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O-Acylation of Heteropolyanions Containing Two Adjacent Vanadium Atoms

Chul Wee Lee and Hyunsoo So*

Department of Chemistry, Sogang University, Seoul 121-742

Kyu Ryong Lee

Department of Chemistry, Hallym University, Chuncheon 200-010. Received June 27, 1988

Reaction of Keggin- or Dawson-type heteropolyanions containing two adjacent vanadium atoms with acetic anhydride in the presence of acid produced acylated anions. Heteropolyanions with one or no vanadium atom do not react under the same conditions, indicating that the acyl group is attached to the bridging oxygen atom between the two vanadium atoms. A characteristic infrared band at 1760 cm^{-1} was observed for the acylated anions. The 8-line EPR spectrum shows that one of the vanadium atoms is reduced to V(IV). The acylated heteropolyanions are easily hydrolyzed, and its acyl group can also be transferred to aniline.

Introduction

An interesting, new development in the chemistry of heteropolyanions is preparation of heteropolyanions attached with organic groups.[1] Since the surface of a heteropolyanion is similar to those of some metal oxides extensively used as heterogeneous catalysts for various organic reactions, organic derivatives of heteropolyanions may be useful in clarifying the mechanism of catalysis by metal oxides.

Most organic derivatives of the Keggin-structure heteropolyanions involve replacement of peripheral metal oxygen groups by other metal-ligand groups.[2-4] A rare type involves organic groups attached to the surface oxygen atoms of heteropolyanions, a good example being the O-alkylated anions.[5]

We have been trying to attach an acyl group to the surface oxygen atoms of heteropolyanions. So far we have not been able to obtain a crystalline product, the crystal structure of which may provide direct evidence for such acylation. But various experimental data indicate that such acylation occurs for heteropolyanions containing two adjacent vanadium atoms. Details are reported in this paper.

Experimental

Preparation of Compounds. a-1,2-$K_6[PV_2W_{10}O_{40}]$ (PV_2), a-1,2,3-$K_6[PV_3W_9O_{40}]$ (PV_3), a-1,2,3-$(Bu_4N)_4H_3[PV_3W_9O_{40}]$, a-1,2,3-$(Bu_4N)_4H_3[SiV_3W_9O_{40}]$ (SiV_3) and 1,2,3-$(Bu_4N)_3KH_3[P_2V_3W_{15}O_{62}]$ (P_2V_3) were prepared according to the methods in the literature.[6-8] PV_2 or PV_3 dissolved in water
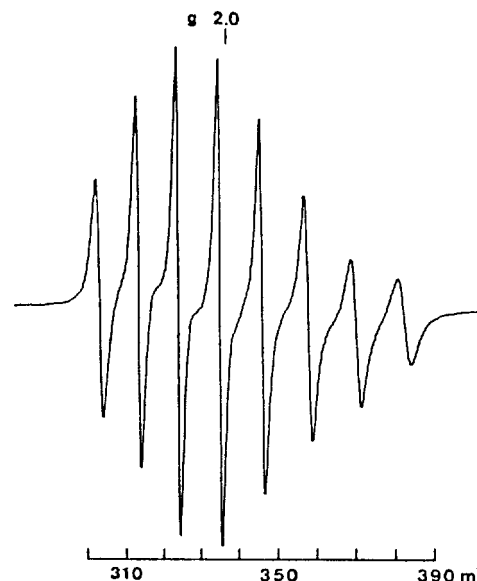
Figure 1. Solution EPR spectrum of $[(CH_3CO)PV(IV)VW_{10}O_{40}]^{5-}$.

was reduced by one equivalent of hydrazine dihydrochloride, and the potassium salt of $[PV(IV)VW_{10}O_{40}]^{6-}$ or $[HPV(IV)V_2W_9O_{40}]^{6-}$ was precipitated by adding potassium chloride.[14,16]

Acylation. All of the above heteropolyanions or their one electron reduction products were acylated in the same manner. Here the procedure for PV_2 is described. 10 m*l* of acetic anhydride was added to 1g of PV_2. When a small amount (~0.3 m*l*) of boron trifluoride etherate was added to

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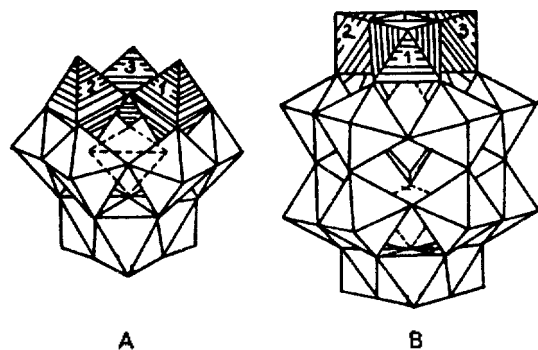
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Figure 2. Polyhedral representations of (A) Keggin structure and (B) Dawson structure. Two or three tungsten atoms in the octahedra with hatched lines are replaced by vanadium atoms.

