A Dimeric Titanium-Containing Polyoxometalate. Synthesis, Characterization, and Catalysis of H_2O_2-Based Thioether Oxidation

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The previously unknown titanium(IV)-containing μ-hydroxo dimeric heteropolytungstate $(Bu_4N)_7[(PTiW_{11}O_{39})_2OH]$ (TBA salt of H**1**) has been synthesized, starting from $H_5PTiW_{11}O_{40}$, and characterized by elemental analysis, multinuclear (^{31}P, ^{17}O, ^{183}W) NMR, IR, FAB-MS, cyclic voltammetry, and potentiometric titration. ^{31}P NMR reveals that H**1** (δ −12.76) readily forms in MeCN from the Keggin monomer (POM), $PTiW_{11}O_{40}^{5-}$ (**2**, δ −13.34), upon the addition of 1.5 equiv of H^+, via the protonated species, $P(TiOH)W_{11}O_{39}^{4-}$ (H**2**, δ −13.44). The ratio of H**1**, **2**, and H**2**, which are present in equilibrium in MeCN solution at 25 °C, depends on the concentration of both H^+ and H_2O. The Ti−O−Ti linkage readily reacts with nucleophilic reagents, such as H_2O and ROH, to yield monomeric Keggin derivatives. μ-Hydroxo dimer H**1** shows higher catalytic activity than **2** for thioether oxidation by hydrogen peroxide in acetonitrile. The reaction proceeds readily at room temperature and affords the corresponding sulfoxide and sulfone in ca. quantitative yield. The addition of H_2O_2 to H**1** or H**2** results in the formation of a peroxo complex, most likely the hydroperoxo complex $P(TiOOH)W_{11}O_{39}^{4-}$ (**I**), which has ^{31}P NMR resonance at −12.43 ppm. The rate of the formation of **I** is higher from H**2** than from H**1**. When H**1** is used as a catalyst precursor, the rates of the thioether oxidation and peroxo complex formation increase with increasing H_2O concentration, which favors the cleavage of H**1** to H**2**. H_2O_2 in MeCN slowly converts **2** to another peroxotitanium complex, $P(TiO_2)W_{11}O_{39}^{5-}$ (**II**), which has ^{31}P NMR resonance at −12.98 ppm. Peroxo complexes **I** and **II** differ in their protonation state and interconvert fast on the ^{31}P NMR time scale. Addition of 1 equiv of H^+ completely converts **II** to **I**, while 1 equiv of OH^- completely converts **I** to **II**. ^{31}P NMR confirms that **I** is stable under turnover conditions (thioether, H_2O_2, MeCN). Contrary to two-phase systems such as dichloroethane/aqueous H_2O_2, no products resulting from the destruction of the Keggin POM were detected in MeCN in the presence of H_2O_2 (a 500-fold molar excess). The reactivity of **I**, generated in situ from **II** by adding 1 equiv of H^+, toward organic sulfides under stoichiometric conditions was confirmed using both ^{31}P NMR and UV−vis spectroscopy. This is a rare demonstration of the direct stoichiometric oxidation of an organic substrate by a titanium peroxo complex.

Introduction

The selective catalytic oxidation of organic compounds is of both academic and industrial interest.[1−5] d-Electron-transition-metal-substituted polyoxometalates (POMs), so-called inorganic metalloporphyrins, have attracted much attention as oxidation catalysts because they are thermodynamically stable against oxidative degradation, unlike metalloporphyrins and other metal complexes with organic ligands; yet their d-metal “active sites” can be extensively modified synthetically.[6−10] These compounds combine the selectivity advantages of homogeneous catalysts with the stability advantages of heterogeneous catalysts. Since they consist of a closely packed array of oxide anions, they can be regarded as discrete fragments of extended metal oxide lattices and, thus, can function as tractable homogeneous probes of heterogeneous catalytic oxidation reaction mechanisms.[6,7,10,11]

Much work has been reported on these complexes as catalysts for the oxidation of organic compounds by various oxygen donors, such as PhIO,[12−16] H_2O_2,[8,17−24] *t*-BuOOH,[15,25] $NaIO_4$,[26]

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NaClO,[8,14] and O_2 in the presence of different reductants.[27−29] More than 50 papers have addressed the oxygenation or oxidation of a wide variety of substrates in the presence of POM derivatives, and this literature has been recently reviewed.[7,8,15,30,31] Since H_2O_2 is one of the most attractive oxidants from both economic and environmental perspectives,[1,2,7,8] Ti(IV)-containing POMs are of particular interest because they can be regarded as homogeneous oxidatively stable models[32,33] for TS-1 and Ti-containing mesoporous materials, including Ti−MCM-41, which are highly efficient heterogeneous catalysts for the oxidation of organic substrates by H_2O_2.[34−40] Despite the number of mechanism and structure−activity studies of TS-1 and related materials, the mechanism of their catalytic action and the nature of the active oxidizing species still remain a matter of discussion. Several Ti(IV)-containing POMs are known.[41−53] These include monosubstituted and disubstituted Keggin-type POMs, including peroxo complexes,[41−49] Walls−Dawson-type POMs,[50] and more complicated but commonly observed anhydride forms of POMs, such as $Si_2Ti_6W_{18}O_{77}{}^{14-}$,[51] $Ge_2Ti_6W_{18}O_{77}{}^{14-}$,[52] $P_4Ti_6W_{32}O_{132}{}^{36-}$,[54] and $P_8W_{60}Ti_{12}O_{242}{}^{36-}$.[54] The latter compounds are members of an emerging class of POMs that involve condensation−dimerization through substituted addenda atoms (both d^0 and d^n, $n > 1$).[51−55]

