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Modeling Reactive Metal Oxides. Kinetics, Thermodynamics, and Mechanism of M_3 Cap Isomerization in Polyoxometalates

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An investigation of M_3O_{13} unit (“M_3 cap”) isomerization in the classical polytungstodiphosphates α- and β-$P_2W_{18}O_{62}^{6-}$ has been undertaken because cap isomerism is an important and structurally well-studied phenomenon in many polyoxometalate families. The relative thermodynamic stabilities of the α (more stable) versus β isomers were established both in the solid state by differential scanning calorimetry (4.36 ± 0.64 kcal/mol) and in solution by ^{31}P NMR (3.80 ± 0.57 kcal/mol). The isomerization of β-$P_2W_{18}O_{62}^{6-}$ to α-$P_2W_{18}O_{62}^{6-}$, followed by ^{31}P NMR, has a bimolecular rate constant k_2 of 9.3×10^{-1} M^{-1} s^{-1} at 343 K in pH 4.24 acetate buffer. Several lines of evidence establish the validity of suggestions in the literature that isomerization goes through a lacunary (defect) intermediate. First, the rate is proportional to $[OH^-]$. Second, isomerization increases at higher ionic strengths, and a Debye–Hückel plot is consistent with a rate-limiting reaction between β-$P_2W_{18}O_{62}^{6-}$ and OH^- (two species with a charge product of 6). Third, alkali-metal cations stabilize the bimolecular transition state ($K^+ > Na^+ > Li^+$), consistent with recent ion-pairing studies in polyoxometalate systems. Fourth, the monovanadium-substituted products α_1- and α_2-$P_2VW_{17}O_{62}^{7-}$ (^{51}V NMR δ –554 ppm) form during isomerization in the presence of VO^{2+}. The known lacunary compounds (α_1- and α_2-$P_2W_{17}O_{61}^{10-}$) also react rapidly with the same vanadium precursor. Fifth, solvent studies establish that isomerization does not occur when OH^- is absent. A mechanism is proposed involving attack of OH^- on β-$P_2W_{18}O_{62}^{6-}$, loss of monomeric W(VI) from the M_3 (M_3O_{13}) terminal cap, isomerization of the resulting lacunary compound to α-$P_2W_{17}O_{61}^{10-}$, and finally reaction of this species with monomeric W(VI) to form the thermodynamic and observed product, α-$P_2W_{18}O_{62}^{6-}$.

Introduction

Heterogeneous catalysis by metal oxides and by supported or solid transition-metal oxide clusters (polyoxometalates or POMs for convenience)[1] have a number of similarities. A number of processes, and in particular oxidations, catalyzed by both types of materials are commercially significant, and both types of catalysts and catalytic processes continue to be the subject of considerable ongoing research.[2−10] Because many reactive POMs have both elemental compositions and structures similar to or virtually identical with their corresponding reactive metal oxides, the former have been repeatedly invoked as structural models of the latter.[1,11−14] However, comparisons between the *dynamic* properties of reacting or catalytically active metal oxides and POMs are lacking. This derives in good measure from the fact that while there is much recent work on characterization of the structural and physicochemical changes in metal oxide surfaces under turnover conditions (with a number of in situ spectroscopic and structural methods now in use to elucidate these

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structural changes),[3,15−18] the comparable situation does not exist for POMs and heterogeneous reactions catalyzed by POMs.

There are limited data on the kinetics and mechanism of POM reactions (rearrangements, isomerizations, polymerizations) and ion pairing, information fundamental to understanding not just catalysis by POMs but to a number of other applications of this sizable and growing class of inorganic compounds as well. A few solid-state and solution-state studies have been reported. Wachs and co-workers described in situ Raman spectroscopy and thermogravimetric analysis (TGA) evidence for the formation and subsequent breakdown of Keggin POMs under typical heterogeneous catalytic oxidation conditions.[19] Trifirò, Finke, and co-workers documented (FTIR, XRD, TGA, and TEM) evidence for the solid-state rearrangement of the Wells−Dawson POM, $K_6P_2W_{18}O_{62}\cdot 10H_2O$, to a stable Keggin-type heteropolyanion phase,[20] and Kawafune and Matsubayashi reported the solid-state isomerization of A-β-$PV_3W_9O_{40}^{6-}$ to its corresponding α-isomer.[21] In the latter work, rate constants, activation parameters, and the kinetic impact of some ion pairing effects were reported. Mechanistic studies of POMs in solution fall into two categories. Early kinetic studies provide some insight into POM formation and degradation (not POM rearrangements, isomerizations, or reactions of POM units themselves), but the electronic absorption spectral[22−26] or electrochemical[27] methods used could not unequivocally define many of the species present. Studies using ^{17}O NMR and higher resolution (i.e. species specific) methods by Klemperer and co-workers (documentation of structural changes in α-$Mo_8O_{26}^{4-}$, $C_6H_5AsMo_7O_{25}^{4-}$, and $(C_6H_5As)_2Mo_6O_{24}^{4-}$),[28] Tézé and co-workers (sequential formation of polytungstosilicates),[29] and others on actual POM rearrangements provided substantial information on species present during transformation but little or no kinetic or thermodynamic data.

