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Sterically Controlled Esterification on Bis(μ-hydroxo) Dioxovanadium Site in γ-$H_2SiV_2W_{10}O_{40}{}^{4-}$

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The esterification of a bis(μ-hydroxo) dioxovanadium site in divanadium-substituted silicotungstate, γ-$H_2SiV_2W_{10}O_{40}{}^{4-}$, with alcohols is sterically controlled: The secondary and tertiary alcohol esters are hardly formed (equilibrium constant < 0.01), and a large equilibrium constant of 75 is observed for the reaction with methanol.

Vanadate esters (or vanadium alkoxides) are important complexes as oxidants or oxidation catalysts, oxide precursors, and analogues of phosphate esters in the fields of organic[1] and inorganic syntheses,[2] and bioinorganic chemistry,[3] respectively. They are also reported to be a key intermediate for the aerobic oxidation of alcohols with vanadia catalysts.[4] Therefore, dependence of reactivity of the vanadium site with alcohols is interesting. The aqueous chemistry of vanadium oxoanion is complex, and the complexity in part arises from the ability of the vanadate ion to undergo protonation and oligomerization.[5−7] Also, the esterification of bis(μ-hydroxo) dioxovanadium site with alcohols was previously unknown. The incorporation of vanadium centers to the more stable, rigid polyoxometalate framework may avoid the complex equilibrium. Keggin-type ($XW_{12}O_{40}{}^{n-}$) and Dawson-type ($X_2W_{18}O_{62}{}^{m-}$) polyoxotungstates show stability toward the hydrolysis or isomerization when dissolved in organic solvents such as acetonitrile.[8] Although there are various kinds of Keggin- and Dawson-type vanadium-substituted polyoxotungstates,[9] the esterification reaction was reported only for trivanadium-substituted $H_4P_2V_3W_{15}O_{62}{}^{5-}$.[9g,10] In this paper, we report the sterically controlled esterification of the bis(μ-hydroxo) dioxovanadium site in divanadium-substituted silicotungstate, γ-$H_2SiV_2W_{10}O_{40}{}^{4-}$ (**1**),[9h,11] with alcohols: The secondary and tertiary alcohol esters are hardly formed, and a large equilibrium constant of 75 is observed for the reaction with methanol.

The methyl monoester of **1** (**2**) was easily formed by addition of methanol to the acetonitrile solution of **1**. The formation of **2** was highly selective, and no diester was formed even in the presence of excess methanol. The esterification reaction was reversible, and the hydrolysis of **2** readily proceeded in the presence of water. The single

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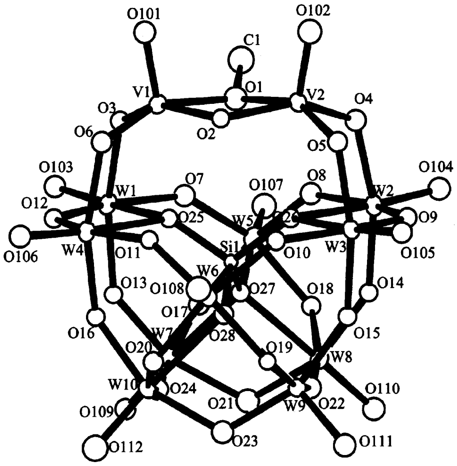

Figure 1. ORTEP view of CEK-**2**, showing 50% probability ellipsoids. Hydrogen atoms and CEK moieties were omitted for clarification.

crystals of **2** were obtained by vapor diffusion of diethyl ether to the acetonitrile solution of the 18-crown-6-potassium salt derivative of **1** (CEK-**1**) containing methanol.[12] As shown in Figure 1, the anionic cluster **2** retained the γ-Keggin structure, and the two vanadium atoms were bridged with one oxygen atom and one methoxo group.

The bond valence sum (BVS) value of O2 was 1.16 and clearly different from those of the other oxygen atoms (1.53−2.10), indicating that the oxygen atom remained protonated.[11,13] The ^{1}H NMR spectrum of CEK-**2** in CD_3CN showed two lines at 4.44 ppm (sharp, 3H per anion) and 5.18 ppm (broad, 1H per anion) in addition to the lines assignable to the solvent and countercation. The ^{13}C NMR showed a line at 69 ppm (1C per anion), of which the value falls in the range of those reported for diamagnetic metal methoxides.[14] These results show that the formula of **2** is γ-$HSiV_2W_{10}O_{39}(\mu\text{-}OCH_3)^{4-}$. The ^{183}W NMR spectrum showed six lines at −80.9, −93.3, −94.5, −122.8, −124.8, and −134.9 ppm with intensities of 2(br):1:2(br):1:2:2, respectively (Figure S1). The ^{51}V NMR spectrum showed one line at −549 ppm (Figure S2). These NMR results are in accord with the structure with the C_s symmetry in Figure 1.