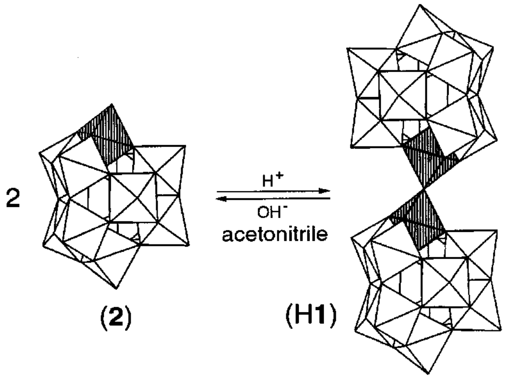

Figure 1. Polyhedral representation of the monomeric Keggin-type POM $PTiW_{11}O_{40}{}^{5-}$ (**2**), the μ-hydroxo dimer $[(PTiW_{11}O_{39})_2OH]^{7-}$ (H**1**), and their pH-dependent interconversions. The TiO_6 octahedra are shaded.

The tetraalkylammonium salts of $PTiW_{11}O_{40}{}^{5-}$ (**2**) were found to catalyze alkene oxidation by H_2O_2 in two-phase systems[17,19] but not in homogeneous MeCN.[18,19] Recently, we have found that some samples of **2** show high catalytic activity in the oxidation of methyl phenyl sulfide by H_2O_2.[24] We have studied a relationship between the POM countercation and catalytic activity in the above reaction and found that protons are needed to form a peroxo POM that is active in MPS oxidation.[56]

Here we report on the preparation and characterization of the new titanium(IV)-containing μ-hydroxo dimeric heteropolytungstate $[(PTiW_{11}O_{39})_2OH]^{7-}$ (H**1**) formed in acidic MeCN from the well-known Keggin POM **2** (Figure 1), the monomer−dimer interconversion chemistry, and the role of peroxo Ti POMs in thioether oxidation by H_2O_2.

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Experimental Section

Materials. Acetonitrile (Fluka, HPLC quality) was dried and stored over activated 3 Å molecular sieves. Methyl phenyl sulfide (MPS), methyl *p*-tolyl sulfide (MTS), and the corresponding sulfoxides were purchased from Fluka and used without additional purification. Tetra-*n*-butylammonium hydroxide (TBAOH) (1.0 M solution in MeOH, Aldrich) and trifluoromethanesulfonic acid (TfOH, Merck) were commercial samples and were titrated prior to use. Hydrogen peroxide (35%) was concentrated in vacuo to 68−86% and was titrated iodometrically prior to use. All the other compounds were the best available reagent grade and were used without further purification.

The Na salt of $PW_{11}O_{39}^{7-}$ was prepared by adding $^{1}/_{11}$ mol of H_3PO_4 to 1 mol of $H_3PW_{12}O_{40}$ dissolved in water and adjusting the pH to 4.0 with NaOH (the ^{31}P NMR spectrum in H_2O shows a single line at −10.7 ppm[57]) (stoichiometry: $11H_3PW_{12}O_{40} + H_3PO_4 + 84NaOH \rightarrow 12Na_7PW_{11}O_{39} + 60H_2O$). $H_5TiPW_{11}O_{40}$ was synthesized by the electrodialysis method described previously (^{31}P NMR in H_2O: −13.68 ppm).[58,59]

Instrumentation and Methods. Gas chromatographic analyses were performed using a gas chromatograph equipped with a flame ionization detector and a 15 m × 0.3 mm SE-30 capillary column (Ar, 100−200 °C, 10 °C/min). GC-MS analyses of organic products were conducted using an LKB-2091 instrument. FAB-MS spectra of the POMs were obtained in a 2-nitrophenyl octyl ether (NPOE) matrix using the negative ion mode on a JEOL SX102/SX102A/E mass spectrometer. ^{31}P, ^{17}O, and ^{183}W NMR spectra were recorded at 161.98, 54.24, and 16.67 MHz, respectively, on an MSL-400 Brüker spectrometer. Chemical shifts, δ, were referenced to 85% H_3PO_4, H_2O, and 1 M aqueous Na_2WO_4, respectively. Chemical shifts upfield from the reference are reported as negative. In ^{31}P NMR measurements, a secondary standard, 0.1 M aqueous $H_4PVMo_{11}O_{40}$, was used. Its δ, -3.70 ± 0.03 ppm relative to concentrated H_3PO_4, was corrected for the solution magnetic susceptibility difference. The error in measuring δ was in the range of ±0.04, ±3, and ±0.1 ppm for ^{31}P, ^{17}O, and ^{183}W NMR spectra, respectively. Electronic absorption spectra were run on a Shimadzu UV-300 spectrophotometer using 1 cm thermostated quartz cells. Infrared spectra were recorded for 0.5−1.0 wt % samples in KBr pellets or for MeCN solutions in KBr cells on a Specord 75 IR or a Nicolet 510M FTIR spectrometer. All the cyclic voltammetric measurements were performed at 25 °C under argon using a BAS CV-50W voltammetric analyzer, a three-electrode cell, a glassy-carbon working electrode, a platinum auxiliary electrode, and a Ag/$AgNO_3$ (0.01 M in MeCN) reference electrode. $TBAPF_6$ (0.1 M) was used as the supporting electrolyte. The sweep rate in all cases was 100 mV/s. C, H, and N analyses were performed at Atlantic Microlab Inc., Norcross, GA. All other elemental analyses were performed at E&R Microanalytical Laboratory, Inc., Corona, NY.

