Isolation and Spectroscopic Properties of A-β-$[PV_3W_9O_{40}]^{6-}$ Anion Salts and Their Isomerization to the α-Isomers

Isao Kawafune* **and Gen-etsu Matsubayashi**[†]

Osaka Municipal Technical Research Institute, 1-6-50, Morinomiya, Joto-ku, Osaka 536

†Department of Applied Chemistry, Faculty of Engineering, Osaka University,
1-16, Machikaneyama, Toyonaka, Osaka 560

(Received August 9, 1995)

β-Isomers of A-type vanadium-trisubstituted nonatungstophosphate anion salts were synthesized by a condensation of $NaVO_3$ and A-$Na_9[PW_9O_{34}]\cdot7H_2O$ in an aqueous hydrochloric acid and 1,4-dioxane mixed solution. Their geometries were characterized by IR, ^{31}P, ^{51}V, and ^{183}W NMR spectroscopies. The tetrabutylammonium salt of the β-isomer, A-β-$(NBu^n{}_4)_4H_2[PV_3W_9O_{40}]$, isomerizes to the corresponding α-isomer both in the solid state and in solution under mild conditions, which can be directly followed by FT-IR and ^{31}P NMR spectroscopies. The kinetics of the isomerization in the solid state had a first-order rate constant at 40 °C, $k_1 = 2.19\times10^{-7}$ (s^{-1}), together with $\Delta H^\ddagger = 93.3$ ($kJ\,mol^{-1}$) and $\Delta S^\ddagger = -77.3$ ($J\,K^{-1}\,mol^{-1}$). On the other hand, A-β-$Cs_6[PV_3W_9O_{40}]$ and A-β-$(NBu^n{}_4)_6[PV_3W_9O_{40}]$, which have no protons in the cation part, do not isomerize under the same conditions. The β-to-α isomerization is promoted by protonation at the bridging oxygen atom in the W–O–W bond of the polyanion.

Mixed addenda heteropolyanions, which contain two or more kinds of elements as addenda atoms, have attracted much attention, because their redox properties can be precisely controlled by modifying the constituent addenda atoms[1)] and they are regarded as discrete model complexes of mixed metal catalysts.[1—4)] In the mixed addenda heteropolyanions of the Keggin type, there are numerous possibilities for positional isomerisms[5)] as well as geometrical ones.[6)] Hence, for a few of them, their structures, especially the location of the different metal atoms, have been confirmed by multinuclear (^{29}Si, ^{31}P, ^{51}V, ^{183}W) NMR spectroscopies[7—10)] and by X-ray structural analyses.[11—14)] Stereospecific syntheses of trisubstituted tungstosilicate compounds[7,9,10)] have been done by using structurally well-characterized trivacant lacunary nonatungstosilicate precursors, the A-α-$[SiW_9O_{34}]^{10-}$ [15)] and A-β-$[SiW_9O_{34}]^{10-}$ anion salts.[16)] On the other hand, it is uncertain whether the trivacant lacunary nonatungstophosphate anion, $[PW_9O_{34}]^{9-}$, is an α- or β-isomer.[8)] By using the A- and B-$[PW_9O_{34}]^{9-}$ anion salts as precursors, two α-isomers of trivanadononatungstophosphate compounds, the A-α-$[PV_3W_9O_{40}]^{6-}$ [7)] and B-α-$[PV_3W_9O_{40}]^{6-}$ anion salts,[8)] have been synthesized. In contrast, by using the A-$[PW_9O_{34}]^{9-}$ anion salt as a precursor we previously reported the synthesis of the A-β-$[PMo_3W_9O_{40}]^{3-}$ anion salt,[14)] which is the first example containing a β-isomer of an A-type trisubstituted PW_9 unit.

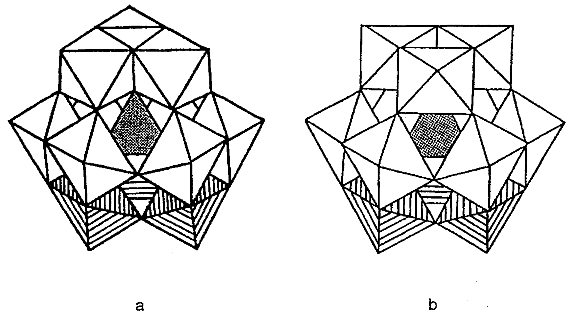

Fig. 1. Polyhedral representations of the A-β-$[PV_3W_9O_{40}]^{6-}$ (a) and A-α-$[PV_3W_9O_{40}]^{6-}$ anions (b). (Plain and hatched parts indicate WO_6 and VO_6 octahedra, respectively.)

In this study, we extended these findings to the synthetic procedures for vanadium-trisubstituted nonatungstophosphate anion salts and newly isolated some A-β-$[PV_3W_9O_{40}]^{6-}$ anion salts (Fig. 1a). This β-isomer, A-β-$(NBu^n{}_4)_4H_2[PV_3W_9O_{40}]$, isomerizes to the corresponding α-one (Fig. 1b) both in the solid state and in solution under mild conditions. Furthermore, the isomerization process can be directly followed by Fourier transform-IR (FT-IR) and ^{31}P NMR spectroscopies, affording its kinetics as the first report of the β-to-α isomerization in the solid state.

