Formation of α- and β-Keggin-Type $[PW_{12}O_{40}]^{3-}$ Complexes in Aqueous Media

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The formation process of the α- and β-Keggin-type $[PW_{12}O_{40}]^{3-}$ complexes was investigated in an aqueous 50 mM (M = mol dm^{-3}) W(VI)–5.0 mM P(V) system. The ^{31}P NMR study confirmed the formation of A-α-$[PW_9O_{34}]^{9-}$, A-β-$[PW_9O_{34}]^{9-}$, α-$[PW_{11}O_{39}]^{7-}$, and β_1-$[PW_{11}O_{39}]^{7-}$ on acidification of an alkaline solution of $WO_4{}^{2-}$ and $HPO_4{}^{2-}$ to pH 7.5 or below. An isomeric mixture of α- and β-$[PW_{12}O_{40}]^{3-}$ was obtained on further acidification of such solutions containing both α- and β-type lacunary complexes to pH 1 or below. On the other hand, heating of the W(VI)–P(V) system caused A-α-$[PW_9O_{34}]^{9-}$, A-β-$[PW_9O_{34}]^{9-}$, and β_1-$[PW_{11}O_{39}]^{7-}$ to disappear completely, leaving α-$[PW_{11}O_{39}]^{7-}$. Acidification of the α-$[PW_{11}O_{39}]^{7-}$ solution produced only α-$[PW_{12}O_{40}]^{3-}$.

Tungstophosphate complexes have received increasing attention in recent catalytic and electrocatalytic researches.[1,2] Almost all the tungstophosphate complexes have been prepared by acidification of an aqueous W(VI)–P(V) system. As far as the Keggin anions are concerned, we have recently reported that an isomeric mixture of α- and β-$[PW_{12}O_{40}]^{3-}$ is formed on acidification of an aqueous W(VI)–P(V) system;[3] the β-isomer is derived by rotating one of the edge-shared W_3O_{13} groups by $\pi/3$. According to Weinstock et al.,[4] the kinetic and thermodynamic stabilities of β-Keggin anions depend on the kind of heteroatom and on the ionic charge; the stabilities of β-$[XW_{12}O_{40}]^{n-}$ are in the order of X = Al(III) > Si(IV) > P(V) where $n = 5$–3. Owing to its low stability, β-$[PW_{12}O_{40}]^{3-}$ isomerizes spontaneously into the stable α-isomer in aqueous media.

It is known that aqueous solutions of α-$[PW_{12}O_{40}]^{3-}$ are kinetically stable only at pH < 2. When the pH is raised, this ion is converted into the so-called lacunary anion, α-$[PW_{11}O_{39}]^{7-}$; the crystallographic structure of α-$[PW_{11}O_{39}]^{7-}$ has been determined.[5–7] Further increase of the pH leads to the formation of A-type $[PW_9O_{34}]^{9-}$.[8–11] Indeed, several tungstophosphate anions that contain the A-α- or A-β-type Keggin fragment in the structure have been prepared.[12–17] On the other hand, B-$[PW_9O_{34}]^{9-}$ is obtained by heating A-$[PW_9O_{34}]^{9-}$ in the solid state.[18–22]

The speciation of such lacunary anions should be the basis for the formation of α- and β-$[PW_{12}O_{40}]^{3-}$ in aqueous solution. Because most studies have been devoted to the isolation of tungstophosphate complexes rather than to the solution chemistry of the W(VI)–P(V) system, little is known about the formation conditions of lacunary Keggin anions. Besides, the existence of some lacunary anions in solution has not been demonstrated.

The present study focused on the formation of α- and β-$[PW_{12}O_{40}]^{3-}$ in aqueous solution. In this study, ^{31}P NMR was successfully utilized for detecting kinetically unstable lacunary anions including β_1-$[PW_{11}O_{39}]^{7-}$, A-α-, and A-β-$[PW_9O_{34}]^{9-}$ in solution. We found that the short-lived β-type lacunary anions: β_1-$[PW_{11}O_{39}]^{7-}$ and/or A-β-$[PW_9O_{34}]^{9-}$, acted as a precursor of β-$[PW_{12}O_{40}]^{3-}$.