$TBA_7[(PTiW_{11}O_{39})_2OH]$ (TBA salt of H1). Synthesis of the TBA salt of H**1** was carried out as follows: To 9 mmol of $H_5PTiW_{11}O_{40}$ in 45 mL of water was added 31.5 mmol of TBABr dissolved in 30 mL of H_2O. The resulting mixture was vigorously stirred (5−7 min); then the white precipitate was separated by centrifugation, washed with H_2O, and dried at 70 °C. The resulting solid was dissolved in MeCN, filtered to remove insoluble impurities, and reprecipitated by the addition of a 5-fold v/v excess of water. The resulting white solid was separated, washed, dried at 70 °C until the weight remained constant, and then placed under vacuum (1−2 Torr) for 4 h at 100 °C. No additional weight was lost (yield: 36 g; 98% based on initial POM). The TBA salt of H**1** is reasonably soluble (up to about 0.05 M) in dry MeCN. The number of TBA cations, determined by the ignition of the product salts at 600 °C, was ca. 3.5 per P atom. Anal. Calcd for $C_{112}H_{253}N_7O_{79}P_2Ti_2W_{22}$: C, 18.78; H, 3.56; N, 1.37; O, 17.64; P, 0.86; Ti, 1.34; W, 56.45. Found: C, 19.11; H, 3.58; N, 1.37; P, 0.66; Ti, 1.16; W, 56.33. IR (1200−400, cm^{-1}): δ 1076, 971, 891, 815, 655, 594, 515. ^{31}P NMR (0.05 M in dry MeCN at 20 °C): δ −12.76 ($\Delta\nu_{1/2} = 2$ Hz). ^{17}O NMR (0.05 M in MeCN at 45 °C): δ 767, 743, 727 (W=O), 547 (W−O−Ti), 417, 408, 403, 394 (W−O−W), 62 (PO_4); the approximate intensity ratio of terminal to bridging oxygen atoms is 1:2. ^{183}W NMR, (0.05 M in MeCN at 20 °C): $-\delta$ 89.5, 98.5, 99.2, 101.5, 105.4, 108.7, with the approximate intensity ratio of 2:2:1:2:2:2. The negative-anion FAB-MS spectrum (*m/z* 4000−8000) gave *m/z* 5408 ± 5 as the most intense peak. This is strong evidence of a dimeric structure and may be attributed to $[H\mathbf{1} + 6H - 4O]^-$. The molecular ion peak $[TBA_7H\mathbf{1} - H]^-$ at *m/z* 7163 ± 4 observed in the FAB-MS spectrum of the TBA salt of H**1** is in agreement with the value of 7165 calculated for the molecular weight of the TBA salt of H**1**. The fragmentation patterns are dominated by loss of multiple TBA (*m/z* 242), O (*m/z* 16), and WO_3 (*m/z* 232) units. Potentiometric titration of H**1** (0.05 mmol) in MeCN (5 mL) with 1 M methanolic TBAOH, carried out as described in the literature,[11,60] shows a sharp breakpoint at 1 equiv of OH^-, indicating a $[H^+]/[H\mathbf{1}]$ ratio of 1.0. Repeated attempts to grow diffraction-quality single crystals of the TBA salt of H**1** failed. Many solvents, including alcohols and water, cleave the dimeric structure, and monomeric Keggin POM species crystallize in cubes from mixtures of MeCN with these solvents.

$TBA_5PTiW_{11}O_{40}$ (TBA salt of 2). The TBA salt of **2** was prepared by two different procedures. The first procedure is a slight modification of that in the literature.[47] $Ti(SO_4)_2$ (6 mmol, 1 M solution in 2 M H_2SO_4) was added to an aqueous solution (20 mL) of $Na_7PW_{11}O_{39}$ (6 mmol). After the pH of the resulting solution was adjusted to 5.6 by adding small aliquots of $NaHCO_3$, the product was precipitated by adding a 5-fold molar excess of TBABr (30 mmol). The white precipitate was separated, purified, and dried as described for H**1**. The elemental analyses were satisfactory and consistent with the formula $TBA_{4.6}Na_{0.4}PTiW_{11}O_{40}$. The second procedure provides a route to the pure TBA_5 (Na^+-free) salt of **2**. In this procedure, 3 equiv of methanolic TBAOH was added to a MeCN solution of H**1**. A white solid, precipitated by the addition of a 5-fold v/v excess of water to the MeCN solution, was separated, washed, dried at 70 °C, and analyzed (satisfactory elemental analysis as $TBA_5PTiW_{11}O_{40}$). The samples from both procedures had identical IR and ^{31}P NMR spectra. IR (1200−400 cm^{-1}): 1089, 1062, 960, 886, 705 (weak), 660 (weak), 593, 513. ^{31}P NMR (dry MeCN): δ −13.34 ($\Delta\nu_{1/2} = 1$ Hz). ^{17}O NMR (0.1 M in MeCN at 45 °C): δ 963 (Ti=O), 723, 716, 706 (W=O), 536, 523 (W−O−Ti), 420, 407, 389 (W−O−W), 70 (PO_4). ^{183}W NMR (0.1 M in MeCN at 20 °C): $-\delta$ 62.4, 94.7, 103.7, 108.1, 112.7, 119.6, with the approximate intensity ratio 2:2:1:2:2:2. The negative-anion FAB-MS spectrum exhibited no peaks in the *m/z* 4000−8000 range, consistent with the presence of only a monomeric Keggin structure. Potentiometric titration with methanolic TBAOH revealed no acid protons.