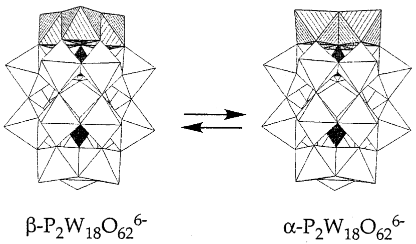

Figure 1. Isomerization of β-$P_2W_{18}O_{62}^{6-}$ to α-$P_2W_{18}O_{62}^{6-}$ shown in polyhedral notation. The two central tetrahedra in each molecule represent P^VO_4 units, and the octahedra represent $W^{VI}O_6$ units.

In 1999, the first energy differences for α- and β-isomers of Keggin POMs under equilibrium conditions in solution were reported.[30] Recent research also quantifies both the thermodynamics and kinetics of ion pairing in reactive POM systems.[31,32] This work supersedes informative POM ion pairing studies by several groups that focused primarily on the structural consequences of these interactions.[29,33−36] The earlier structural studies revealed unprecedented control of heteropolyanion isomers in solution by selection of an appropriate cation.[35,37] Significantly, there are no detailed reports of POM reactions using species-specific techniques such as NMR methods that include quantification of both thermodynamic and kinetic properties.

We report here such a study. We focus on isomerism of the Wells−Dawson POMs of the formula $P_2W_{18}O_{62}^{6-}$ for several reasons (the net reaction is given in Figure 1). First, there have been many synthetic and structural studies on these isomers.[11,38−41] Among the six isomers postulated by

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Baker and Figgis for $P_2W_{18}O_{62}{}^{6-}$, only four have actually been observed.[42−44] α- and β-$P_2W_{18}O_{62}{}^{6-}$, the two most common isomers, are always produced together upon acidification of Na_2WO_4. The structure of β-$P_2W_{18}O_{62}{}^{6-}$ and the two other known isomers, γ- and γ^*-$P_2W_{18}O_{62}{}^{6-}$, were inferred from ^{31}P and ^{183}W NMR solution studies.[43,45−50] Second, these studies ranging in time from 1920 to the present do not address and thus complement the information in this study on quantification of key thermodynamic and kinetic values and features. Third, the dominant isomerism in these POMs involves M_3 (or M_3O_{13}) units that occur in many structural families of POMs and approximate those in close-packed metal oxide domains occurring on the steps and corners of reactive metal oxide surfaces. Fourth, the study of $P_2W_{18}O_{62}{}^{6-}$ facilitates use of ^{31}P NMR, an informative and species-specific spectroscopic handle whose utility in POM chemistry is well-established.[43,46−52]

Experimental Section

General Methods. All materials used were reagent grade, with the exception of sodium tungstate dihydrate, which was Folin reagent grade. ^{31}P and ^{51}V NMR spectra were acquired on Varian INOVA 400 MHz and Unity 600 MHz spectrometers, respectively. Differential scanning calorimetric and thermogravimetric data were collected on ISI DSC 550 and ISI TGA 1000 instruments, respectively. α- and β-$(NH_4)_6P_2W_{18}O_{62}$ were prepared according to the literature methods.[53]

NMR Procedures. The ^{31}P NMR data were collected at 161.9 MHz. Chemical shifts are reported relative to 85% phosphoric acid. T_1 values for both α- and β-$(NH_4)_6P_2W_{18}O_{62}$ were determined (from oxygen-free solutions) to be 11 s. The following spectral parameters were used: 90° pulse, pulse width, 13 μs; sweep width, 20 000 Hz; delay, 55 s; 36 scans. The NMR software NUTS (1-D version, distributed by Acorn NMR Inc., Fremont, CA) was used for baseline correction and integration. NMR data were collected over a wide spectral window to detect any decomposition products and, subsequently, over a narrow spectral window for the most accurate integration. No decomposition products were detected. The reaction proceeds at rates amenable for accurate ^{31}P NMR measurement of the concentrations of starting β-$P_2W_{18}O_{62}{}^{6-}$ and product α-$P_2W_{18}O_{62}{}^{6-}$ at the indicated time intervals. The sum of the integration of the corresponding β-isomer peaks (−10.9 and −11.5 ppm) was divided by the sum of all three peaks (including that for the α-isomer at −12.2 ppm) to determine the fraction of the β-isomer present in solution. This value was multiplied by the initial concentration of the β-isomer to give the concentration at the indicated time intervals. Sensitivity was enhanced for certain experiments by moving to a higher field (from 400 MHz to 600 MHz) and by using a different type probe designed to give greater sensitivity. The ^{51}V NMR data were collected at 157.6 MHz. A 10 mM solution of $H_4PVMo_{11}O_{40}$ in 0.60 M NaCl was used as the external reference (δ −533.6 ppm relative to neat $VOCl_3$; chemical shifts are reported relative to $VOCl_3$ at δ 0 ppm). The following spectral parameters were used: 90° pulse, pulse width, 6 μs; sweep width, 75 000 Hz; delay, 1 s; 500 scans.