The formation constants (K's) of the ester ($K = \{[\mathbf{2}][H_2O]\}/\{[\mathbf{1}][MeOH]\}$) in water (buffered with 0.1 M $NaHSO_4$/ 0.1 M Na_2SO_4, pH = 1.67) and acetonitrile at 298 K were determined to be 75 ± 2 and 75 ± 5, respectively, by the ^{51}V NMR. These values are much larger than those reported for methyl monovanadate ($H_2VO_4^- + MeOH$, $K_1 = 5.2 \pm 0.1$, $K_2 = 1.2 \pm 0.1$),[15] methyl divanadate ($(HO)O_2VOVO_2(OH)^{2-} + MeOH$, $K_1 = 3.0 \pm 0.3$, $K_2 = 3.1 \pm 0.3$),[15] methyl ester of Dawson-type trivanadium-substituted phosphotungstate ($HP_2V_3W_{15}O_{59}(\mu\text{-}OH)_3^{5-} + MeOH$, $K_1 = 2.0 \pm 0.2$, $K_2 = 1.3 \pm 0.2$, $K_3 = 0.37 \pm 0.08$),[10a] methyl acetate (5.9 ± 0.2),[16] and monoethyl phosphate ($K_1 = 0.46$).[17] Unlike $HP_2V_3W_{15}O_{59}(\mu\text{-}OH)_3^{5-}$ and **1**, the β-Keggin-type trivanadium-substituted silicotungstate β-1,2,3-$H_xSiV_3W_9O_{40}^{(7-x)-}$ has been reported to be inactive for the esterification[9g] although the V−(μ-OH)−V bridge is present in all these three polyoxometalates. The order of reactivity of the bridging hydroxo groups with the vanadium-substituted polyoxotungstates decreased in the following order: $\mathbf{1} > H_4P_2V_3W_{15}O_{62}^{5-} > \beta$-1,2,3-$H_xSiV_3W_9O_{40}^{(7-x)-}$. The order is possibly explained by the difference of the V−OR−V bond angles. The V−OR−V bond angle in **1** (106°) is closer to the ideal angle for sp^3 electronic state (109°) than that in β-1,2,3-$H_xSiV_3W_9O_{40}^{(7-x)-}$ (150°).[18] The sp^3-like character of the V−OMe−V oxygen atom in **1** may stabilize the ester. This explanation is supported by the following calculation: The formation energies (ΔE's) of methyl ester were calculated with B3LYP density functional[19,20] to be +2.6 and +30.4 kJ mol^{-1} for γ-$HSiV_2W_{10}O_{39}(OMe)^{4-}$ and β-1,2,3-$SiV_3W_9O_{39}(OMe)$,$^{6-}$ respectively, where ΔE was expressed by $\Delta E = E(\mathbf{2}) + E(H_2O) - E(\mathbf{1}) - E(MeOH)$. By using these ΔE values in combination with the formation constant of γ-$HSiV_2W_{10}O_{39}(OMe)^{4-}$, the formation constant of β-1,2,3-$SiV_3W_9O_{39}(OMe)^{6-}$ is calculated to be 1.0×10^{-3}, in agreement with the fact that $H_xSiV_3W_9O_{40}^{(7-x)-}$ was inactive for the esterification.

We investigated the esterification of **1** with various alcohols, and the results are summarized in Table 1. The K

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(11) Yellow single prismatic crystals of the tetramethylammonium salt of $[\gamma\text{-}1,2\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$ were grown from the aqueous solution by slow evaporation at room temperature. The crystallographic data follow: $[(CH_3)_4N]_4H_2SiV_2W_{10}O_{40}{\cdot}3H_2O$, fw = 2959.07, monoclinic, space group $P2_1/n$ (No. 14). At 113 K, a = 11.7992(7) Å, b = 37.804(2) Å, c = 12.7372(8) Å, β = 110.308(3)°, V = 5328.4(6) Å^3, Z = 4, D_{calcd} = 3.688 g cm^{-3}, μ(Mo Kα) = 219.76 cm^{-1}. Data were collected on a Rigaku Saturn CCD area detector with graphite monochromated Mo Kα radiation (0.71070 Å) to a maximum 2θ value of 55°. There were 118316 measured and 12403 unique reflections (R_{int} = 0.039). R1 = 0.022 and wR2 = 0.025 for 10946 reflections ($I > 3\sigma(I)$). The distance between the two vanadium atoms was 3.116(2) Å. The existence of 4 Me_4N^+ countercations per **1** was identified. The bond valence sum (BVS) values of tungsten (6.02−6.17), vanadium (5.06, 5.11), and silicon (3.91) indicate that the oxide cluster of **1** is composed of V(V), W(VI), and Si(IV) ions. Therefore, two protons are associated with the anionic cluster of **1** on the basis of the charge balance. The BVS values of oxygen atoms (1.17 and 1.39) bridging two vanadium atoms are different from those of the other oxygen atoms (1.68−2.07). These facts indicate that two oxygen atoms between vanadium are protonated resulting in hydroxo ligands as has been reported.[9h]