$TBA_5PTiW_{11}O_{41}$ (II). The peroxo complex **II** was prepared by the reaction of the TBA salt of **2** with 30% aqueous H_2O_2 in MeCN at 20 °C ($[H_2O_2]/[\mathbf{2}] = 15$) over a period of 3 days. The yellow solid, which had precipitated when H_2O was added to the MeCN solution, was centrifuged, collected, washed twice with water, and dried in a vacuum desiccator overnight. ^{31}P NMR (dry MeCN): δ −12.98 ($\Delta\nu_{1/2} = 18$ Hz). The peroxo complex is quite stable (only 10% decomposition to **2** is observed after it is stored in the dark at room temperature for 6 months). The $[\mathbf{II}]/[\mathbf{2}]$ ratio can be easily quantified by the integration of ^{31}P NMR signals at −12.98 and −13.34 ppm, respectively.

Catalytic Oxidation of Thioethers. Oxidations of MPS and MTS were carried out in a thermostated glass reactor equipped with a magnetic stirrer, a reflux condenser, and an inlet for argon. The initial rates of thioether (0.5 M) oxidation by H_2O_2 (0.1 M, added as 86 or 35 wt % aqueous solution) at 25 °C in MeCN were used to assess the relative catalytic activities of the different Ti-containing POMs (5×10^{-4} M). Aliquots (1 mL) were taken, and the H_2O_2 consumption vs time was determined by iodometric titration in an AcOH−H_2O (70/30, v/v) medium. The organic reactants and products were monitored by gas chromatography as a function of time. Products were identified from their ^{1}H NMR and mass (GC-MS) spectra. The yields of sulfoxide and sulfone products as well as the conversion of initial sulfides were quantified by GC using biphenyl as the internal standard.

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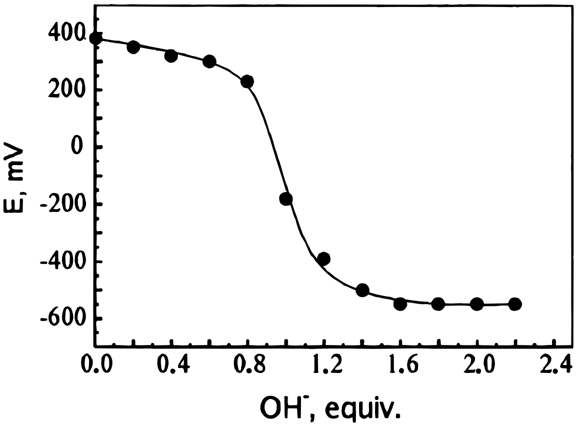

Figure 2. Typical curve for the potentiometric titration of H**1** (0.05 mmol) in MeCN (5 mL) with 1.0 M methanolic TBAOH. The potentials are relative to a standard Ag/AgCl electrode.

Stoichiometric Oxidations by the Peroxo POMs. To further investigate the mechanism of the catalytic H_2O_2-based thioether oxidation, we examined stoichiometric reactions of the peroxotitanium complexes. Peroxo complex **II** does not react with MPS at room temperature over a period of several days (no changes were observed in the ^{31}P NMR and UV−vis spectra of **II**, and no conversion of MPS was detected). To transform **II** (0.02 M, δ −12.98) to the active complex **I** (δ −12.43), we added 1 equiv of acid ($HClO_4$ or TfOH) as a 0.2 M solution in MeCN. Then MPS or MTS (0.1 M) was added to **I**, and the disappearance of the signal at δ −12.43 and the appearance of the peaks of the monomeric POMs at −13.34 and −13.44 ppm were monitored by ^{31}P NMR. The disappearance of **I** (maximum at 25 000 cm^{-1}) was simultaneously monitored using UV−vis spectroscopy. The interaction of **I** with MPS, giving MPSO, was confirmed by GC.

Results and Discussion

Synthesis and Hydrolytic Chemistry of $[(PTiW_{11}O_{39})_2OH]^{7-}$ (H1). We observed previously that tetralkylammonium salts of $PTiW_{11}O_{40}^{5-}$ (**2**) precipitated from aqueous solutions with different acidities, showing significantly different catalytic activities in MPS oxidation by H_2O_2 in MeCN.[24,56] To understand this phenomenon, we have studied the effect of the POM preparation procedure on the composition of the catalyst and its activity in this typical polar organic medium.

The presence of the μ-hydroxo dimer, H**1**, a new complex, was first indicated by a potentiometric titration of the TBA salt of the titanopolytungstophosphate (precipitated from $H_5PTiW_{11}O_{40}$) in MeCN with methanolic TBAOH. Figure 2 shows a typical potentiometric titration curve for **1**, with a sharp breakpoint at 1 equiv of OH$^-$, indicating $[H^+]/[H\mathbf{1}] = 1.0$. Further addition of TBAOH results in a slow response of the glass electrode, consistent with cleavage of the μ-oxo dimer, a result borne out by all the additional experimental data (vide infra). In general, the dimer (H**1**) forms upon acidification of **2** by strong acids (e.g., $HClO_4$ or triflic acid).

Several lines of evidence convincingly establish that the μ-hydroxo dimeric formulation of H**1** is correct, that H**1** and **2** are interconvertable by reversible, pH-dependent reactions (addition of base forms **2**; addition of acid forms H**1**), and that the dimer can be isolated in both basic (Ti−O−Ti = **1**) and protonated (Ti−OH−Ti = H**1**) forms. Each line of experimental evidence will now be succinctly presented. The reader should refer to the Experimental Section for details.