Rate Law Determination. Solutions of β-$(NH_4)_6P_2W_{18}O_{62}$ (10 mM) were prepared in 100 mM acetate buffer at pH 4.24 and placed in glass vials with sealed caps. The solutions were degassed as liquids and purged with Ar. The vials were heated in a mineral oil bath at 343 K and the contents stirred magnetically at a constant speed of 300 rpm. Aliquots (0.7 mL) were removed from the vial at set time intervals, immediately cooled in an ice−water bath, and then analyzed by ^{31}P NMR. The concentration of β-$(NH_4)_6P_2W_{18}O_{62}$ was varied over a 10-fold range (from 5 to 50 mM). The total ionic strength (0.648 M) and pH (4.24) were kept constant by careful addition of appropriate quantities of NaCl and CH_3COOH/$NaOOCCH_3$, respectively. Solutions of β-$(NH_4)_6P_2W_{18}O_{62}$ (10 mM) were also prepared in 100 mM acetate buffer at varying pH values (from pH 4.1 to 5.2). The ionic strength was held constant by adjustment with NaCl. All pH values were corrected for temperature. Control experiments were run by substituting citrate buffer for the acetate buffer. A pH titration was performed to determine if the POM protonates over the pH range in question.

Ionic Strength Dependence. Solutions of β-$(NH_4)_6P_2W_{18}O_{62}$ were prepared in acetate buffer (100 mM) as described in Rate Law Determination. The ionic strength was adjusted from 0.2 to 2.2 M by adding appropriate quantities of NaCl to each vial while the pH was kept constant at 4.24 by careful addition of CH_3COOH and $NaOOCCH_3$. The ionic strength due to the buffer was accounted for in all reactions. Initial rate data were collected and plotted in accordance with Debye−Hückel theory (see the Supporting Information).[54−56]

Activation Parameters. Solutions of β-$(NH_4)_6P_2W_{18}O_{62}$ (10 mM) were prepared in 100 mM acetate buffer at pH 4.24 and ionic strength 0.3 M, purged with Ar, and placed in glass vials with sealed caps. The vials were heated in a mineral oil bath at fixed temperatures from 314 to 373 K, and each was stirred at 300 rpm. Aliquots (0.7 mL) were removed from the vials at set time intervals and immediately cooled in an ice−water bath. The samples were analyzed by ^{31}P NMR and the data plotted using the Eyring and Arrhenius equations.

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Alkali-Metal Cation Dependence. Solutions (13 mM) of β-$(NH_4)_6P_2W_{18}O_{62}$ were prepared in 100 mM buffer at pH 4.24 by careful addition of $CH_3COOH/MOOCCH_3$, where M = Li^+, Na^+, K^+. The chloride salts of Li^+, Na^+, and K^+ were added to each sample in equal molar amounts (0.18 M) to keep the total ionic strength of the solution (including the POM, countercations, alkali-metal salts, and acetate buffer) constant at 0.48 M. The total alkali-metal concentration was also kept constant at 0.18 M. Aliquots (0.7 mL) were removed from the vial and analyzed as described in Rate Law Determination.

Vanadyl Incorporation Experiments. $VOSO_4$ (0.016 g) was dissolved in 7 mL of 100 mM aqueous acetate buffer solution at pH 4.24, and 0.388 g of β-$(NH_4)_6P_2W_{18}O_{62}$ was added. The resulting solution (pH 3.0) was degassed, placed in a glass vial with a sealed cap, heated to 343 K, and stirred at 300 rpm while it was monitored with time. Aliquots (0.7 mL) were removed from the vial and analyzed by ^{31}P and ^{51}V NMR. Control experiments were run analogously using α-$(NH_4)_6P_2W_{18}O_{62}$ instead of β-$(NH_4)_6P_2W_{18}O_{62}$. Authentic samples of α_2-$P_2VW_{17}O_{62}^{7-}$ were prepared and purified according to literature methods.[57]

Solid-State Experiments. A partially dehydrated sample of β-$(NH_4)_6P_2W_{18}O_{62}$ (10.5 mg) was placed in an aluminum pan and heated from 298 to 873 K at a rate of 20 K/min in a differential scanning calorimeter (DSC). Peaks due to loss of lattice waters were assigned by thermogravimetric analysis (TGA). No decomposition products were detected, as determined by ^{31}P NMR analysis. Pure samples of α- and β-$(NH_4)_6P_2W_{18}O_{62}$ were heated at a rate of 20 K/min (up to 583 K) in a muffle furnace for 6 h, and samples were removed every 1 h and redissolved for ^{31}P NMR analysis.

Solvent Effects. Solutions of β-$(NH_4)_6P_2W_{18}O_{62}$ (5 mM) were prepared in 100 mM acetate buffer (pH 4.24) with percentages of acetonitrile varying between 5 and 100 vol %. The contents of the vials were heated and stirred as described in Rate Constant Determination. Initial rate data (^{31}P NMR) were collected as described above.