Experimental

Apparatus and Materials. ^{31}P and ^{183}W NMR spectra were obtained with a Bruker Model AVANCE 500 spectrometer at 202.46 and 20.835 MHz, respectively. The ^{31}P NMR spectra were recorded in a 5 mm diameter NMR tube with a concentric capillary containing D_2O for instrumental lock. Chemical shifts are expressed in parts per million with respect to 85% (v/v) H_3PO_4. The ^{183}W NMR spectra were obtained in a 10 mm diameter tube, and chemical shifts were referenced to 1 M $Na_2WO_4 \cdot 2H_2O$ in D_2O. The ^{31}P and ^{183}W NMR spectra were measured at 25 °C. Stock solutions of W(VI) and P(V) were prepared by dissolving appropriate amounts of $Na_2WO_4 \cdot 2H_2O$ and $NaH_2PO_4 \cdot 2H_2O$, respectively. All the chemicals were of analytical grade and were used without further purification.

The β-Keggin-type $(n\text{-}Bu_4N)_3[PW_{12}O_{40}]$ complex was prepared and purified according to our previous method.[3] Figure 1 shows a ^{183}W NMR spectrum for the β-Keggin isomer dissolved in CD_3COCD_3. The β-structure is confirmed by the appearance of three ^{183}W resonances at −92.2, −100.4, and −109.4 ppm with a ratio of 1:2:1.[23]

For the sake of brevity, the Keggin-series tungstophosphate complexes are sometimes referred to by their P/W ratios as the PW_{12}, PW_{11}, and PW_9 complexes.

Results

Detailed ^{31}P NMR measurements of aqueous W(VI)–P(V) solutions were made as a function of the concentrations of W(VI) and/or P(V), acidities, and the reaction temperature. In the available range of acidity, the total concentrations of W(VI) and P(V) were varied in the range of 50 ≤ [W(VI)] ≤ 300 mM and 5.0 ≤ [P(V)] ≤ 300 mM.

Formation of α-Tungstophosphates in a Heated 50 mM

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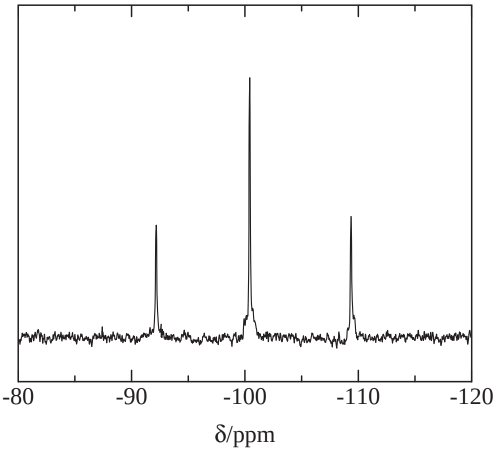


Fig. 1. A ^{183}W NMR spectrum for β-$(n\text{-}Bu_4N)_3[PW_{12}O_{40}]$ dissolved in CD_3COCD_3. Numerical data are given in the text.

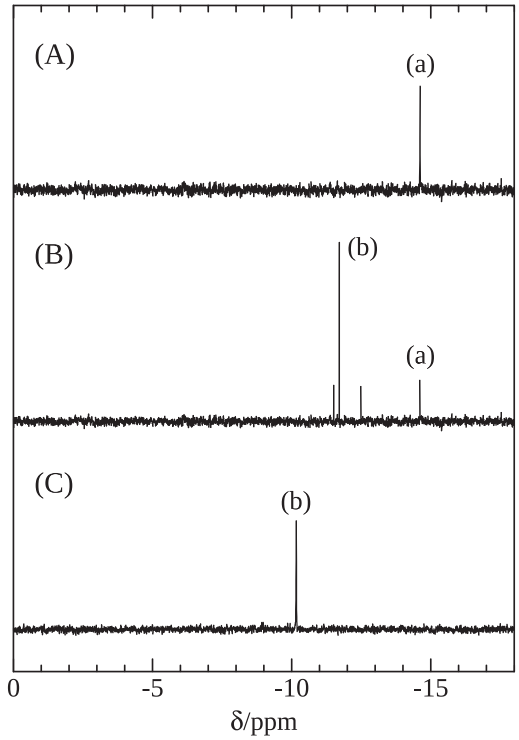


Fig. 2. ^{31}P NMR spectra for a 50 mM W(VI)–5.0 mM P(V)–0.1 M malonate buffer system of various acidities. (A) 0.4 M HCl; (B) pH 2.5; (C) pH 4.0. (a) α-PW_{12}; (b) α-PW_{11}. Measured after heating at 90 °C for two days.

