crystallography. After 6 h, the IR spectrum of the pale yellow sample showed V═O vibration bands at 1006 and 995 cm^{-1} and a broad O−H vibration band at 3489 cm^{-1} (Figure S11A). The solid-state ^{51}V MAS NMR spectrum of the pale yellow sample showed a signal at −559.6 ppm (Figure S8B). The cold-spray ionization mass spectrum (CSI-MS) showed the most intense parent ion peak (centered at m/z 3822.58) with an isotopic distribution that agrees with the pattern calculated for the monolabeled {(TBA)$_5$[H$_2$SiV$_2$W$_{10}$O$_{39}$(^{16}O)]}$^+$ (centered at m/z 3822.61) (Figure S12). All these data were in good agreement with those of the starting (TBA)$_4$[γ-H$_2$SiV$_2$W$_{10}$O$_{40}$]. On the other hand, upon exposure of **1** to H$_2{}^{18}$O vapor for 6 h, the IR spectrum showed V═O vibration bands at 1005 and 994 cm^{-1} and an O−H vibration band at 3484 cm^{-1} (Figure S11B). The V═O vibration bands appeared at almost the same positions as those found upon exposure of **1** to H$_2{}^{16}$O vapor, whereas the O−H vibration band appeared at a lower wavenumber. Upon dissolution in CH$_3$CN, the cold-spray ionization mass spectrum (CSI-MS) showed the most intense parent ion peak (centered at m/z 3824.43) that agrees with the position calculated for the monolabeled {(TBA)$_5$[H$_2$SiV$_2$W$_{10}$O$_{39}$(^{18}O)]}$^+$ (m/z 3824.61) (Figure S13). These results show that the syn-linear (VO)$_2$-(μ-O) core in **1** reacts with water to form the bis(μ-hydroxo)-divanadium core.

There are four possible reaction mechanisms for reaction of **1** with water: (a) the nonradical mechanisms (a-1) protonation at the bridging oxo ligand by water followed by coordination to the vanadium center and (a-2) coordination of water to the vanadium center followed by proton transfer to the bridging oxo ligand; (b) the radical mechanisms (b-1) homolytic dissociation of water (H$_2$O → H$^\bullet$ + $^\bullet$OH) followed by reaction with **1** and (b-2) formation of the triplet V(V)−(O$^\bullet$)−V(IV) species followed by reaction with water. Since compound **1** is stabilized by the partial double bond character of the linear V(V)−(O)−V(V) bond, which hides the potential coordination sites on the vanadium centers, reaction a-2 is not possible. Neither is reaction b-1, because the triplet species cannot react with the singlet species. In addition, the activation energies for a-1, b-1, and b-2 were 139.40, 493.40, and 280.12 kJ mol^{-1}, respectively (Figure S14). Therefore, path a-1 is the most probable. No signals of the paramagnetic species or intermediates were observed by solid and solution ^{51}V NMR experiments for reaction of **1** with water, supporting this idea.

The energies of the reaction steps are summarized in Figure 3. The interaction of water with the bridging oxo ligand and the successive coordination of water to the vanadium center led to the formation of **TS1** (V···O = 2.219 (2.235) Å, O···H = 1.406 (1.369) Å). Successive proton transfer resulted in the formation of the bis(μ-hydroxo)divanadium substituted polyoxometalate **3**. The valence of the vanadium did not change in each step. Thus, the water dissociation reaction proceeds heterolytically. The calculated activation and formation energies were 130.40 and −16.54 kJ mol^{-1}, respectively, and the latter value was much lower than those of the homolytic and heterolytic dissociation of water.

In conclusion, heterolytic water dissociation by a polyoxometalate with the previously unknown syn-linear (VO)$_2$(μ-O) core was investigated by crystal-to-crystal transformation. Our results give direct experimental evidence for the heterolytic dissociation of water on the metal oxide surface at the atomic

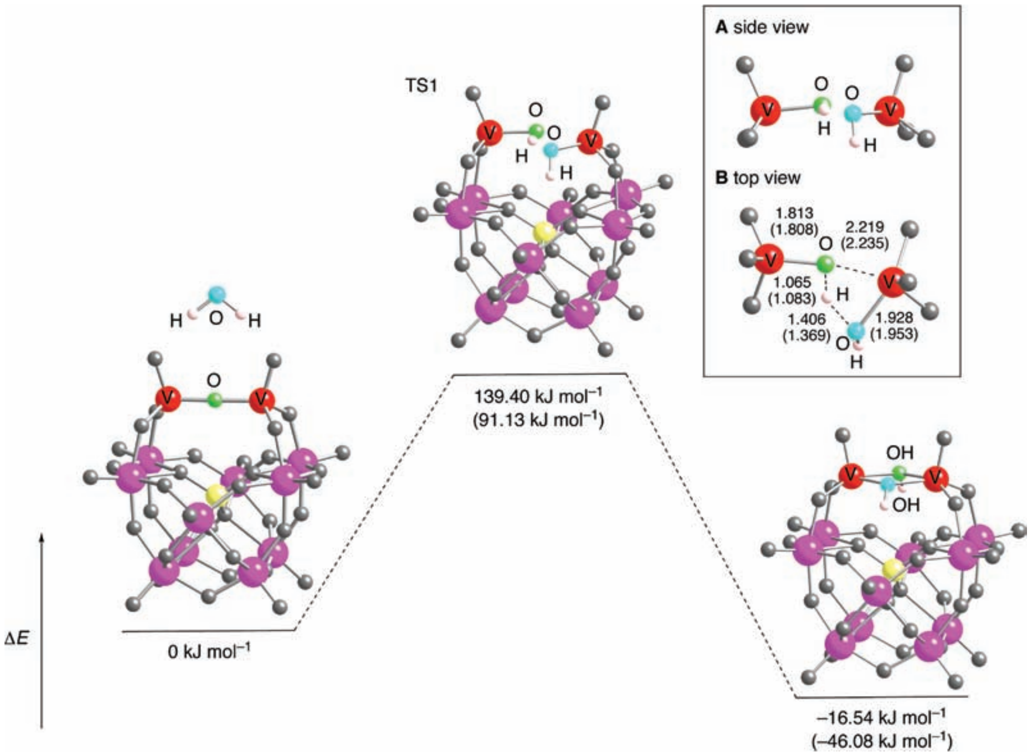

Figure 3. Energy diagram of water dissociation reaction with **1**: (A) side view of the core structure of **TS1**; (B) top view of the core structure of **TS1**. The lengths are given in angstroms. Energies and lengths in parentheses are those obtained under vacuum conditions.

level. The heterolytic dissociation of water proceeds in a cooperative way: (i) protonation at the bridging oxo ligand by water followed by coordination to the vanadium center (**TS1**) and (ii) successive proton transfer followed by the formation of a bis(μ-hydroxo)-divanadium core.

■ ASSOCIATED CONTENT

Supporting Information. CIF files giving crystallographic data of **1**−**3** and text, tables, and figures giving experimental procedures, details of DFT calculations, and the complete ref 18. This material is available free of charge via the Internet at http://pubs.acs.org.

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NOTE ADDED AFTER ASAP PUBLICATION

In the version published ASAP January 7, 2011, references 8 and 9 were switched; the correct version reposted January 13, 2011.