Experimental

Preparation of Trivanadononatungstophosphate Anion Salts. A-β-$Cs_6[PV_3W_9O_{40}]$ (Abbreviated β-Cs_6). To an aqueous (90 cm^3) solution of $NaVO_3$ (4.23 g, 34.4 mmol) was added 50 cm^3 of 12 $mol\,dm^{-3}$ HCl and then 50 cm^3 of 1,4-dioxane. To the vigorously stirred pale yellow solution, A-$Na_9[PW_9O_{34}]\cdot7H_2O$[8)] (14.2 g, 5.54 mmol) was added slowly in small portions (about 50 mg) to turn red immediately. After stirring for 1 h at room temperature, CsCl solids (13.2 g, 78.4 mmol) were added to the solution. The resulting red precipitates were collected by filtration, washed with CH_3OH, and dried in vacuo to afford a red powder (12.5 g). It was dissolved in H_2O (350 cm^3), yellow insoluble materials being removed by centrifugation. The supernatant solution was evaporated to dryness under reduced pressure to afford a red powder of β-Cs_6 (10.5 g, 58% yield). Anal. Found: P, 0.95; V, 4.3; W, 49%. Calcd for $Cs_6O_{40}PV_3W_9$: P, 0.95; V, 4.67; W, 50.51%.

The condensation of $NaVO_3$ and A-$Na_9[PW_9O_{34}]$ in an aqueous HCl and 1,4-dioxane mixed solution afforded the β-isomer of A-$Cs_6[PV_3W_9O_{40}]$ in contrast to the α-isomer obtained by the same condensation in a buffer solution at pH 4.8.[7,17)]

A-β-$(NBu^n{}_4)_4H_2[PV_3W_9O_{40}]$ (Abbreviated β-TBA_4H_2). To the above supernatant solution of β-Cs_6 was added an aqueous (25 cm^3) solution of $NBu^n{}_4Br$ (6.45 g, 20.0 mmol). The resulting red precipitates were collected by filtration, washed with H_2O and C_2H_5OH, and dried in vacuo to afford a red powder of β-TBA_4H_2 (8.20 g, 43% yield). Anal. Found: C, 22.29; H, 4.20; N, 1.57; P, 0.88; V, 4.1; W, 47%. Calcd for $C_{64}H_{146}N_4O_{40}PV_3W_9$: C, 22.28; H, 4.27; N, 1.62; P, 0.90; V, 4.43; W, 47.96%.

A-β-$(NBu^n{}_4)_6[PV_3W_9O_{40}]$ (Abbreviated β-TBA_6). To a CH_3CN (10 cm^3) solution of β-TBA_4H_2 (1.00 g, 0.290 mmol) was added a CH_3OH solution containing 10 wt% of $NBu^n{}_4OH$ (1.51 g, 0.582 mmol) and the solution was stirred for 5 min at room temperature. After the solvent was evaporated to dryness under reduced pressure, the residue was washed with diethyl ether, collected by filtration, and dried in vacuo to afford a red powder of β-TBA_6 (0.930 g, 81% yield). Anal. Found: C, 30.17; H, 5.70; N, 2.17%. Calcd for $C_{96}H_{216}N_6O_{40}PV_3W_9$: C, 29.32; H, 5.54; N, 2.14%.

A-α-$(NBu^n{}_4)_4H_2[PV_3W_9O_{40}]$ (Abbreviated α-TBA_4H_2). A-α-$[PV_3W_9O_{40}]^{6-}$ was prepared by the condensation of A-$Na_9[PW_9O_{34}]\cdot 7H_2O$[8)] and $NaVO_3$ in a buffer solution at pH 4.8 and isolated as a cesium salt, A-α-$Cs_6[PV_3W_9O_{40}]$, according to the procedure in the literature.[7,17)] A-α-$Cs_6[PV_3W_9O_{40}]$ (7.10 g, 2.17 mmol) was dissolved in H_2O (1000 cm^3) and followed by addition of an aqueous (25 cm^3) solution of $NBu^n{}_4Br$ (6.45 g, 20.0 mmol). The resulting red precipitates were collected by filtration, washed with H_2O and C_2H_5OH, and dried in vacuo to afford a red powder of α-TBA_4H_2 (3.40 g, 45% yield). Anal. Found: C, 22.30; H, 4.11; N, 1.70%. Calcd for $C_{64}H_{146}N_4O_{40}PV_3W_9$: C, 22.28; H, 4.27; N, 1.62%.

Isomerization of the β-Isomers. The solid samples of the β-isomers were sealed in a glass tube under reduced pressure and left at a constant temperature. They were dissolved in a solvent and ^{31}P NMR spectra were measured. The progress of the isomerization of the β-isomer to the α-one was followed by the intensity ratio of their ^{31}P NMR signals.