Results and Discussion

Assessment of Isomer Distribution (α versus β) at Equilibrium. It is helpful, if not essential, in many cases to have some knowledge of the thermodynamics ($\Delta H°$, $\Delta S°$, $\Delta G°$) of a process before undertaking a detailed study of the kinetics and mechanism. After the evaluation of various techniques, we determined that two provided the relative stabilities of the α- and β-isomers, one for solids (the powdered POMs) and one for solutions. After long reaction times in solution (>64 h), it was determined that the concentrations of β- and α-$P_2W_{18}O_{62}^{6-}$ remain unchanged (times up to 700 h were assessed). At equilibrium in aqueous solution at 343 K, 99.6% of β-$P_2W_{18}O_{62}^{6-}$ converts to α-$P_2W_{18}O_{62}^{6-}$ and 0.4% of β-$P_2W_{18}O_{62}^{6-}$ remains. These small equilibrium quantities of β-$P_2W_{18}O_{62}^{6-}$ made it necessary to move to a higher field NMR spectrometer (600 MHz versus 400 MHz) with greater sensitivity and still use a saturated solution in order to accurately quantify all POM concentrations.[58] If we assume this system is indeed at equilibrium, then $\Delta G°$ is 3.80 ± 0.57 kcal/mol at 343 K. To first assess whether this assumption is valid, the temperature of the system (at equilibrium) was changed to 328 K for 36 h.[59] The concentration of β-$P_2W_{18}O_{62}^{6-}$ increased to 0.8% (99.2% α-$P_2W_{18}O_{62}^{6-}$) at this temperature. Once the system was reequilibrated at 343 K over 14 h, the original 0.4% β-$P_2W_{18}O_{62}^{6-}$ was again present (within experimental error). When a solution of 100% α-$P_2W_{18}O_{62}^{6-}$ was heated at 328 K for 36 h, approximately 0.6% β-$P_2W_{18}O_{62}^{6-}$ was present (within experimental error). Therefore, it is reasonable to assume that within the uncertainty of the integrations the two product distributions (from 100% α and 100% β) are in agreement.

Differential scanning calorimetry (DSC) data show a number of endothermic peaks below 473 K. Thermogravimetric analyses of the same samples establish that these peaks correspond to loss of lattice water molecules. No decomposition is observed by ^{31}P NMR. No peaks (corresponding to a temperature change) appear again until 583 K, which ^{31}P NMR establishes is the actual isomerization process. The reaction of 100% β-$(NH_4)_6P_2W_{18}O_{62}$ proceeds to 30% α and 70% β at 583 K with no detectable decomposition products. The heating rate was varied between 20 K/min and 100 K/min to establish the reproducibility of the data.[60] The percentages of α and β in the resulting product mixtures were unchanged, as observed in their corresponding peak integrations and confirmed by ^{31}P NMR. A $\Delta H°$ value of 4.36 ± 0.64 kcal/mol was determined after corrections for loss of lattice water molecules (4 wt % according to TGA) for a system where 30% of β-$P_2W_{18}O_{62}^{6-}$ is converted to α-$P_2W_{18}O_{62}^{6-}$. It is significant experimentally to note that this DSC-based method does not rely on the attainment of equilibrium, since ^{31}P NMR analysis on the redissolved sample permits the quantification of the amount of the bulk sample of β-$P_2W_{18}O_{62}^{6-}$ that is actually undergoing a thermal transformation. Therefore, this method provides an alternative to the use of equilibrium values for the assessment of $\Delta H°$. The DSC-based method for evaluation of solid-state reaction enthalpies is especially useful for the phosphotungstate POMs, where it is well-established that the β-isomers are not as stable as their aluminum counterparts (i.e. the ratio of concentrations of the α-isomer to the β-isomer is a large number) and therefore not as amenable to equilibrium constant determination in solution by NMR.[30] Attempts were also made to characterize the solid-state thermal chemistry of α-$(NH_4)_6P_2W_{18}O_{62}$ by DSC; however, its transformations are complex and a mixture of α-, β-, and γ-$(NH_4)_6P_2W_{18}O_{62}$ result.[61] From the data obtained in these experiments, it was concluded that the differences in energy between β-$P_2W_{18}O_{62}^{6-}$

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(57) Harmalker, S. P.; Leparulo, M. A.; Pope, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 4286−4292.

(58) Sensitivity was enhanced not only by moving to a higher field but also by using a different type of probe with coils in closer proximity to the sample.

(59) (a) Pettersson, L. In *Topics in Molecular Organization and Engineering—Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*; Pope, M. T., Müller, A., Eds.; Kluwer Academic: The Netherlands, 1993; pp 27−40. (b) Attempts to assess the equilibrium at a higher temperature (363 K) were unsuccessful because the concentration of β-$P_2W_{18}O_{62}^{6-}$ was nearly undetectable.

(60) Varying heating rates is a common means of establishing the reproducibility of DSC data. Slow heating rates can identify if successive reactions are present, while fast heating rates can determine if there is partial decomposition of the sample (see: Wendlandt, W. W. *Thermal Analysis*; Wiley-Interscience: New York, 1986).

and α-$P_2W_{18}O_{62}{}^{6-}$ are not substantially different in the solid state and in solution. Slight variations in the value of $\Delta G°$ could certainly reflect solvation effects. If we assume entropic effects are negligible,[62a] then the $\Delta G°$ value of isomerization would be ca. 4 kcal/mol (within experimental error) for both the solid-state and solution systems.