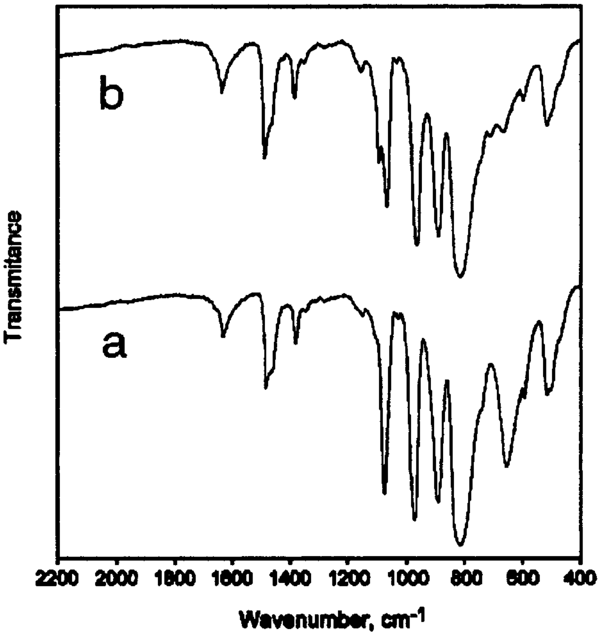

Figure 3. IR spectra of (a) H**1** and (b) **2**. Both samples are at 0.5−1.0 wt % in KBr.

First, the infrared spectra show that the Keggin unit in **2** is retained in H**1** (Figure 3 compares the two spectra in the informative 2200−400 cm^{-1} region). The solid (KBr pellet) and solution (MeCN) spectra of H**1** are practically identical, indicating that the same structure is present in both phases. The spectra for H**1** and **2** differ significantly in two locations. The triply degenerate PO_4 stretching mode is split in **2** (1089 and 1062 cm^{-1}) but not in H**1** (1076 cm^{-1}), indicating a higher symmetry around the central PO_4 tetrahedron in H**1** than in **2**. This phenomenon, first elaborated by Rocchiccioli-Deltcheff and Thouvenot[61] and probed in several subsequent studies,[43,44,47,62−66] gives a useful indication of the distortion induced by the replacement of a $(M(VI){=}O)^{4+}$ (M = W,Mo) unit in the parent Keggin structure with other atoms or groups, such as $(Ti(IV){=}O)^{2+}$. The band at 665 cm^{-1} in H**1** is most likely the asymmetric stretching fundamental of the Ti−O−Ti unit in this dimer for two reasons: first, this band is absent in **2**, and second, this band is in the same region as the M−O−M stretches in β-$(TBA)_{7.5}H_{6.5}Si_2Ti_6W_{18}O_{77}$ (Ti−O−Ti at 700 cm^{-1}),[51] $K_{19}H_9P_4Ti_6W_{32}O_{132}$ (Ti−O−Ti at 683 cm^{-1}),[53] and $TBA_{12}H_4P_4W_{30}Nb_6O_{123}$ (Nb−O−Nb at 683 cm^{-1}),[55a,b] a complex recently confirmed by X-ray crystallography to be a tri-μ-oxo dimer[55e]

Second, the number, δ range, and intensity ratios of the ^{17}O and ^{183}W NMR resonances (see Experimental Section) confirm the retention of the Keggin structure of the $PTiW_{11}O_{40}$ units in H**1**. The ^{17}O signal for the terminal oxygen atom on Ti is not seen in the spectrum of H**1** (Figure 4a) but appears (δ 963) after the addition of 3 equiv of TBAOH in MeOH (Figure 4b). Previously, the signal of the terminal Ti═O in **2** was observed in aqueous solution at 919 ppm.[47] In addition, the relative line widths in the ^{17}O NMR spectra of H**1** and **2** support the dimeric formulation of H**1**.

Third, the negative-ion FAB-MS spectrum recorded in the range of *m/z* 4000−8000 in an inert 2-nitrophenyl octyl ether

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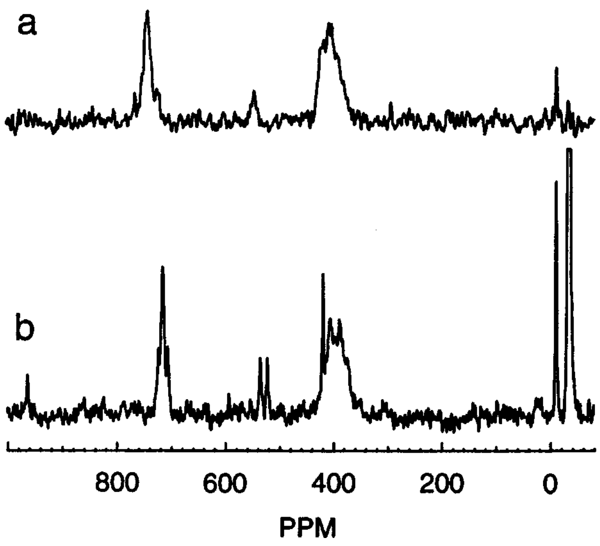

Figure 4. ^{17}O NMR spectra of H**1** (0.05 M in MeCN) (a) before and (b) after addition of 3 equiv of methanolic TBAOH.

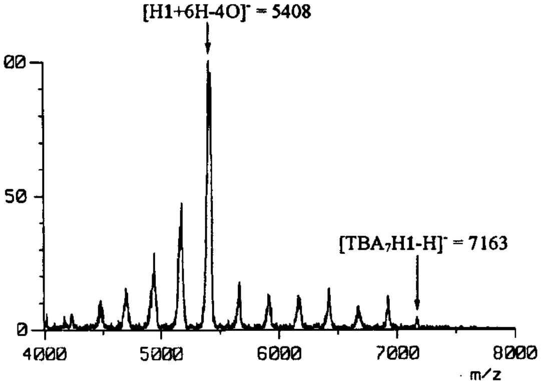

Figure 5. Negative ion FAB-MS spectrum of H**1** dissolved in a NPOE matrix.