W(VI)–5.0 mM P(V) System. Since the formation of tungstophosphate complexes was pH- and temperature-dependent, ^{31}P NMR spectra were recorded after heating 50 mM W(VI)–5.0 mM P(V) systems of various pH values at 90 °C for two days. Below pH 2, the 50 mM W(VI)–5.0 mM P(V) system showed a ^{31}P NMR line at −14.6 ppm (Fig. 2A), and the appearance of a single ^{183}W NMR line at −94.2 ppm indicated that all the tungsten atoms are structurally equivalent. These results clearly show the formation of α-PW_{12}.

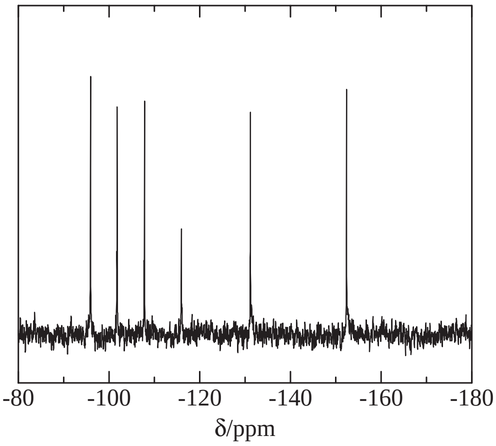


Fig. 3. A ^{183}W NMR spectrum for a 100 mM W(VI)–10 mM P(V)–0.1 M malonate buffer (pH 5) system. Measured after heating at 90 °C for two days. Numerical data are given in the text.

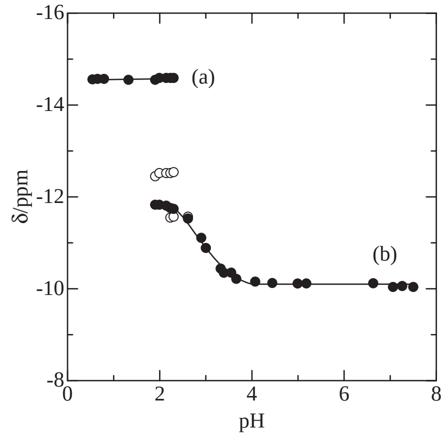


Fig. 4. ^{31}P NMR chemical shifts as a function of pH for a 50 mM W(VI)–5.0 mM P(V)–0.1 M malonate buffer system. (a) α-PW_{12}; (b) α-PW_{11}. The ^{31}P NMR measurements were made after heating at 90 °C for two days. Open circles denote undefined ^{31}P NMR lines.

In addition to the −14.6 ppm line, a new line appeared at −11.8 ppm around pH 2. Simultaneously, we found two smaller lines at both downfield and upfield sides of the new line (Fig. 2B); no assignments were made to the small lines. As the pH was raised, the major −11.8 ppm line grew with a downfield shift, to a limit of −10.2 ppm. In the pH range of 4.0–7.5, the 50 mM W(VI)–5.0 mM P(V) system was characterized by the −10.2 ppm line (Fig. 2C). As shown in Fig. 3, the 100 mM W(VI)–10 mM P(V) solution (pH 5) gave six ^{183}W NMR lines at −96.1, −101.9, −107.9, −116.1, −131.3, and −152.6 ppm with the intensity ratio of 2:2:2:1:2:2,[24–26] indicating that the ^{31}P resonance at −10.2 ppm corresponds to the monolacunary derivative, α-PW_{11}.[9] In Fig. 4 are plotted the respective ^{31}P NMR chemical shift values against pH. The downfield shift of the α-PW_{11} line can be ascribed to the deprotonation. Similar downfield shifts were also observed for α-PMo_{11}.[27]

Formation of α- and β-Tungstophosphates in a Fresh 50 mM W(VI)–5.0 mM P(V) System. Because we found no