Rate Constant and Overall Rate Behavior. The loss of β-$P_2W_{18}O_{62}{}^{6-}$ and the formation of α-$P_2W_{18}O_{62}{}^{6-}$ versus time was monitored by ^{31}P NMR peak integrations. The data rigorously follow pseudo-first-order processes for reactant consumption and product formation (eqs 1 and 2, respectively).

$$[\beta\text{-POM}]_t = [\beta\text{-POM}]_0 e^{-kt} \tag{1}$$

$$[\alpha\text{-POM}]_t = [\alpha\text{-POM}]_0 (1 - e^{-kt}) \tag{2}$$

The value of k_{obs} ($(5.3 \pm 0.4) \times 10^{-5}$ s^{-1}) at 343 K is the same within experimental error as that obtained from a linear plot of the data. Dividing k_{obs} by the concentration of the species held constant, OH^-, yields a bimolecular rate constant: k_2 at 343 K $= 9.3 \times 10^{-1}$ M^{-1} s^{-1}.[62b] Further, no decomposition is detectable by ^{31}P NMR, and the sum of the product (α-$P_2W_{18}O_{62}{}^{6-}$) plus remaining β-$P_2W_{18}O_{62}{}^{6-}$ is always equal to the initial concentration of β-$P_2W_{18}O_{62}{}^{6-}$.

The kinetic van't Hoff plot for the dependence of the β-$P_2W_{18}O_{62}{}^{6-}$ isomerization rate on POM concentration has a slope of 1.0 (see the Supporting Information). The linear fit of the data is good, with $R^2 = 0.992$. The data contain an ionic strength correction (i.e. the ionic strength was kept constant throughout by adjusting the NaCl concentration).[63a] This was appropriate, given the high charge (6−) on the POM, since a 10-fold increase in POM concentration represents a 360-fold increase in ionic strength. The result, corrected for ionic strength, indicates the reaction is first order in POM (slope 1.0).

The kinetic van't Hoff plot for the pH dependence also has a slope of 1.0 ($R^2 = 1.0$) at constant ionic strength. In short, the reaction is proportional to $[OH^-]$. This supports the proposal by the groups of Hervé and Crouch that isomerization occurs via lacunary intermediates.[24,29] Experiments were performed to assess whether OH^- or OAc^- is the actual species reacting with the POM by replacing the acetate buffer with a citrate buffer under identical conditions (pH, ionic strength, and temperature). $k_{obs} = (4.9 \pm 0.5) \times 10^{-5}$ s^{-1} at 343 K for the citrate-buffered solution is the same as k_{obs} for the acetate-buffered solution within experimental error, suggesting that OH^- is most likely reacting with the POM. A pH titration confirms the POM is not protonated over the pH range of these experiments.

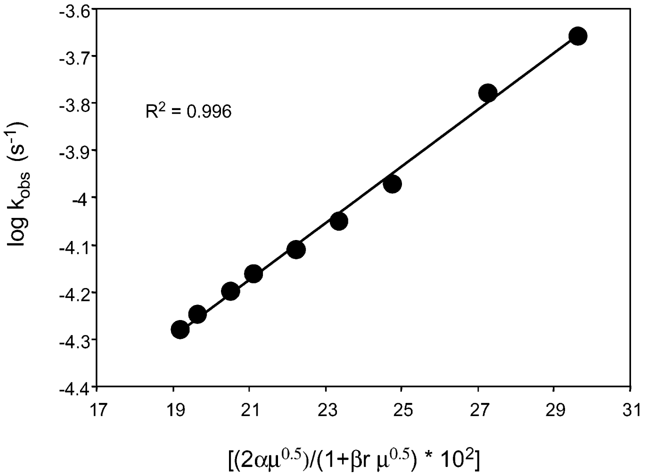

Figure 2. Debye−Hückel plot for the ionic strength dependence of β-$P_2W_{18}O_{62}{}^{6-}$ isomerization. Initial rate data were taken over an 11-fold range in ionic strength (from 0.2 to 2.2 M). The slope of the Debye−Hückel plot (5.92) is equal to $z_1{*}z_2$, the product of the interacting charges (see the Supporting Information).

Ionic Strength Effects. Figure 2 gives the Debye−Hückel plot for the ionic strength dependence. The rate increases with ionic strength. This is consistent with the fact that increasing the ionic strength can enhance the rate of exchange of ions (i.e. H^+ and OH^-) with the solvent and, therefore, facilitate the interaction of OH^- with the POM.[54,64] The slope of the Debye−Hückel plot shown in Figure 2 is equal to $z_1{*}z_2$, the product of the interacting charges, when log k_{obs} is plotted against $2\alpha\mu^{0.5}/(1 + \beta r\mu^{0.5})$ (see the Supporting Information). The numerical values of α and β used are 0.412 (at 343 K) and 0.329×10^8 cm, and the hydrodynamic radius of $P_2W_{18}O_{62}{}^{6-}$ is 6.4 Å.[55] A best-fit analysis of the data gives a straight line with a slope of 5.92 and a R^2 value of 0.996. This value is expected for the interaction of β-$P_2W_{18}O_{62}{}^{6-}$ and OH^- in the rate-limiting transition state.