Physical Measurements. IR spectra were measured with a Perkin–Elmer 983G spectrophotometer in KBr pellets. FT-IR spectra in solution were measured with a Nicolet 5DX spectrophotometer using a KRS-6 cell with a 0.1-mm light path. ^{31}P and ^{183}W NMR spectra were measured as previously reported.[18)] ^{51}V NMR spectra were measured with a JEOL JNM-EX270 spectrometer operating at 71.04 MHz. ^{51}V parameters: pulse width, 5.1 μs; sweep width, 60000 Hz; number of acquisitions, 200. For all NMR measurements, the tetrabutylammonium salts and the cesium salts were dissolved in CD_3CN (0.01—0.05 mol dm^{-3}) and in D_2O (0.003—0.004 mol dm^{-3}), respectively. ^{31}P, ^{51}V, and ^{183}W NMR chemical shifts were referenced to 85% H_3PO_4, $VOCl_3$ (neat), and Na_2WO_4 in D_2O (2 mol dm^{-3}), respectively, using the sample replacement method.[19)]

Results and Discussion

Geometries of the β-Isomers. Figure 2 shows the IR spectrum of the β-TBA_4H_2 salt, together with that of the α-TBA_4H_2 salt. In the region of 1200—600 cm^{-1} in both the spectra, there occur four major bands characteristic of the Keggin-type structure. They are assigned to P–O (O_p band), M=O (terminal oxygen, O_t band, M = V and W), M–O–M (corner-sharing oxygen, O_{bc} band), and M–O–M (edge-sharing oxygen, O_{be} band) stretching modes on the basis of the analogy to the assignments of the Keggin-type polyanions.[20)] The distinctions between the spectra of these α- and β-isomers are as follows. First, α-TBA_4H_2 develops well-separated O_{bc} (883 cm^{-1}) and O_{be} (805 cm^{-1}) bands, while the O_{bc} band (880 cm^{-1}) of β-TBA_4H_2 is weak and obscured by the broad O_{be} band (805 cm^{-1}). Second, the O_p band of β-TBA_4H_2 (1077 cm^{-1}) appears in the lower frequency region compared with that of α-TBA_4H_2 (1086 cm^{-1}). Third, in a lower frequency region (500—300 cm^{-1}), a strong band is observed for α-TBA_4H_2 (382 cm^{-1}), and three broad ones for β-TBA_4H_2 (406, 374, and 328 cm^{-1}). These findings are in good agreement with the spectral behavior characteristic of α- and β-isomers of $[XM_{12}O_{40}]^{n-}$ polyanions (X = P, Si, Ge, and As, M = Mo and W).[20)] The β-Cs_6 salt also showed the IR spectral pattern characteristic of the β-isomer.

The reaction solution for the condensation of $NaVO_3$ and A-$Na_9[PW_9O_{34}]$ as described for the preparation of the β-Cs_6 salt in the experimental section using D_2O instead of

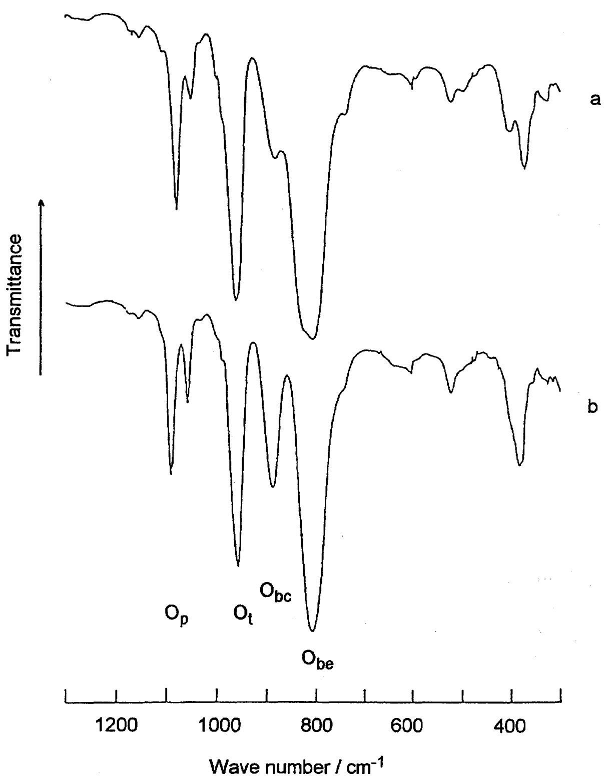

Fig. 2. IR spectra of the β-TBA_4H_2 salt (a) and the α-TBA_4H_2 salt (b) in KBr pellets.

H_2O showed only a single sharp ^{31}P NMR signal at -11.65 ppm and two ^{183}W NMR signals at -106.7 and -117.9 ppm with integrated intensities in the ratio 1 : 2, as depicted in Fig. 3. These spectral patterns are consistent with the formation of a single species of a β-isomer of an A-type vanadium-trisubstituted nonatungstophosphate polyanion. That is, the higher field ^{183}W NMR signal can be assigned to the six "belt" tungsten atoms and the other signal to the three "cap" ones, in comparison with those observed for the A-β-$[SiV_3W_9O_{40}]^{7-}$ [10] and A-β-$[PMo_3W_9O_{40}]^{3-}$ anions.[14] The lower field signal shows satellites due to the spin-spin coupling ($^2J_{W-O-W}$ = ca. 16 Hz), although the higher field one is broadened by the quadrupolar influence of the ^{51}V nuclei.