Figure 3. The infrared spectra of (A) $(Bu_4N)_4H_3[SiV_3W_9O_{40}]$ and (B) its acylated product.

this mixture, the solid started to dissolve immediately. (Boron trifluoride colud be replaced by phosphoric acid or sulfuric acid, but the purest product was obtained when BF_3 was used.) After the solid dissolved completely, 0.5g of tetrabutylammonium bromide was added to the solution. Adding diethyl ether to the solution produced a dark brown precipitate. The precipitate was collected, dried, and recrystallized several times in acetonitrile. The infrared spectrum of the product showed a band at 1760 cm^{-1} ascribable to the C = O stretch, in addition to the bands characteristic of the Keggin structure (see below). And the product dissolved in acetonitrile showed an 8-line EPR spectrum characteristic of an oxovanadium(IV) compound; see Figure 1. Anal. Calcd for $(Bu_4N)_2K_3[(CH_3CO)PV(IV)VW_{10}O_{40}]\cdot H_2O$: C, 12.5; H, 2.30; N, 0.86. Found: C, 13.6; H, 2.48; N, 0.89.

$K_3[PW_{12}O_{40}]$, $K_3[PMo_{12}O_{40}]$, and $K_4[PVW_{11}O_{40}]$ did not react with acetic anhydride in the presence of acid.

Hydrolysis. An 8-line EPR spectrum was observed for the acylation product of PV_3. When it was dissolved in water, the solution showed a 43-line EPR spectrum[9,10] characteristic of a-1,2,3-[HPV(IV)V_2W_9O_{40}]^{6-}$. The precipitate obtained by adding potassium chloride to the aqueous solution showed no IR band at 1760 cm^{-1}.

Reaction with Aniline. 15g of an acylated heteropolyanion and 0.4 ml of aniline were added to 80 ml of dichloromethane. The mixture was stirred for 6 hours at room temperature, and then was separated into solid and solution by filtration. The 1760 cm^{-1} band almost disappeared in the IR spectrum of the solid. The filtrate was evaporated and white crystals were collected. The IR and NMR spectra of the product agreed with those of acetanilide.

Measurements. IR spectra were obtained from KBr discs on a Shimadzu IR-440 spectrometer. EPR spectra were measured using a Bruker EPR spectrometer(ER 200E) operating at 9.7GHz. NMR spectra were recorded on a Varian NMR spectrometer(EM 360).

Results and Discussion

The structures of Keggin- and Dawson-type heteropolyanions are shown in Figure 2.[17,18] For the heteropolyanions studied here, two or three tungsten atoms in the octahedra with hatched lines are replaced by vanadium atoms.[6-8]

The reactivities of heteropolyanions toward acylation were clearly distinguished depending upon whether two adjacent vanadium atoms exist or not. When BF_3, a Lewis acid,
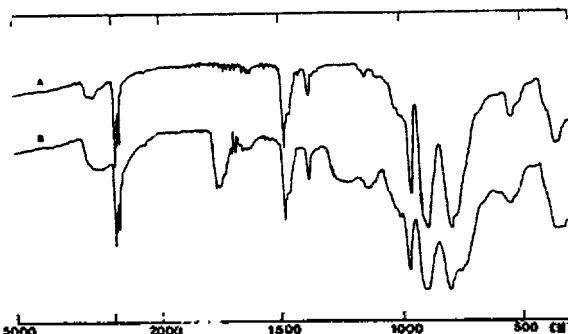
or an ordinary acid was added to the mixture of acetic anhydride and heteropolyanions, only those containing two adjacent vanadium atoms dissolved. Both Keggin- and Dawson-type anions behaved in the same manner. This indicates that the bridging oxygen atom between the two vanadium atoms is involved in the reaction.

The infrared spectrum of the acylated SiV_3 is compared with that of the tetrabutylammonium salt of SiV_3 in Figure 3. The bands at 1000-700 cm^{-1} characteristic of the Keggin structure remain intact, and new bands appear at 1760 and 1300-1100 cm^{-1} in the acylated SiV_3. The band at 1760 cm^{-1} may be ascribed to the carbonyl group of CH_3CO- attached to the heteropolyanion. The frequency of this band precludes the existence of any acylium ion (showing a carbonyl band at 2300 cm^{-1}) or a solvated acetic anhydride (showing two bands at 1830-1800 and 1780-1750 cm^{-1}).

Since only those heteropolyanions containing two adjacent vanadium atoms are acylated, it is reasonable to assume that the acetyl group is attached to the bridging oxygen atom between the two vanadium atoms. The reactivity of this atom may be explained in terms of its high negative charge. When a hexavalent tungsten atom in a heteropolyanion is replaced by a pentavalent vanadium atom, the bridging oxygen atoms bonded to the vanadium atom get extra negative charges.[11] In a heteropolyanion containing two adjacent vanadium atoms, the bridging oxygen atom between the two vanadium atoms will have a higher negative charge and thus act as a stronger nucleophile than other bridging atoms.