Debye−Hückel theory seems to account quite nicely for the ionic strength dependence of the reaction. Previously, the Debye−Hückel equation has held for POM solutions with ionic strength values up to 0.616 M for α-$PW_{12}O_{40}{}^{3-}$ and 1.49 M for α-$P_2W_{18}O_{62}{}^{6-}$.[55] The highest ionic strength value in this study is 2.2 M. Typically this equation is limited to more dilute solutions (<0.50 M), while the original form of the equation was derived for even more dilute solutions (<0.01 M).[54,64] While the application of conventional Debye−Hückel theory to such high concentrations should be suspect, it is important to point out that the charge densities on POMs are not only far lower than in nearly all conven-

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(61) Maksimovskaya and Maksimov obtained similar results in the transformation of α-$H_6P_2W_{18}O_{62}{}^{6-}$. They attribute this to a reverse isomerization reaction catalyzed by the H^+ countercations. See: Maksimovskaya, R. I.; Maksimov, G. M. *Zh. Neorg. Khim.* **1995**, *40*, 1363−1368. In contrast, Kawafune and Matsubayashi have observed that H^+ ions catalyze the isomerization of β-$TBA_4H_2PV_3W_9O_{40}$ (where TBA = tetra-*n*-butylammonium) to α-$TBA_4H_2PV_3W_9O_{40}$.[21]

(62) (a) Entropy is assumed to be negligible, since there is no net change in charge or phase of the system. Furthermore, since $\Delta S = (\Delta H - \Delta G)/T$, the entropic change would be negligible if ΔH and ΔG are approximately the same value. (b) One needs to divide k_{obs} by the reagent whose concentration is constant during the reaction (OH^- in the present case), even if it is the lower of the two concentrations initially. This is the fundamental meaning of pseudo-first-order kinetics and the only way to obtain a meaningful value for the rate constant. (c) Pseudo-first-order rate constants were used to obtain the Eyring plots. As a result, a different value of $\Delta S^‡$ will be obtained at each value of pH, although the $\Delta H^‡$ value (obtained from the slope) will be unchanged. We thank an anonymous reviewer for comments.

(63) (a) The buffer concentration was kept sufficiently high to maintain a constant pH throughout the reaction. (b) Previous reports have shown the gradual addition of vanadate to α-$P_2W_{18}O_{62}{}^{6-}$ leads to the very slow (i.e. on the order of months) formation of a mixture of α_1 and α_2 isomers of $P_2VW_{17}O_{62}{}^{7-}$.[50]

(64) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*; 3rd ed.; Wiley: New York, 1981.

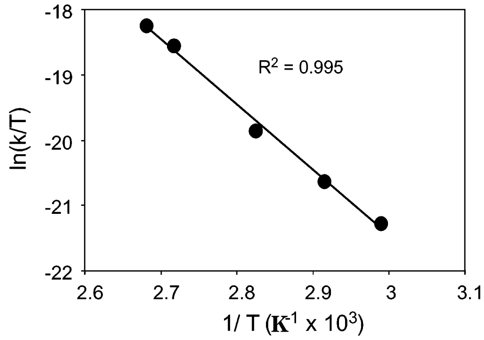

Figure 3. Temperature dependence of the isomerization of β-$P_2W_{18}O_{62}^{6-}$ (Eyring plot).

Table 1. Cation Dependence of the Initial Rate of β-$P_2W_{18}O_{62}^{6-}$ Isomerization[a]

MCl[b]	init. rate[c] (10^6 M s^{-1})
LiCl	1.05
NaCl	1.68
KCl	2.10

[a] [POM] = 13 mM in 100 mM acetate buffer at pH 4.24 and 343 K. [b] [LiCl] = [NaCl] = [KCl] = 0.18 M. [c] Aliquots (0.7 mL) were removed and analyzed by ^{31}P NMR.

tional ions, including those used to derive Debye−Hückel theory in the first place, but also that these very low POM charges exert their electrostatic effects over a far larger ion surface area than for conventional ions. As a consequence, solvation (including hydration) energies, hydrogen bonding, and hydrodynamic radii of POMs are all minimal (smaller than those of conventional complex ions in solution).

Activation Parameters. The Eyring plot for the isomerization of β-$P_2W_{18}O_{62}^{6-}$ is given in Figure 3. From the slope and *y* intercept, the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 19.9 ± 1.4 kcal mol^{-1} and −30.4 ± 2.1 cal K^{-1} mol^{-1} at pH 4.24, respectively. From $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$, $\Delta G^{\ddagger}$ is 28.9 ± 2.0 kcal mol^{-1} at 298 K and pH 4.24.[62c] The fit of the data is good ($R^2 = 0.995$), and the linearity of the plot implies that only one reaction is taking place throughout this temperature range.

Alkali-Metal Cation Dependence. Table 1 gives the initial rate data for the isomerization of β-$P_2W_{18}O_{62}^{6-}$ at equal cation concentrations and the same temperature, pH, buffer concentration, and ionic strength. Precautions were taken to minimize error due to the pairing of the cations with acetate by keeping concentrations of these species well below their K_{sp} values. These systems show rates that vary as a function of the hydrodynamic radius of the alkali metals in aqueous solution. In other words, the rate of isomerization increases as the hydrodynamic radius of the cation decreases. Lithium, despite having the smallest crystallographic radius, has the largest hydrodynamic radius of the alkali metals and is least able to intimately pair with the POM in aqueous solution.[31,32] On the other hand, potassium has the smallest hydrodynamic radius of these three alkali-metal cations and is most able to intimately pair with the POM. These data are consistent with cation stabilization of the increasing charge in the rate-limiting transition state complex. That is, the more highly charged POM (the lacunary β-$P_2W_{17}O_{61}^{10-}$ versus the parent β-$P_2W_{18}O_{62}^{6-}$) and the charged monomeric W(VI) species are forming in the activated complex.