The isolated β-Cs_6 salt gave a single sharp ^{31}P NMR signal at -10.98 ppm in D_2O. The ^{31}P, ^{51}V, and ^{183}W NMR spectra of the β-TBA_4H_2 salt in CD_3CN vary with the amount of added H_2O, as demonstrated in Fig. 4. The broad ^{183}W NMR

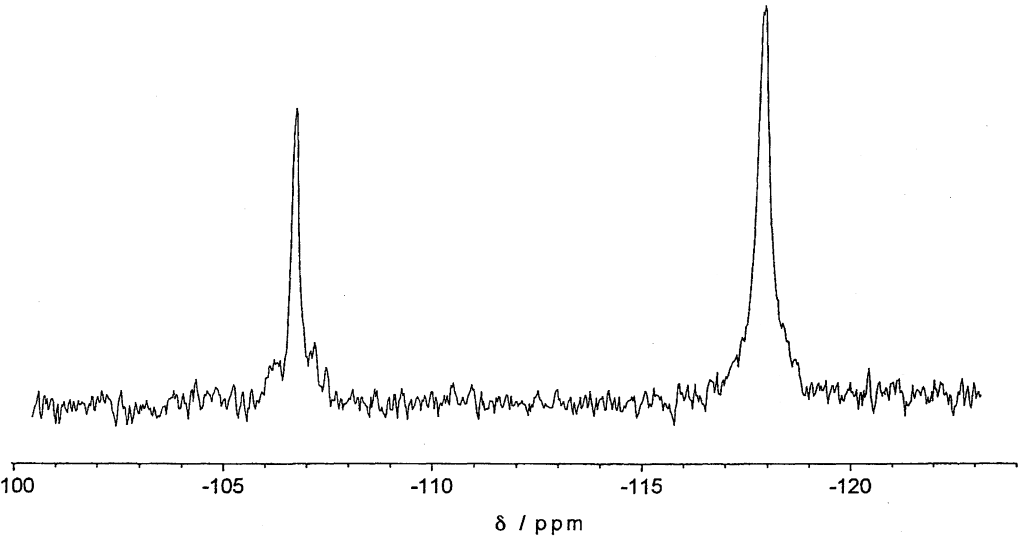

Fig. 3. ^{183}W NMR spectrum of the reaction solution for the condensation of $NaVO_3$ and A-$Na_9[PW_9O_{34}]$ in a mixture of HCl/D_2O and 1,4-dioxane.

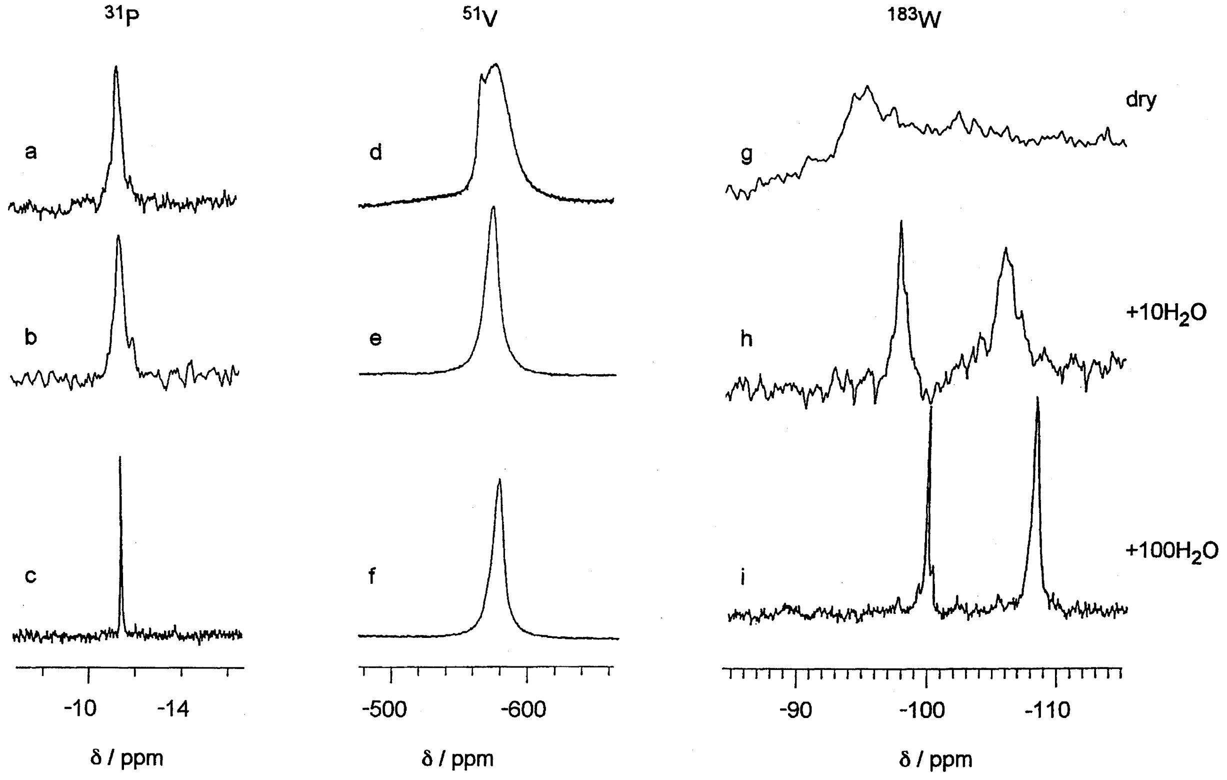

Fig. 4. ^{31}P (a, b, c), ^{51}V (d, e, f), and ^{183}W NMR spectra (g, h, i) of the β-TBA_4H_2 salt in CD_3CN. The amount of added H_2O is 0 (a, d, g), 10 (b, e, h), and 100 equivalent (c, f, i) of H_2O to the salt.