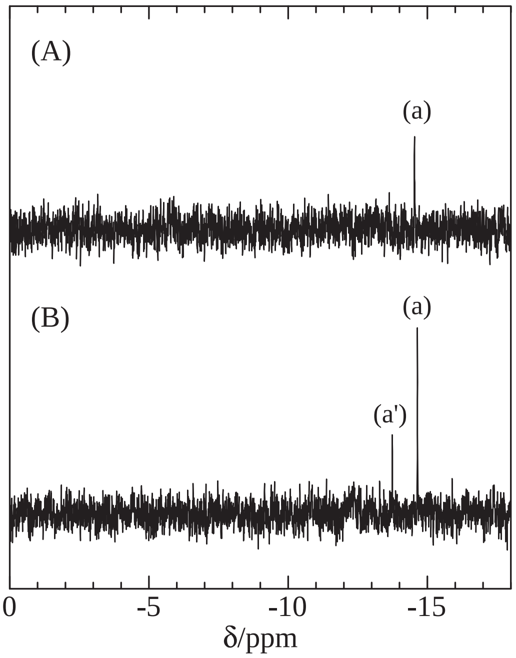


Fig. 5. ^{31}P NMR spectra for a 50 mM W(VI)–5.0 mM P(V)–0.4 M HCl system. Measured (A) immediately; (B) after two hours.

evidence for the existence of β-PW_{12} in the heated system, ^{31}P NMR spectra were recorded for a 50 mM W(VI)–5.0 mM P(V)–0.4 M HCl system without heating. The test solution was prepared by transferring the W(VI) and P(V) stock solutions into a volumetric flask (pH ca. 8), followed by the addition of an aliquot amount of 10 M HCl. The fresh solution exhibited the α-PW_{12} line at −14.6 ppm (Fig. 5A). As time elapsed, the α-PW_{12} line grew slowly with the appearance of a new line at −13.7 ppm (Fig. 5B), indicating the formation of β-PW_{12}.[3] The β-PW_{12} line decreased with time, and finally it disappeared completely after 24 h. This observation can explain the absence of the β-PW_{12} line in the heated 50 mM W(VI)–5.0 mM P(V) system. We have recently found that β-PW_{12} is markedly stabilized by the presence of CH_3CN at concentrations $>$ 15% (v/v) in the reaction mixture, and this finding led us to the preparation of β-PW_{12}.[3]

In order to study the formation process of β-PW_{12}, we recorded ^{31}P NMR spectra for a freshly prepared 50 mM W(VI)–5.0 mM P(V) system of various acidities. In the pH range of 1–3.5, the α-PW_{12} and α-PW_{11} lines appeared with unidentified small lines (Fig. 6A). As shown in Fig. 6B, a pair of lines appeared at −10.2 (α-PW_{11}) and −8.6 ppm around pH 4. Above pH 5, a new line appeared at −5.1 ppm, accompanied by an additional line at −3.2 ppm (Fig. 6C). Further increase of pH caused the −5.1 ppm line to grow in relation to the −10.2 ppm line. Simultaneously, the −8.6 ppm line disappeared, leaving the −3.2 ppm line (Fig. 6D). At pH values $>$ 4, all the chemical shift values are independent of pH, indicating that no protonation of the tungstophosphate complexes occurs (Fig. 7). It must be stressed that the −8.6, −5.1, and −3.2 ppm lines are transient.

As shown in Fig. 5B, acidification of the 50 mM W(VI)–5.0 mM P(V) system (pH ca. 8) yielded β-PW_{12} very slowly. On acidification of each solution in Figs. 6B–D, however, the ^{31}P NMR spectrum exhibited −14.6 and −13.7 ppm lines below pH 1.0 (Fig. 6E), indicating that α- and β-PW_{12} occurs rapidly even at ambient temperature. These results indicate that some of the tungstophosphates responsible for the −10.2, −8.6, −5.1, and −3.2 ppm lines may act as precursors of α- and β-PW_{12}. As already described, the −10.2 ppm line is assigned to α-PW_{11}.