(NPOE) matrix (Figure 5) strongly supports the presence of a dimer in H**1**. The most intense peak at *m/z* 5408 ± 5 may be attributed to $[H1 + 6H - 4O]^-$. The observed molecular ion peak $[TBA_7H1 - H]^-$ at *m/z* 7163 ± 5 is in excellent agreement with the molecular weight of 7165 calculated for $TBA_7[(PTiW_{11}O_{39})_2OH]$ (TBA_7H1). This peak is completely absent in the negative-anion FAB-MS spectrum of **2**, consistent with the presence of only a monomeric Keggin unit. The fragmentation patterns for both **1** and **2** are dominated by the loss of multiple TBA (*m/z* 242), O (*m/z* 16), and WO_3 (*m/z* 232) units characteristic of the FAB mass spectra of POMs.[67,68] The spectra for each complex were recorded at least three times and were of excellent reproducibility, establishing that no monomer−dimer conversions were taking place during desorption or other aspects of the analytical process.[69]

Fourth, ^{31}P NMR spectra, under a range of conditions, afford corroboration of the implications of the infrared, ^{17}O NMR, ^{183}W NMR, and FAB-MS data and provide additional information about the titanopolytungstophosphates in MeCN. A peak at −13.34 ppm was previously assigned to the TBA salt of the monomer, **2**.[24] The μ-hydroxo dimer, H**1**, shows a single peak at −12.76 ppm in dry MeCN. This signal is broadened upon dilution ($\Delta\nu_{1/2} = 2$, 4, 11, and 25 Hz at 0.05, 0.005, 0.0025, and 0.00125 M, respectively). Such broadening in dry MeCN may be explained by the slow proton mobility on the polyanion surface in polar nonaqueous solvents.[11,70−72] Dilution of H**1** to beyond ca. 0.001 M results in the reversible generation of **2** (a peak at −13.44 ± 0.04 ppm).

^{31}P NMR facilitated the direct observation of μ-oxo (hydroxo) dimer formation and cleavage. Stepwise addition of small quantities of a strong acid ($HClO_4$ or TfOH) gives rise to **2** in a different protonation state and additional species, each with distinct resonances (Figure 6). Initially, the addition of acid causes the appearance of a new NMR signal at −13.44 ppm at the expense of the signal at −13.34 ppm (Figure 6b). Note that the chemical shifts of both resonances are not effected by the addition of small quantities of H_2O. Upon the further addition of acid, the intensity of the signal at −13.44 ppm decreases, and a new signal appears at about −13.2 ppm, which then moves downfield (Figure 6c). When 1.5 equiv of acid is added, the chemical shift coincides with that of H**1** (Figure 6d,e). These results are entirely consistent with the initial protonation of the Ti═O oxygen (δ −13.34) in forming $P(TiOH)W_{11}O_{40}^{4-}$ (H**2**, δ −13.44), since the protonation of Ti−O−W bridges should be expected to result in a downfield shift of the ^{31}P resonance, analogous to the shift in vanadium-containing POMs.[73] Protonation of the Ti═O bond prior to Ti−O−W formation was proposed previously for the Ti-substituted Well−Dawson POMs[50] as well as for $H_5PTiW_{11}O_{40}$.[58] It is not possible to isolate pure H**2**, since, on the basis of ^{31}P NMR spectra, this species reacts further.

The formation of Ti−O−Ti units upon the acidification of hydrolyzed Ti(IV) compounds is well known and used in sol−gel processing.[74,75] Furthermore, the μ-oxo dimer A-β-$(TBA)_{7.5}H_{6.5}Si_2W_{18}Ti_6O_{77}$ forms in acidic medium (pH 1−4).[51] By analogy, it is reasonable to suggest that the monomeric species H**2** is a key intermediate in the transformation of **2** to the dimer, **1**. Protonation of the Ti−O−Ti bridge occurs upon the further addition of acid, which results in the downfield shift of the ^{31}P resonance to −12.76 ppm at 1.5 equiv of H^+ per **2**. The protonated dimer, H**1**, then predominates. The plausible mechanism for the formation of H**1** upon acidification of **2** may be described by eqs 1−3

$$P(TiO)W_{11}O_{39}^{5-} + H^+ \rightleftharpoons P(TiOH)W_{11}O_{39}^{4-} \quad (1)$$

$$P(TiOH)W_{11}O_{39}^{4-} + P(TiOH)W_{11}O_{39}^{4-} \rightleftharpoons [(PTiW_{11}O_{39})_2O]^{8-} + H_2O \quad (2)$$

$$[(PTiW_{11}O_{39})_2O]^{8-} + H^+ \rightleftharpoons [(PTiW_{11}O_{39})_2OH]^{7-} \quad (3)$$

Further addition of acid causes a downfield shift of the signal of H**1** to −12.18 ppm, evidently due to the protonation of the

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(69) It is interesting to note that $H_5PTiW_{11}O_{40}$, the synthetic precursor to **1**, appeared to be monomeric in aqueous solution according to FAB-MS data. However, it appears to be dimeric in the solid state, since the intense band at 665 cm^{-1} is observed in its KBr pellet IR spectrum. Previously, this band was erroneously assigned to the Ti−O−W bonds.[58]