resonance in dry CD_3CN is gradually transformed to the two peaks with addition of H_2O. With 100 equivalent amounts of H_2O, two sharp signals are observed at −99.4 and −107.6 ppm with integrated intensities in the ratio 1 : 2, which is similar to the signals observed for the reaction solution shown in Fig. 3. The lower field signal shows unambiguous spin-spin coupling satellites ($^2J_{W-O-W} = 18.1$ Hz). The value of the coupling constant agrees with those observed for pairs of tungsten atoms via the corner-sharing oxygen atom ($^2J_{W-O-W} = 13$—30 Hz), which is larger than those via an edge-sharing one ($^2J_{W-O-W} = 5$—12 Hz) as previously reported for the Keggin-type heteropoly tungstates.[7,10] Concomitantly, the broad ^{51}V NMR resonance consisting of two or more components in dry CD_3CN is transformed to a single broad signal (−574.6 ppm) with 10 equivalent amounts of H_2O. In the ^{31}P NMR spectra, the broad signal (−11.64 ppm) in dry CD_3CN is also sharpened and shifted to a lower field with addition of H_2O. These results indicate that the bridging oxygen atoms of the β-TBA_4H_2 salt are protonated, as observed for A-β-$(NBu^n{}_4)_4H_3[SiV_3W_9O_{40}]$.[10] In dry CD_3CN the protonation site is rather localized on the NMR time scales and the C_{3v} symmetry for the naked A-β-$[PV_3W_9O_{40}]^{6-}$ anion is lowered, leading to broadening of ^{31}P, ^{51}V, and ^{183}W NMR signals of the β-TBA_4H_2 salt. The presence of H_2O accelerates the exchange process between the protonation sites of the bridging oxygen atom. Hence, the A-β-$[H_2PV_3W_9O_{40}]^{4-}$ anion is observed as an overall average C_{3v} symmetry.

The β-TBA_4H_2 salt was deprotonated in CH_3CN by addition of 2 equivalent amounts of $NBu^n{}_4OH$. The obtained β-TBA_6 salt afforded a sharp single ^{31}P NMR signal at −10.90 ppm in wet CD_3CN (about 100 equivalent amounts of H_2O to the salt added). Furthermore, upon the reaction of β-TBA_4H_2 with 3 equivalent amounts of $NBu^n{}_4OH$, the product gave the same ^{31}P NMR signal as that of β-TBA_6. Therefore, the fully deprotonated β-TBA_6 salt did not decompose in the presence of additional OH^-. The distinction between the ^{31}P NMR resonances of β-TBA_4H_2 (−11.42 ppm) and of β-TBA_6 (−10.90 ppm) is assumed to reflect the structural difference between these polyanions; the polyanion moiety

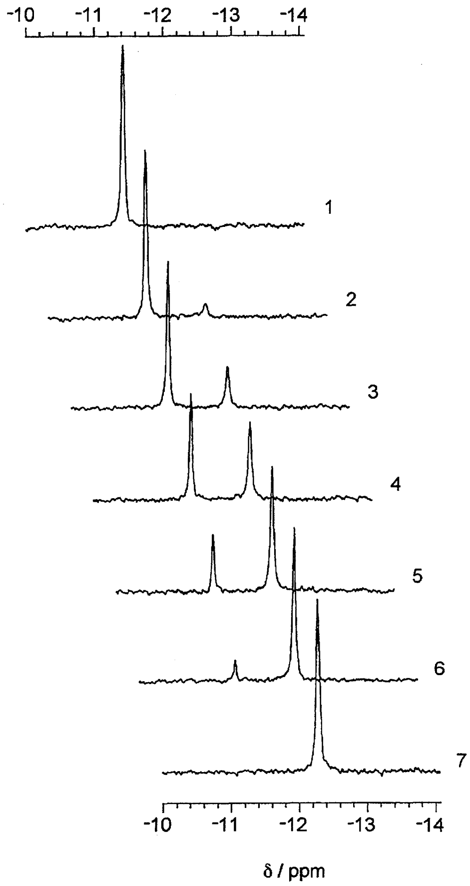

Fig. 5. ^{31}P NMR spectra of the wet CD_3CN solutions of the β-TBA_4H_2 salt heated at 80 °C in the solid state. (heating time; 0 (1), 2 (2), 8 (3), 19 (4), 39 (5), 94 (6), and 160 h (7)).

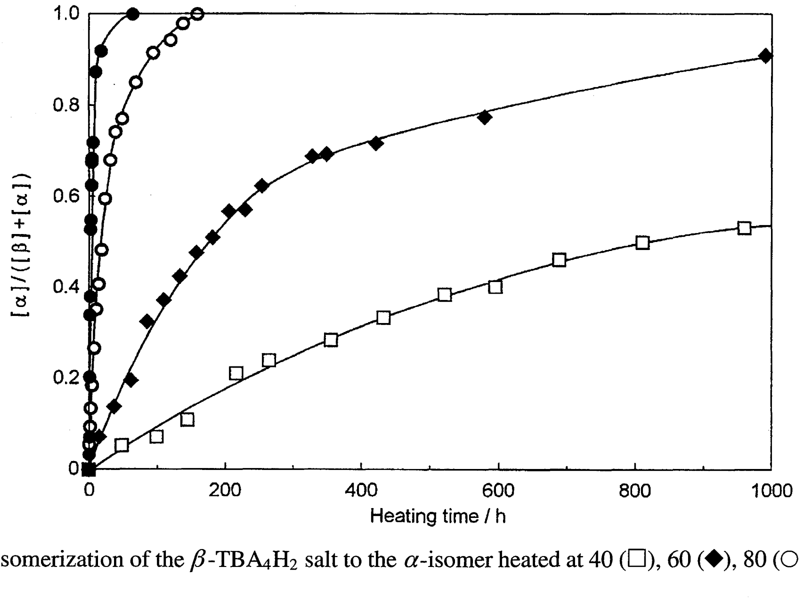

Fig. 6. Progress of the isomerization of the β-TBA_4H_2 salt to the α-isomer heated at 40 (□), 60 (◆), 80 (○), and 100 °C (●) in the solid state.