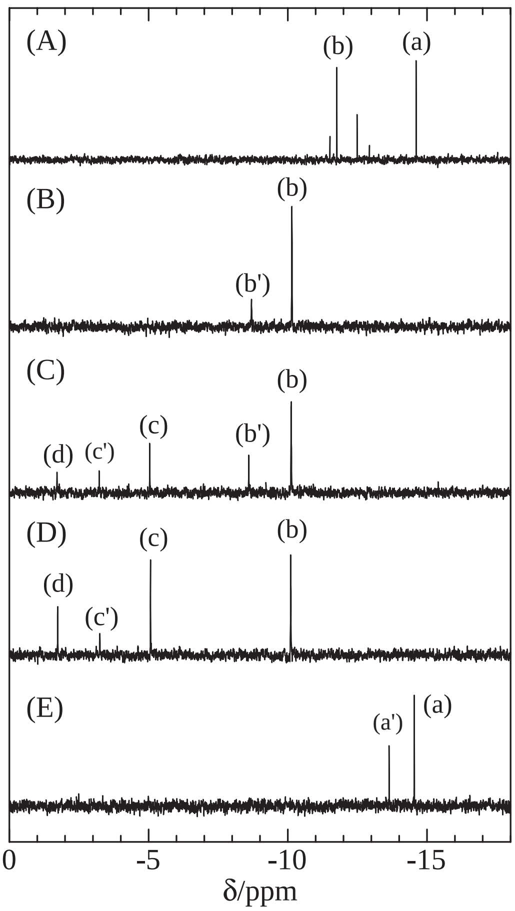


Fig. 6. ^{31}P NMR spectra upon the preparation of a 50 mM W(VI)–5 mM P(V)–0.1 M malonate buffer system. (A) pH 2.3; (B) pH 4.0; (C) pH 5.5; (D) pH 7.3; (E) 0.4 M HCl. (a) α-PW_{12} (−14.6 ppm); (a′) β-PW_{12} (−13.7 ppm); (b) α-PW_{11} (−10.2 ppm); (b′) β_1-PW_{11} (−8.6 ppm); (c) A-α-PW_9 (−5.1 ppm); (c′) A-β-PW_9 (−3.2 ppm); (d) P_2W_5 (−1.7 ppm).

In the pH range of 4.5–7.5, as shown in Figs. 6C, D, and 7, there was an additional line at −1.7 ppm, which can be tentatively assigned to $[P_2W_5O_{23}]^{6-}$ (P_2W_5).[28] No further discussion on the tungstophosphate complex with the −1.7 ppm line is made, because the complex is not directly related to the formation of the α- and β-Keggin complexes.

α-Type Lacunary Complexes: The following ^{31}P NMR measurements were made to identify the transient tungstophosphate species giving the −8.6, −5.1, and −3.2 ppm lines. First, a 50 mM W(VI)–5.0 mM P(V)–0.4 M HCl solution was heated at 90 °C for two days, and then cooled to room temperature. As shown in Fig. 8A, the solution gave only α-PW_{12}. Then, ^{31}P NMR was measured upon raising the pH to

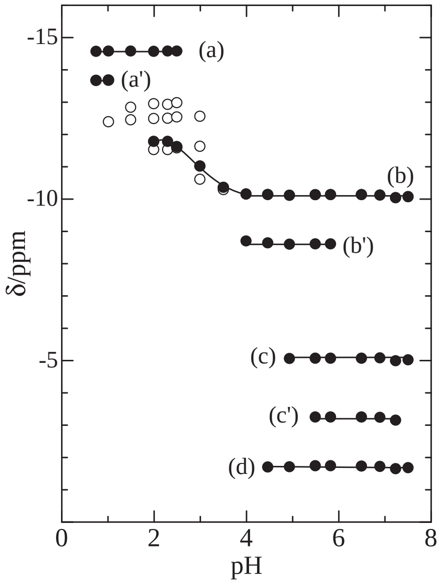


Fig. 7. ^{31}P NMR chemical shifts as a function of pH for a fresh 50 mM W(VI)–5.0 mM P(V)–0.1 M malonate buffer system. (a) α-PW_{12}; (a′) β-PW_{12}; (b) α-PW_{11}; (b′) β_1-PW_{11}; (c) A-α-PW_9; (c′) A-β-PW_9; (d) P_2W_5. For each solution of pH < 1, the ^{31}P NMR measurements were made after one hour. Open circles denote undefined ^{31}P NMR lines.