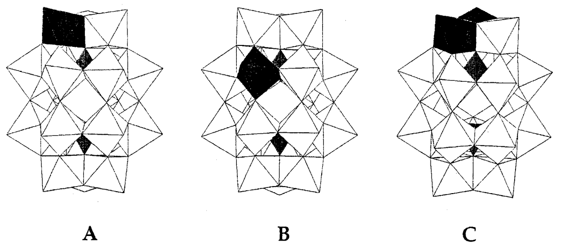

Figure 4. Vanadyl incorporation products: (**A**) α_2-$P_2VW_{17}O_{62}^{7-}$; (**B**) α_1-$P_2VW_{17}O_{62}^{7-}$; (**C**) α-$P_2V_2W_{16}O_{62}^{8-}$.

Vanadyl Incorporation Experiments. The presence of $VOSO_4$ in a solution of β-$P_2W_{18}O_{62}^{6-}$ at pH 4.24 (acetate buffer) at 343 K initially produces two new species, each with two symmetry-inequivalent P atoms due to the incorporation of vanadium atom(s) (Figure 4). One complex is identified as α_2-$P_2VW_{17}O_{62}^{7-}$ (ca. 19% yield; **A** in Figure 4). First, ^{31}P NMR gives two peaks (−10.9 and −13.0 ppm) which are the same within experimental error as the reported literature values for α_2-$P_2VW_{17}O_{62}^{7-}$.[57] Second, the ^{51}V NMR spectrum has one peak (−554 ppm) which is also very similar to the reported literature value for α_2-$P_2VW_{17}O_{62}^{7-}$.[57] This isomer assignment was verified by preparation and evaluation of an authentic sample of α_2-$P_2VW_{17}O_{62}^{7-}$. Furthermore, control experiments with α-$P_2W_{18}O_{62}^{6-}$ show that α_2-$P_2VW_{17}O_{62}^{7-}$ is formed to some extent in the absence of isomerization (approximate yield 6%).[63b] The second species was identified as α_1-$P_2VW_{17}O_{62}^{7-}$ (approximate yield 13%; **B** in Figure 4) by comparison with literature values (^{31}P NMR gives two peaks at −11.9 and −12.9 ppm, and ^{51}V NMR has one peak at −564 ppm).[57] A third species, which only appears in solution after 24 h, was identified as α-$P_2V_2W_{16}O_{62}^{8-}$ (approximate yield 7%, **C** in Figure 4), also by comparison with literature values (^{31}P NMR gives two peaks at −9.0 and −13.5 ppm, and ^{51}V NMR has one peak at −525 ppm).[57] In summary, after 45% of β-$P_2W_{18}O_{62}^{6-}$ is consumed, 19% of the final mixture is α_2-$P_2VW_{17}O_{62}^{7-}$, 13% of the product mixture is α_1-$P_2VW_{17}O_{62}^{7-}$, 7% is α-$P_2V_2W_{16}O_{62}^{8-}$, and 6% is α-$P_2W_{18}O_{62}^{6-}$.

The data are consistent with the proposal in the literature that isomerization occurs via lacunary intermediates.[24,29] The hydrolytic (OH^- induced) loss of the monomeric W(VI) species forms a lacunary compound which rapidly reacts with many monomeric hydrated metal species, including $V{=}O^{2+}$.[1,29,40] Wells−Dawson POMs have two types of WO_6 units by symmetry, those in the belts (indicated by a 1 subscript) and those in the caps (indicated by a 2 subscript). Previous reports have established that either belt or cap WO_6 sites can be substituted with another metal.[65,66] Further studies have shown, however, that α_1-substituted Wells−Dawson POMs are less reactive than the α_2-substituted isomers.[67] If base attack on a belt W leads to a α_1-species, a "hole migration" can take place where the molecule rearranges to

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(65) Contant, R.; Ciabrini, J. P. *J. Chem. Res., Synop.* **1977**, 222.
(66) Lyon, D. K.; Miller, W. K.; Novet, T.; Domaille, P. J.; Evitt, E.; Johnson, D. C.; Finke, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7209−7221.

move the free site onto the cap.[68] Further, the presence of $V{=}O^{2+}$ inhibits the rate of isomerization, which is also consistent with the reversible loss of $W{=}O^{4+}$ during the reaction.[68] Attempts to determine if WO_4^{2-} influences the rate of reaction were unsuccessful, since this species reacts rapidly to form the thermodynamically stable metatungstate over this pH and temperature range.[11] The presence of the disubstituted derivative in aged solutions is not unexpected, as the presence of a single vanadium atom is shown to influence subsequent metal incorporation.