(12) Crystallographic data follow: $[K(C_{12}H_{24}O_6)]_4[\gamma\text{-}HSiV_2W_{10}O_{39}(OCH_3)]{\cdot}1.5CH_3CN$, fw = 3814.06, triclinic, space group $P\bar{1}$ (No. 2). At 183 K, a = 15.107(7) Å, b = 17.440(8) Å, c = 21.742(12) Å, α = 81.44(2)°, β = 84.21(2)°, γ = 67.64(2)°, V = 5232.6(43) Å^3, Z = 2, D_{calcd} = 2.421 g cm^{-3}, μ(Mo Kα) = 113.67 cm^{-1}. Data were collected on a Rigaku Mercury CCD area detector with graphite monochromated Mo Kα radiation (0.71070 Å) to a maximum 2θ value of 55°. There were 67858 measured and 21485 unique reflections (R_{int} = 0.061). R1 = 0.064 and wR2 = 0.072 for 10511 reflections ($I > 3\sigma(I)$). The distances between V1 and O25 and between V2 and O26 were 2.60(2) and 2.52(2) Å, respectively.

(13) BVS values of atoms in CEK-**2** (atom, BVS): V1, 4.85; V2, 4.95; W1, 5.66; W2, 5.81; W3, 5.95; W4, 5.80; W5, 5.96; W6, 5.73; W7, 5.66; W8, 5.70; W9, 5.82; W10, 5.69; Si, 3.70; O1, 2.10; O2, 1.16; O3, 1.90; O4, 1.80; O5, 1.90; O6, 1.80; O7, 1.94; O8, 1.86; O9, 1.85; O10, 1.70; O11, 1.85; O12, 1.91; O13, 1.86; O14, 1.91; O15, 1.93; O16, 1.91; O17, 1.91; O18, 1.94; O19, 1.88; O20, 1.93; O21, 1.78; O22, 1.98; O23, 1.85; O24, 1.96; O25, 1.72; O26, 1.71; O27, 1.87; O28, 1.86; O101, 1.68; O102, 1.83; O103, 1.66; O104, 1.70; O105, 1.61; O106, 1.66; O107, 1.75; O108, 1.75; O109, 1.57; O110, 1.53; O111, 1.66; O112, 1.74.

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Table 1. Esterification of 1 with Various Alcohols in Acetonitrile at 298 K

alcohol	δ (^{51}V) of ester/ppm	K^a
methanol	−549	75 ± 5
ethanol	−550	20 ± 2
1-propanol	−547	9.5 ± 0.5
2-propanol	−552	<0.01
1-butanol	−547	9.7 ± 0.9
isobutyl alcohol	−538	1.0 ± 0.1
tert-butyl alcohol	*b*	0
benzyl alcohol	−544	5.5 ± 0.2
4-methylbenzyl alcohol	−544	6.7 ± 0.2
4-methoxybenzyl alcohol	−544	8.9 ± 0.3
4-fluorobenzyl alcohol	−544	9.3 ± 0.3
4-chlorobenzyl alcohol	−544	8.9 ± 0.5
4-(trifluoromethyl)benzyl alcohol	−544	8.3 ± 0.5
4-nitrobenzyl alcohol	−542	9.5 ± 0.5

[a] K = ([ester][H_2O])/([**1**][alcohol]) (no dimension). [b] No ester was formed.

values decreased in the order methanol > ethanol > 1-propanol ≈ 1-butanol and primary alcohols ≫ secondary alcohols ≥ tertiary alcohols = 0, and those for secondary and tertiary alcohols were much smaller than those for monovanadate esters ($K_1 = 5.0$ (2-propanol); 3.4 (*tert*-butyl alcohol)).[7] Such smaller K values observed for the secondary and tertiary alcohols are probably caused by the steric crowding resulting from introduction of secondary carbon center at the bridging oxygen site. The K values for *para*-substituted benzyl alcohols were smaller than that of ethanol while pK_a values for *para*-substituted benzyl alcohols (14.89−15.64) are smaller than that of ethanol (15.9),[21,22] supporting the idea. It has also been reported that secondary and tertiary alcohol ester formation on the Nb−O−Nb bridging site in $Nb_2W_4O_{19}^{4-}$ is prevented by the steric repulsion.[23]

The structural model for isopropyl ester constructed by the addition of two methyl groups to the carbon center of **2** illustrated the steric crowding between the methyl groups and O101, O102, O3, O4, O7, and O8 atoms. Such a steric effect results in much smaller K values for isopropyl and *tert*-butyl esters.

In summary, the esterification of bis(μ-hydroxo) dioxovanadium site in divanadium-substituted silicotungstate, γ-$H_2SiV_2W_{10}O_{40}^{4-}$, with alcohols is sterically controlled: The secondary and tertiary alcohol esters are hardly formed (equilibrium constant < 0.01), and a large equilibrium constant of 75 is observed for the reaction with methanol.

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Supporting Information Available: Experimental details, calculation details, Figures S1−S4 (for determination of K), Table S1 (crystallographic data for TMA-**1** and CEK-**2**), and Tables S2−S5 (for calculation of ΔE). This material is available free of charge via the Internet at http://pubs.acs.org.

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