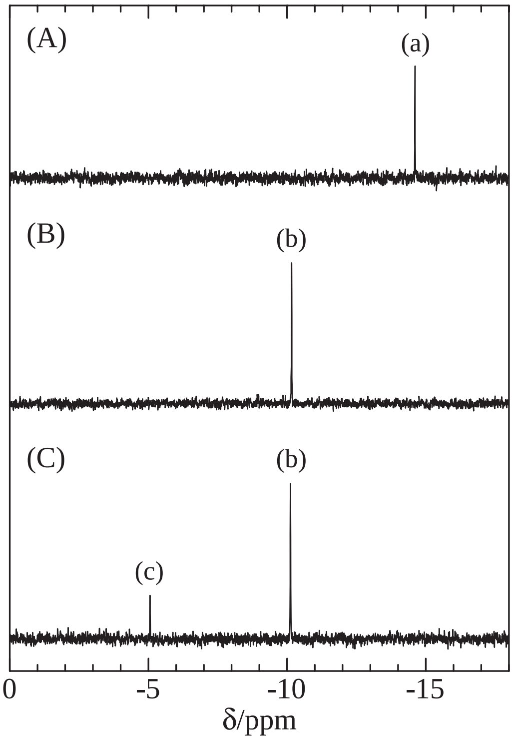


Fig. 8. ^{31}P NMR spectra after heating a 50 mM W(VI)–5.0 mM P(V)–0.4 M HCl–0.1 M malonate buffer system at 90 °C for two days. Measured (A) after cooling to room temperature; (B) upon raising the pH of (A) to 4; (C) upon raising the pH of (A) to 6. (a) α-PW_{12}; (b) α-PW_{11}; (c) A-α-PW_9.

3.5–5 with NaOH. The appearance of a single line at -10.2 ppm indicates the complete transformation of α-PW_{12} into α-PW_{11} (Fig. 8B). When the pH was raised to 5–7.5, the α-PW_{11} line was accompanied by a small line at -5.1 ppm (Fig. 8C). As time elapsed, the -5.1 ppm line was decreased, leaving the stable α-PW_{11} line. Thus, the tungstophosphate complex corresponding to the -5.1 ppm line belongs to the α-type series. It is reasonable to assign the -5.1 ppm line to A-α-PW_9, a degradation product of α-PW_{11}.

As far as the α-Keggin-type series are concerned, as shown in Fig. 7a, b, and c, the respective formation conditions can be given as a function of pH: α-PW_{12}, pH < 2.5; α-PW_{11}, pH 2–7.5; A-α-PW_9, pH 5–7.5. During the conversion process of α-PW_{12}, neither of the -8.6 and -3.2 ppm lines was detected, suggesting that both lines are due to the β-type lacunary complexes.

β-Type Lacunary Complexes: When ^{31}P NMR spectra were recorded immediately after the pH of the 50 mM W(VI)–5.0 mM P(V) solution of Fig. 6E was raised again to 4, the original -14.6 (α-PW_{12}) and -13.7 (β-PW_{12}) ppm lines were replaced by the -10.2 (α-PW_{11}) and -8.6 ppm lines, respectively, suggesting that the -8.6 ppm line can be assigned to β-PW_{11}. This assignment was further substantiated by the fact that both -14.6 and -13.7 ppm lines were obtained on acidification of the fresh W(VI)–P(V) solution of pH 4.0, which gave a pair of the -10.2 and -8.6 ppm lines (Fig. 6B). Contrary to α-PW_{11}, β-PW_{11} has not been well characterized because of its limited stability in aqueous media.

The following ^{31}P NMR measurements were made in order to obtain more information on the β-type lacunary complexes. It was found that α- and β-PW_{12} also occurred on acidification of the W(VI)–P(V) solution, showing the -10.2 (α-PW_{11}), -8.6, -5.1 (α-PW_9), and -3.2 ppm lines (pH 5.5) (Fig. 6C) or the -10.2 (α-PW_{11}), -5.1 (α-PW_9), and -3.2 ppm lines (pH 7.3) (Fig. 6D). These results confirm that the tungstophosphates responsible for the -8.6 and -3.2 ppm lines belong to the β-type series.