Solvent Effects. The isomerization reaction was studied by varying the mole fraction of acetonitrile in water. Acetonitrile strongly inhibits the rate of isomerization. Rate retardation by addition of organic solvents to aqueous solutions of POMs has been used before for the isolation of kinetically unstable POM isomers. One case in point is the synthesis, isolation, and characterization of β-$PW_{12}O_{40}^{3-}$, a compound which is too short-lived in 100% water, but sufficiently long-lived in water–acetonitrile mixtures, to study.[69] In other studies, it was established that quite labile POMs such as the phosphomolybdates can be stabilized in acetonitrile.[70] This mixed-solvent system could also facilitate the observation of any lacunary intermediates present. No such intermediates were observed in our systems, however. This may be due in part to the much lower lability of the corresponding phosphotungstates.[70] In addition, β-$(NH_4)_6P_2W_{18}O_{62}$ has very low solubility in acetonitrile, making detection of such intermediates extremely difficult.

Mechanism. A theoretical mechanism consistent with all the data is given in eqs 3–7. Under equilibrium conditions

$$\beta\text{-}P_2W_{18}O_{62}^{6-} + OH^- \overset{k_1}{\rightleftarrows} \beta\text{-}HP_2W_{18}O_{63}^{7-} \tag{3}$$

$$\beta\text{-}HP_2W_{18}O_{63}^{7-} + 5OH^- \overset{k_2}{\rightleftarrows} \beta\text{-}P_2W_{17}O_{61}^{10-} + 3H_2O + WO_4^{2-} \tag{4}$$

$$\beta\text{-}P_2W_{17}O_{61}^{10-} \overset{k_3}{\rightleftarrows} \alpha\text{-}P_2W_{17}O_{61}^{10-} \tag{5}$$

$$\alpha\text{-}P_2W_{17}O_{61}^{10-} + WO_4^{2-} + 6H^+ \overset{k_4}{\rightleftarrows} \alpha\text{-}P_2W_{18}O_{62}^{6-} + 3H_2O \tag{6}$$

$$\alpha\text{-}P_2W_{17}O_{61}^{10-} + VO^{2+} + 2H^+ \overset{k_5}{\rightleftarrows} \alpha_2\text{-}P_2VW_{17}O_{62}^{6-} + H_2O \tag{7}$$

(equilibrium is ultimately attained in our solution isomerization reactions), all five steps are reversible. The first step involves nucleophilic attack of 1 equiv of OH^- on the addenda W atom (eq 3) followed by hydrolysis with additional equivalents of OH^- (eq 4).

Free monomeric W(VI) species react rapidly with the lacunary POM (back-reaction to re-form the starting β-$P_2W_{18}O_{62}^{6-}$ or forward reaction with the rearranged lacunary α-$P_2W_{17}O_{61}^{10-}$ to form α-$P_2W_{18}O_{62}^{6-}$). If k_1 is the rate-determining step, the theoretical rate law would be overall second order (first order in $[OH^-]$ and first order in [POM], eq 8). This is consistent with the experimentally

$$\text{rate} = k'[\text{POM}][OH^-] \tag{8}$$

determined rate law, which is also first order in $[OH^-]$ and first order in [POM]. Since the nature of the alkali metal has a strong influence on the overall rate and thus is a part of the rate law, our rate study here is specifically for the association of Na^+ with the POM (i.e. the factor “[POM]” in eq 8 encompasses Na^+ association). It is previously known that the products in some POM syntheses are dependent on the alkali-metal counterion.[65]

This study provides several additional lines of evidence which support proposals in the literature that isomerization occurs via lacunary intermediates (eq 5).[24,29] First, isomerization increases at higher ionic strength values, where the mobility of OH^- ions is increased. In contrast, when the mobility of OH^- is inhibited by mixed solvents, as in acetonitrile–water mixtures, the rate of isomerization decreases. Second, the Debye–Hückel plot indicates that the product of the two interacting charges is 6, consistent with the interaction of β-$P_2W_{18}O_{62}^{6-}$ and OH^- in the rate-limiting transition state complex. Third, the activation parameters (decrease in entropy) are in accord with a bimolecular reaction involving a transition state with increased negative charge and consequent increased ordering of the proximal water molecules of hydration. Fourth, alkali-metal cations stabilize the increased negative charge in the activated complex ($K^+ > Na^+ > Li^+$), consistent with recently established studies in POM systems.[31,32] Fifth, $V{=}O^{2+}$ incorporation is fully consistent with the existence of lacunary intermediates (eq 7), and sixth, solvent effects show that isomerization does not take place when OH^- is absent.

Conclusions. The pH dependence, POM dependence, activation parameters, Debye–Hückel theory, solvent effects, vanadyl substitution experiments, and the alkali-metal cation dependence of the isomerization rate are all consistent with literature proposals that isomerization goes through a lacunary intermediate produced by partial base hydrolysis of addenda tungsten atoms. The lacunary or “defect” species is reconstituted by free monomeric W(VI) species (or VO^{2+}) in subsequent fast steps to give the product, the parent POM α-$P_2W_{18}O_{62}^{6-}$ (or α_1- and α_2-$P_2VW_{17}O_{62}^{7-}$).

Acknowledgment. We thank the NSF (Grant No. CHE-9975453) for support and the Georgia Research Alliance and Emory University for funding the Unity 600 MHz NMR instrument.

Supporting Information Available: Equations for Debye–Hückel theory, data for rate constant determination and [β-$P_2W_{18}O_{62}^{6-}$] and [OH^-] dependence, and an Arrhenius plot. This information is available free of charge via the Internet at http://pubs.acs.org.

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