of β-TBA$_4$H$_2$ is protonated.

Isomerization of the β-TBA$_4$H$_2$ Salt. The β-TBA$_4$H$_2$ salt was heated at 80 °C for 160 h, which had the same IR spectral patterns as those of the α-TBA$_4$H$_2$ salt depicted in Fig. 2. This indicates the isomerization of the β-TBA$_4$H$_2$ salt to the α-isomer in the solid state. Figure 5 shows the ^{31}P NMR spectra of the wet CD$_3$CN solutions of the β-TBA$_4$H$_2$ salt heated at 80 °C in the solid state. The sharp signal observed at -11.42 ppm for the unheated β-TBA$_4$H$_2$ salt decreases in the intensity with the heating time. Concomitantly, a new signal develops at -12.28 ppm; the chemical shift is the same as that of the α-TBA$_4$H$_2$ salt.

Figure 6 shows the progress of the isomerization of β-TBA$_4$H$_2$ to the α-isomer at 40, 60, 80, and 100 °C in the solid state, which was evaluated by the intensity ratios of their ^{31}P NMR signals measured in wet CD$_3$CN (Fig. 5). The first-order rate law (Eq. 1) was applied to the kinetics of this isomerization;

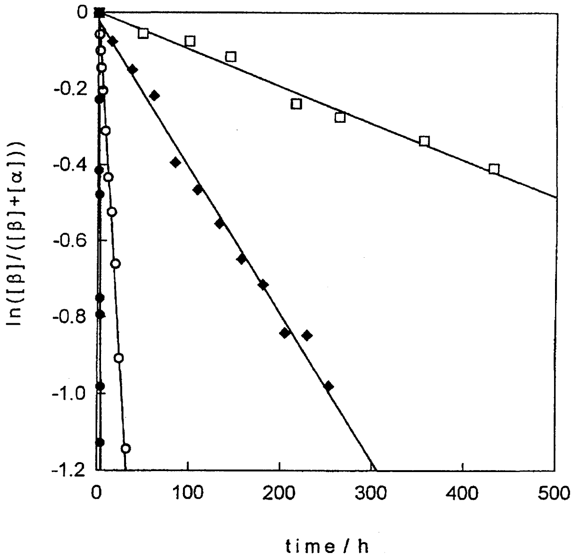

Fig. 7. Plots of ln ([β]/([β]+[α])) vs. time for the isomerization of the β-TBA$_4$H$_2$ salt to the α-isomer heated at 40 (□), 60 (◆), 80 (○), and 100 °C (●) in the solid state.

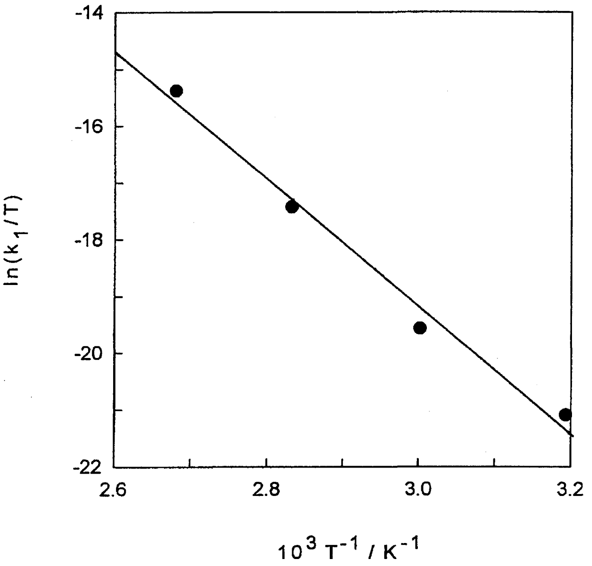

Fig. 8. Eyring plots of the rate constants for the isomerization of the β-TBA$_4$H$_2$ salt to the α-isomer in the solid state.