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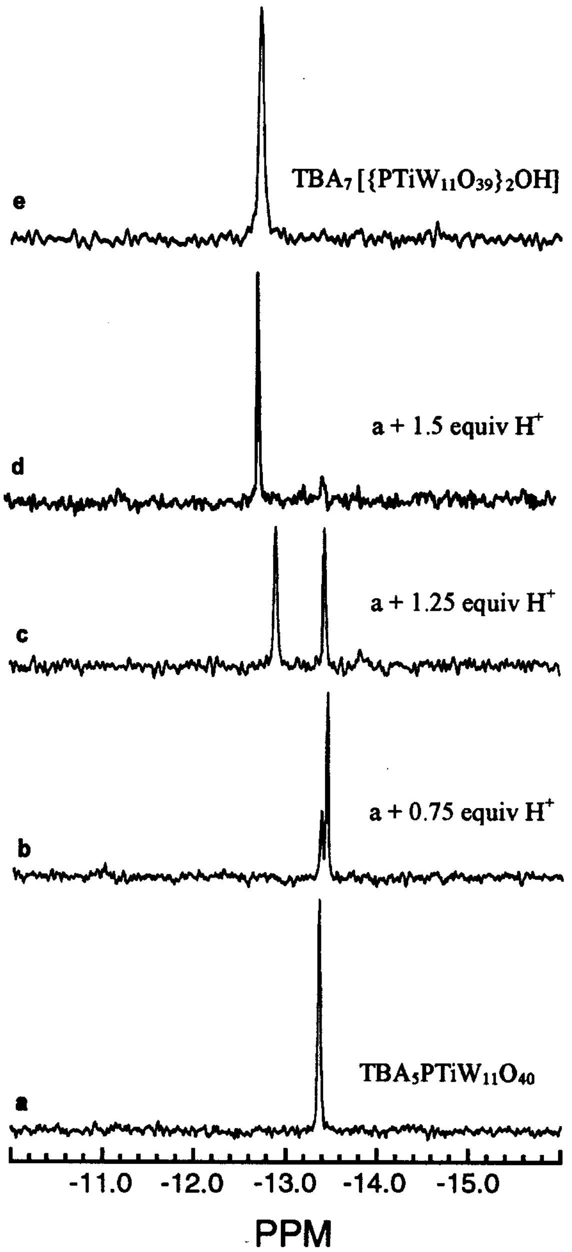

Figure 6. ^{31}P NMR spectra of **2** (5 mM) (a) before acid is added and after the addition of (b) 0.75, (c) 1.25, and (d) 1.5 equiv of $HClO_4$. (e) ^{31}P NMR spectrum of H**1** (5 mM). All spectra were run in MeCN at 20 °C.

Ti−O−W oxygen atoms. The line widths indicate that proton exchange between the different dimeric species still remains fast on the ^{31}P NMR time scale.

Equation 2 predicts that the addition of H_2O to the system would shift the monomer−dimer equilibrium in favor of the monomer, H**2**. ^{31}P NMR experiments confirm that this is precisely what happens. The addition of water to **2** does not effect the chemical shift and width of its resonance, whereas the ^{31}P resonance of H**1** shifts upfield and narrows with increasing H_2O concentration, and the signal at −13.44 ppm for the protonated monomer, H**2**, appears. This signal also appears upon dilution of pure H**1**. Thus, the process opposite to that observed upon the acidification of **2** occurs. Water competes with the μ-oxo dimer for the protons. Since the rate of proton exchange between protonated and unprotonated species increases with H_2O concentration, signal narrowing is observed. H**2** becomes the predominant form at $[H\mathbf{1}]_0 = 0.0025$ M in 9:1 v/v $MeCN:H_2O$. Also consistent with eqs 1−3 is the observation that upon the addition of 3 equiv of methanolic TBAOH to H**1**, **2** is formed immediately in very high selectivity. Note that the tri-μ-oxo dimer $TBA_{12}H_4P_4W_{30}Nb_6O_{123}$ is readily cleaved by 6 equiv of OH^- to yield $TBA_9P_2W_{15}Nb_3O_{62}$.[55b,c] In contrast to **1**, **2** is quite stable against bases in MeCN solution; the addition of 3 equiv of TBAOH causes no change in its ^{31}P NMR spectrum after several days at 25 °C.

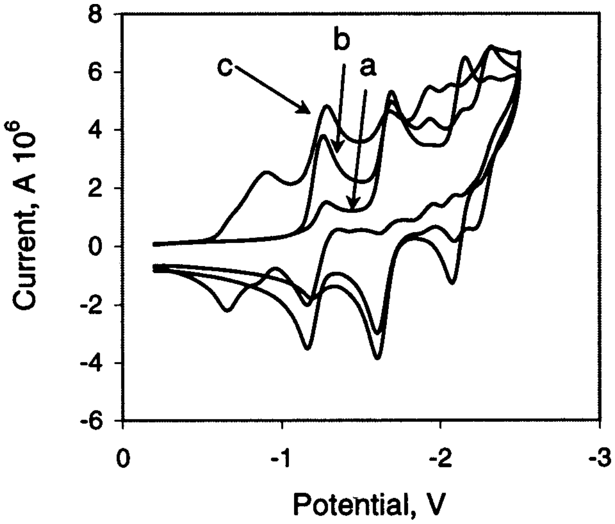

Figure 7. Cyclic voltammetric behavior of **2** (3 mM in MeCN) (a) before acid is added and after addition of (b) 0.5 and (c) 1.5 equiv of TfOH. Potentials are reported relative to $Ag/AgNO_3$ (0.01 M in MeCN). All samples contained 0.1 M $TBAPF_6$ as the supporting electrolyte.