The new bands at 1300-1100 cm^{-1} are also in agreement with the O-acylation, for such bands are expected from the -COO- moiety. In fact, the IR bands of the -COO- moiety in the acylated heteropolyanions are similar to those of esters. For normal esters the C = O stretch occurs at 1735 cm^{-1}, and two or more bands related with the C-O stretch appear at 1300-1000 cm^{-1}. In the spectrum of vinyl acetate, the C = O band is shifted to 1770 cm^{-1}. It has been suggested that the conjugation involving the single-bonded oxygen atom interferes with possible resonance with the carbonyl group leading to an increase in the absorption frequency for the C = O band.[12] The high frequency of the C = O band in the acylated heteropolyanions may be explained in a similar way. Here the bridging oxygen atoms is bonded to three atoms, making resonance with the carbonyl group impossible.

The C = O stretch is found to occur at the same frequency for all heteropolyanions studied here. The VO_6 octahedra share corners in PV_2, PV_3, and SiV_3, and edges in P_2V_3. Thus the bridging oxygen atom between two vanadium atoms in P_2V_3 is different from those in Keggin-type anions.
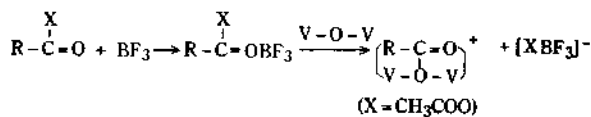
But this difference has little effect on the absorption frequency of the $C=O$ band.

All acylation products showed EPR spectra characteristic of an oxovanadium(IV) compound. This means that one of the vanadium atoms is reduced to V(IV) when the starting material is an oxidized heteropolyanion. It is not clear whether the reduction occurs during the acylation reaction or afterwards. It is known that some heteropolyanions can be reduced photochemically in various media.[13] To avoid photochemical reduction of the heteropolyanion, we have carried out some reactions in the dark. But still the products were EPR-active. The mechanism of the reduction is not understood now.
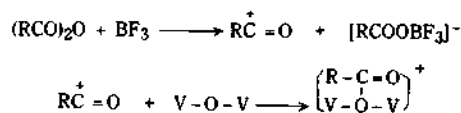
$[PV(IV)VW_{10}O_{40}]^{6-}$ shows a 15-line spectrum, which comes from a hopping electron between two vanadium ($I = 7/2$) atoms.[14] The 8-line EPR spectrum of the acylated PV_2 indicates that the unpaired electron is trapped on one vanadium atom. It is known that the protonated oxygen atom effectively prevents the electron transfer between two vanadium atoms.[15,16] The acylated oxygen atom is expected to behave in a similar way.

PV_2 has one pair of vanadium atoms and thus one site for acylation. But PV_3 has three sites for acylation, and the 8-line EPR spectrum of the acylated product indicates that all sites are either acylated or protonated. On hydrolysis of the acylated PV_3 a monoprotonated species showing a 43-line EPR spectrum was recovered.

The mechanism of acylation is probably an acid-catalyzed nucleophilic substitution with the bridging oxygen atom acting as the nucleophile.

$$\underset{X}{\underset{|}{R-C}}=O + BF_3 \longrightarrow R-\underset{X}{\underset{|}{C}}=OBF_3 \xrightarrow{V-O-V} \left(\underset{V-\overset{|}{O}-V}{R-C=O}\right)^+ + [XBF_3]^-$$
$$(X=CH_3COO)$$

Alternatively, it may proceed as an acylium mechanism

$$(RCO)_2O + BF_3 \longrightarrow R\overset{+}{C}=O + [RCOOBF_3]^-$$

$$R\overset{+}{C}=O + V-O-V \longrightarrow \left(\underset{V-\overset{|}{O}-V}{R-C=O}\right)^+$$
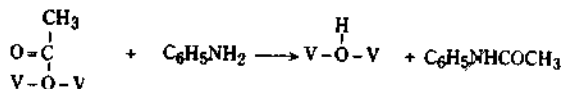
We have no experimental data to distinguish between these two mechanisms now. It is also noted that these two mechanisms do not involve the reduction of one vanadium atom. More work is needed to establish the mechanism.

The acylated heteropolyanions are easily hydrolyzed, and the original heteropolyanions are recovered.

$$\underset{V-O-V}{\underset{|}{R-C=O}} + H_2O \longrightarrow \underset{V-\overset{|}{O}-V}{\overset{H}{V-O-V}} + RCOOH$$
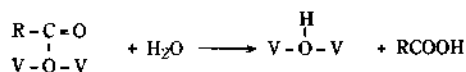
The acyl group attached to the bridging oxygen atom is also transferred to aniline.

$$\underset{V-O-V}{\underset{|}{\overset{CH_3}{\underset{|}{O=C}}}} + C_6H_5NH_2 \longrightarrow \underset{V-\overset{|}{O}-V}{\overset{H}{V-O-V}} + C_6H_5NHCOCH_3$$

We have also tried to acylate $K_4[V_2W_4O_{19}]$ by the same method. It was acylated, but the IR spectrum of the product indicated some structural change in the heteropolyanion.

In summary, we have prepared O-acylated heteropolyanions containing two adjacent vanadium atoms. These anions show characteristic IR band at 1760 cm^{-1}. The acyl group is easily transferred to water or aniline. To our knowledge, this is the first synthesis of O-acylated heteropolyanions.

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