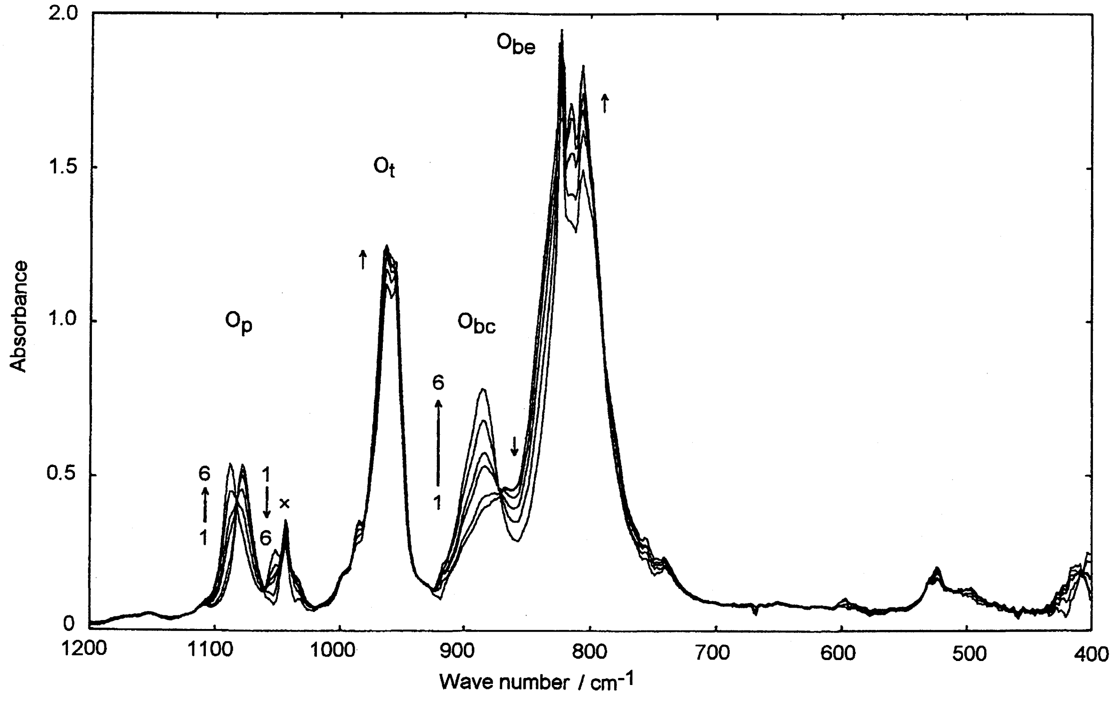

Fig. 9. FT-IR spectral changes of a CH$_3$CN solution containing the β-TBA$_4$H$_2$ salt (2.40×10^{-2} mol dm^{-3}). (reaction time at 60 °C; 0 (1), 20 (2), 98 (3), 164 (4), 315 (5), and 644 h (6), x; peak of the solvent).

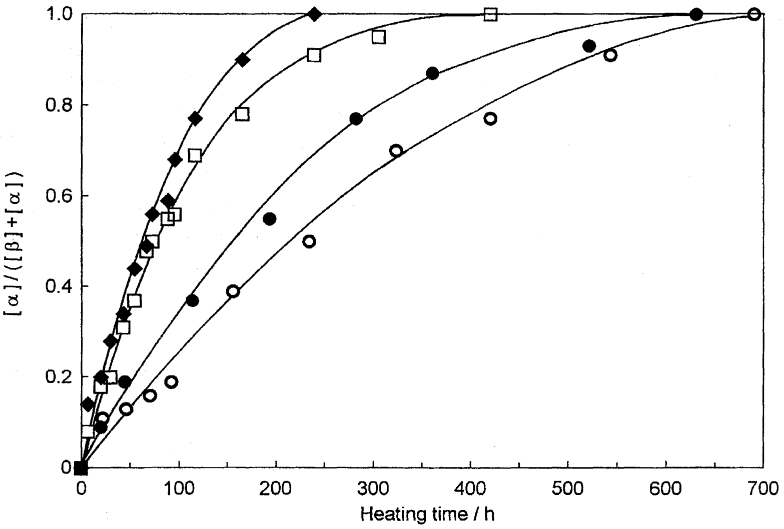

Fig. 10. Progress of the isomerization of the β-TBA_4H_2 salt to the α-isomer in dry CD_3CN (●) at 60 °C and in the presence of H_2O (○), 0.1 M HCl (◆), and 0.1 M DCl (□), where 100 equivalent amounts of the additive to the salt were used.

$$\ln(1-[\alpha]/([\beta]+[\alpha]))=\ln([\beta]/([\beta]+[\alpha]))=-k_1t, \quad (1)$$

where $[\alpha]$ and $[\beta]$ are the concentration of the α- and β-isomers, respectively. Plots of $\ln([\beta]/([\beta]+[\alpha]))$ vs. time for the isomerization at each temperature are shown in Fig. 7. Linear correlations between them are observed up to 60—70% completion of the isomerization. From the slopes of their plots the first-order rate constants, k_1, were evaluated to be 2.19×10^{-7} (s^{-1}) at 40 °C, 1.02×10^{-6} (s^{-1}) at 60 °C, 9.64×10^{-6} (s^{-1}) at 80 °C, and 7.94×10^{-5} (s^{-1}) at 100 °C. Figure 8 shows Eyring plots for the rate constants. The activation parameters were calculated using the Eyring equation: $\Delta H^{\ddagger}=93.3$ (kJ mol^{-1}) and $\Delta S^{\ddagger}=-77.3$ (J K^{-1} mol^{-1}).

The β-Cs_6 and β-TBA_6 salts were also heated at 100 °C in the solid state for several hours. However, the ^{31}P NMR spectra of them measured in wet CD_3CN were identical with those of the respective unheated β-isomers, indicating no isomerization to the α-isomers. These results suggest that protonation to the polyanion of the β-isomer promotes the β-to-α isomerization in the solid state.