These observations can be explained in terms of the conversion of β-PW_{11} (-8.6 ppm) and/or A-β-PW_9 (-3.2 ppm) into β-PW_{12} (-13.7 ppm). Unlike α-PW_{11}, three isomers of β-PW_{11} are possible: β_1-, β_2-, and β_3-type.[29–32] However, the present ^{31}P NMR study indicates the formation of only a single isomer, and we tentatively assign the -8.6 ppm line to β_1-PW_{11}. This assignment is based on the prediction that only β_1-PW_{11} can lead to A-β-PW_9.[1] Figure 7 also shows the respective formation conditions: β-PW_{12}, pH < 1; β_1-PW_{11}, pH 4–6; A-β-PW_9, pH 5.5–7.5.

Discussion

In spite of considerable efforts, no satisfactory correlation between chemical shifts and lacunary structures derived from α- and β-PW_{12} has been reported so far. The present ^{31}P NMR study has demonstrated that the fresh 50 mM W(VI)–5.0 mM P(V) system produces a family of Keggin-type tungstophosphate complexes (α-PW_{12}, α-PW_{11}, A-α-PW_9, β-PW_{12}, β_1-PW_{11}, and A-β-PW_9) as a function of pH and/or the reaction temperature. The chemical shift data of the respective Keggin and lacunary complexes are given in Table 1. Dimerized species such as α- and β-$[P_2W_{18}O_{62}]^{6-}$ (P_2W_{18}) and $[P_2W_{21}O_{71}(H_2O)_3]^{6-}$ (P_2W_{21}) are known to exist at much

Table 1. ^{31}P NMR Chemical Shift Values

Tungstophosphates	Chemical shifts (ppm)	Acidities
α-PW_{12}	−14.6	pH <2.6
β-PW_{12}	−13.7	pH <1
α-PW_{11}	−10.2	pH 2.0–7.6
β_1-PW_{11}	−8.6	pH 4.0–6.0
A-α-PW_9	−5.1	pH 5.0–7.6
A-β-PW_9	−3.2	pH 5.5–7.3
P_2W_{21}	−13.3	1.5 M HCl
α-P_2W_{18}	−12.4	1.5 M HCl
β-P_2W_{18}	−11.6, −10.9	pH 1.3

greater concentrations of W(VI) and/or P(V).[9–11,33–36] Table 1 also lists their chemical shift values, obtained after heating a 300 mM W(VI)–300 mM P(V) system at 90 °C for seven days.

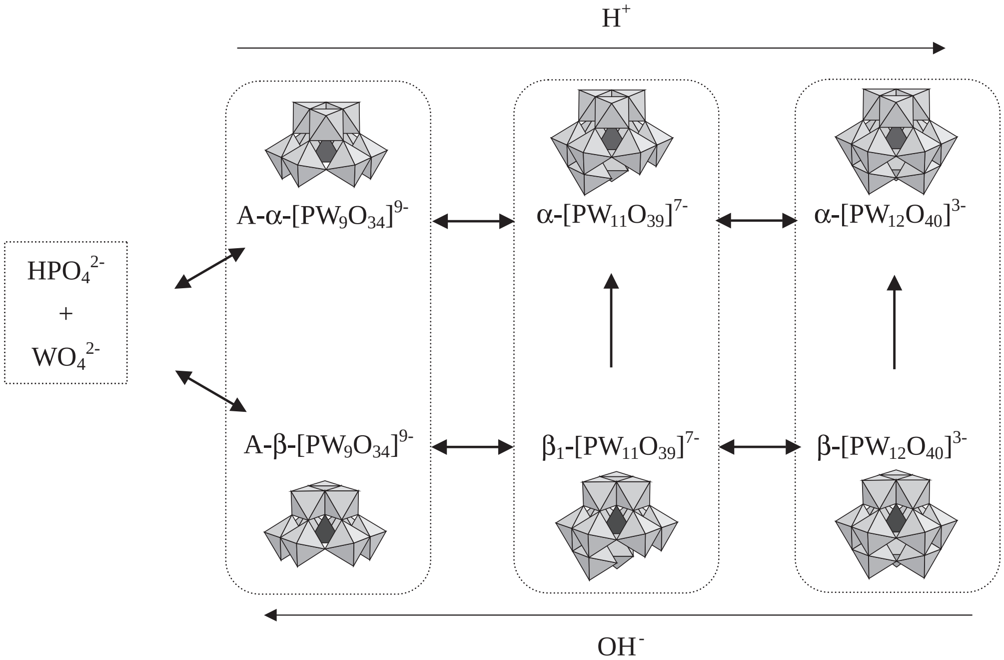
Only α-PW_{12} was formed after heating the 50 mM W(VI)–5.0 mM P(V)–0.4 M HCl system at 90 °C for two days (Fig. 8A), being converted, via α-PW_{11} (Fig. 8B), into A-α-PW_9 as the pH was raised (Fig. 8C). While α-PW_{11} was thermodynamically stable in the W(VI)–P(V) solution (Figs. 2C and 3), A-α-PW_9 formed transiently, being transformed into α-PW_{11}.