Figure 9 shows the FT-IR spectral changes of a CH_3CN solution containing β-TBA_4H_2 at 60 °C. In the region of the obscured O_{bc} band, a new one develops at 885 cm^{-1} with time. Concomitantly, the O_p band (1078 cm^{-1}) decreases, while a new one in the higher frequency (1088 cm^{-1}) increases. The final spectrum in Fig. 9 was changed no more by further heating of the solution at 60 °C and agrees with that of the α-TBA_4H_2 salt.

The ^{31}P NMR spectrum of a CD_3CN solution containing β-TBA_4H_2 showed the spectral changes similar to those observed for the salt heated in the solid state depicted in Fig. 5. These findings indicate that the β-TBA_4H_2 salt also isomerizes to the α-isomer in solution. The progress of the isomerization in CD_3CN was examined in the presence of some kinds of proton sources. It was evaluated by the intensity ratios of the ^{31}P NMR signals of the β- and α-isomers, as depicted in Fig. 10. The rate of the isomerization increases by the addition of HCl. Furthermore, the presence of DCl instead of HCl appreciably decreases the rate, indicating a deuterium effect. These results indicate that the appreciable increase of proton concentration in the solution promotes the protonation to the polyanion and consequently accelerates the β-to-α isomerization. On the other hand, in the presence of a large amount of H_2O the rate of the isomerization decreases compared with that in dry CD_3CN. This is presumably due to the depression of the protonation caused by the addition of H_2O to the solution.

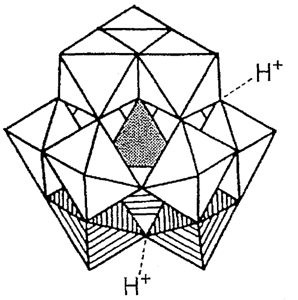

Fig. 11. Polyhedral representation of the A-β-$[H_2PV_3W_9O_{40}]^{4-}$ anion together with probable protonation sites. (Plain and hatched parts indicate WO_6 and VO_6 octahedra, respectively.)

The β-TBA_4H_2 salt has two protons. One of them is probably bound to the bridging oxygen atom in the V–O–V bond, because it is the most basic one among the oxygen atoms in the polyanion, as previously described for the A-β-$[HSiV_3W_9O_{40}]^{6-}$ anion.[10] The other protonation site is considered to be the bridging oxygen atom between "cap" and "belt" tungsten atoms, as illustrated in Fig. 11, on the basis of the finding that the protonation to the A-β-$[PV_3W_9O_{40}]^{6-}$ anion promotes the isomerization of the β-TBA_4H_2 salt to the α-isomer.

References

1) M. Misono, *Proc. Int. Conf. Chem. Uses Molybdenum, 4th*, **1982**, 289.

2) K. Nomiya, H. Saijoh, and M. Miwa, *Bull. Chem. Soc. Jpn.*, **53**, 3719 (1980).

3) R. G. Finke, B. Rapko, and T. J. R. Weakley, *Inorg. Chem.*, **28**, 1573 (1989), and references therein.

4) J. K. Burdett and C. K. Nguyen, *J. Am. Chem. Soc.*, **112**, 5366 (1990), and references therein.

5) M. T. Pope and T. F. Scully, *Inorg. Chem.*, **14**, 953 (1975).

6) L. C. W. Baker and J. S. Figgis, *J. Am. Chem. Soc.*, **92**, 3794 (1970).

7) P. J. Domaille, *J. Am. Chem. Soc.*, **106**, 7677 (1984).

8) P. J. Domaille and G. Watunya, *Inorg. Chem.*, **25**, 1239 (1986).

9) R. G. Finke and M. W. Droege, *J. Am. Chem. Soc.*, **106**, 7274 (1984).

10) R. G. Finke, B. Rapko, R. J. Saxton, and P. J. Domaille, *J. Am. Chem. Soc.*, **108**, 2947 (1986).

11) T. J. R. Weakley, *J. Chem. Soc., Chem. Commun.*, **1984**, 1406.

12) P. J. Domaille and R. L. Harlow, *J. Am. Chem. Soc.*, **108**, 2108 (1986).

13) T. Ozeki and T. Yamase, *Acta Crystallogr., Sect. C*, **47C**, 693 (1991)

14) I. Kawafune and G. Matsubayashi, *Chem. Lett.*, **1992**, 1869.

15) M. M. Mossoba, C. J. O'Connor, M. T. Pope, E. Sinn, G. Hervé, and A. Tézé, *J. Am. Chem. Soc.*, **102**, 6866 (1980).

16) F. Robert and A. Tézé, *Acta Crystallogr., Sect. B*, **37B**, 318 (1981).

17) P. J. Domaille, *Inorg. Synth.*, **27**, 96 (1990).

18) I. Kawafune and G. Matsubayashi, *Bull. Chem. Soc. Jpn.*, **67**, 694 (1994).

19) M. A. Leparulo-Loftus and M. T. Pope, *Inorg. Chem.*, **26**, 2112 (1987).

20) C. Rocchiccioli-Deltcheff, R. Thouvenot, and R. Franck, *Spectrochim. Acta, Part A*, **32**, 587 (1976); C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, and R. Thouvenot, *Inorg. Chem.*, **22**, 207 (1983); R. Thouvenot, M. Fournier, R. Franck, and C. Rocchiccioli-Deltcheff, *Inorg. Chem.*, **23**, 598 (1984).