As shown in Fig. 5, the freshly prepared 50 mM W(VI)–5.0 mM P(V)–0.4 M HCl system slowly produced an isomeric mixture of α- and β-PW_{12}, and β-PW_{12} disappeared as time elapsed. In agreement with the behavior for the α-type series, there was a downfield shift according to the sequence of β-PW_{12} → β_1-PW_{11} → A-β-PW_9 (Figs. 6 and 7). The assignment of the −3.2 ppm line to A-β-PW_9 came from the appearance of β-PW_{12} upon acidification of the W(VI)–P(V) system of pH 7.3, giving the −10.2 (α-PW_{11}), −5.1 (α-PW_9), and −3.2 ppm lines (Fig. 6D and E). Like β-PW_{12}, β_1-PW_{11} and A-β-PW_9 are formed as short-lived intermediates. In a fresh 50 mM W(VI)–5.0 mM P(V) system of pH 4–5, β_1-PW_{11} may be formed by the incorporation of two WO_2 groups in the vacancy of A-β-PW_9. The ^{31}P NMR chemical shift values of the β-type series were 0.9–1.9 ppm downfield from those of the corresponding α-type analogues, and the β-type complexes are formed at narrower pH ranges as compared with the corresponding α-type complexes (Fig. 7).

As shown in Fig. 6, α- and β-lacunary complexes such as α-PW_{11}, β_1-PW_{11}, A-α-PW_9, and A-β-PW_9 are formed instantaneously upon adjusting the pH of the W(VI)–P(V) system to a value between 4 and 7, and the presence of such lacunary complexes leads to the quick formation of α- and β-PW_{12}. It turned out that β_1-PW_{11} isomerized into α-PW_{11}, because the −8.6 ppm line in Fig. 6B disappeared as time passed, leaving the −10.2 ppm line. Because the A-β-PW_9 line was minor and transient, on the other hand, we could not observe its isomerization into A-α-PW_9. These patterns of behavior are in marked contrast to those in a W(VI) and Si(IV) system.[29–32] The acidification of a reaction mixture of W(VI) and Si(IV) leads to A-β-$[SiW_9O_{34}]^{10-}$ (SiW_9), but not to A-α-SiW_9. Further addition of H^+ to the A-β-SiW_9 solution leads to β_1-$[SiW_{11}O_{39}]^{8-}$ (SiW_{11}), which is subsequently transformed according to the sequence of β_1-SiW_{11} → β_2-SiW_{11} → β_3-SiW_{11} → α-SiW_{11}. The alkaline degradation of α-SiW_{11} produces A-α-SiW_9.

Conclusion

The formation process of α- and β-PW_{12} can be proposed as follows. Acidification of an aqueous W(VI)–P(V) system produces a mixture of A-α-PW_9, A-β-PW_9, α-PW_{11}, and β_1-PW_{11} in the early stage before the formation of α- and β-PW_{12}. Among them, A-α-PW_9, A-β-PW_9, and β_1-PW_{11} are formed as short-lived intermediates. The present study shows the importance of β_1-PW_{11} and A-β-PW_9 as key precursors for the formation of β-PW_{12}. When the final pH value is set at < 1, the incorporation of three WO_2 groups in the vacancies



Scheme 1.

of A-α-PW_9 and A-β-PW_9 or of a WO group in vacancies of α-PW_{11} and β_1-PW_{11} leads inevitably to α-PW_{12} and β-PW_{12}, respectively. The β-type lacunary complexes always coexist with the corresponding α-type lacunary complexes (Fig. 7). This finding can explain why an isomeric mixture of α- and β-PW_{12} is always obtained,[3] while α-PW_{12} is formed in the pure form.

Scheme 1 illustrates the sequence of the tungstophosphate species formed in a freshly prepared 50 mM W(VI)–5.0 mM P(V) system.

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