The fifth and final line of experimental observations on the nature of the titanopolytungstophosphate system concerns its electrochemical behavior. The cyclic voltammograms of H**1** and **2**, examined under conditions as close as possible to those in the catalytic thioether oxidations (vide infra), confirm the pH-dependent interconversions of these two POMs. First, upon the addition of 0.5 equiv of triflic acid to **2**, which should result in the formation of H**2**, parallel changes in two reduction peaks were observed. While the peak at $E_{1/2} = -2.12$ V decreases by a factor of 4.9, the peak at $E_{1/2} = -1.23$ V increases in a parallel mode by a factor of 4.8 (Figure 7, traces a and b). The changes in the cyclic voltammograms are consistent with the assignment of the peaks at −2.12 and −1.23 V as the one-electron reduction/oxidation of **2** and H**2**, respectively. The two individual peaks for the reduction of **2** and H**2** (instead of one peak shifting upon addition of acid) are due to slow proton exchange between **2** and H**2** on the CV time scale, which is also consistent with the observation of two individual ^{31}P NMR signals assigned to **2** and H**2** as well (Figure 6b). The further addition of H^+ (up to 1.5 equiv) results in the appearance of two new peaks at $E_{1/2} = -0.90$ and −0.71 V (Figure 7, trace c) presumably corresponding to the one-electron reduction of **1**, H**1**, and possibly other protonated derivatives of **1** that are formed at higher pH. Unlike **2** and H**2**, dimeric derivatives (**1**, H**1**, etc.) were shown from ^{31}P NMR to be in a fast proton exchange in MeCN solution. As a result, more specific assignment of the latter reduction peaks becomes difficult. The addition of 0.5 equiv of OH^- (as methanolic TBAOH) results in the reversible decrease in the peaks at $E_{1/2} = -0.90$ and −0.71 V. The complete disappearance of these peaks is observed after the addition of 1 equiv of OH^-. Under identical conditions, the cyclic voltammetry experiment with the TBA salt of H**1** prepared independently (and not in situ by acidification of **2**) also gave the peaks at $E_{1/2} = -0.90$ and −0.70 V. Again, these disappeared upon the

Table 1. Thioether Oxidation by H_2O_2 in the Presence of H**1** and **2**[a]

catalyst	substrate[b]	initial rate[c] ($\times 10^6$ M s^{-1})
H**1**	MTS	2.9 ± 0.2
H**1**	MTS	5.0 ± 0.3[d]
2	MTS	0.45 ± 0.02
H**1**	–[e]	0.0063
2	–[e]	0.0016
H**1**	MPS	3.0 ± 0.3
H**1**	MPS	4.5 ± 0.3[d]
H**1**	MPSO	1.7 ± 0.1

[a] Reaction conditions: 2.5×10^{-4} M H**1** or 5×10^{-4} M **2**, 0.5 M substrate, 0.1 M (added as 86 wt % solution) H_2O_2, in MeCN, at 25 °C. [b] MTS, MPS, and MPSO are methyl *p*-tolyl sulfide, methyl phenyl sulfide, and methyl phenyl sulfoxides, respectively. [c] Loss of H_2O_2 with time = $(-[H_2O_2]/dt)_o$. [d] With 0.1 M (added as 35 wt % solution) H_2O_2. [e] In the absence of the substrate.

addition of 1 equiv of OH^- (relative to the number of moles of the titanium atoms), which supports the assignments of these peaks as the one-electron reduction of **1** and H**1**.

Data from these five experimental techniques plus potentiometric titration all lead to the same mutually supportive conclusions that **1** in MeCN solution is a previously unknown dimer with a Ti–O–Ti bridge that forms from the dehydration condensation of two Keggin monomers (H**2**) and that acid and base clearly convert the monomers to the μ-oxo dimers and visa versa. Furthermore, **1** is stable in its protonated form (H**1**) with a Ti–OH–Ti bridge, and a protonated form of the monomer, H**2**, is an observable intermediate in these interconversions leading to eqs 1–3 as a summary of this hydrolytic chemistry. Precipitation of the TBA salts of **2** in the pH range of 0.8–2.0 yields various mixtures of H**1**, **2**, and H**2**.

Catalytic Oxidation of Thioethers by H_2O_2 in the Presence of H**1. Active and Inactive Peroxo Complexes.** As we reported previously,[24] thioethers can be efficiently oxidized by H_2O_2 in the presence of titanopolytungstophosphates at room temperature to produce the corresponding oxygenated products (sulfoxides, RR′SO, and sulfones, RR′SO_2) in practically quantitative yield based on both H_2O_2 and substrate consumed. In contrast, the selectivity for sulfoxide, while very high, is not quantitative as in other systems[76–78] because sulfoxide is oxidized further to sulfone at approximately 2% the rate of the thioether oxidation. The selectivity for sulfone starting with 100% sulfoxide is effectively quantitative. In the absence of any titanopolytungstophosphate, neither the thioether MPS nor the sulfoxide MPSO is oxidized by H_2O_2 (even 86%) at ambient temperature. The fact that this system (titanopolytungstophosphates/MeCN/H_2O_2) results in no alkene oxidation even at elevated temperature (50–60 °C) is corroborating evidence that the Keggin units of the titanopolytungstophosphates are stable under these conditions. This follows the patterns of $PW_{11}O_{39}{}^{7-}$ and other polyoxotungstates quickly converted by H_2O_2 to polyperoxotungstates, which result in facile alkene epoxidation by H_2O_2 because these peroxo complexes that form in situ are all very good epoxidation catalysts.[17,18,79,86–88]

Table 1 summarizes the reactivity data for oxidation of two representative thioethers, MPS and MTS, by H_2O_2 in MeCN at room temperature in the presence of H**1** and **2**. It was determined that neither light nor the presence of O_2 affects the rates of these catalytic oxidation reactions. The addition of 20 mol % (relative to H**1**) of the radical scavenger hydroquinone has no demonstrable affect on the rate or other characteristics of these reactions. These facts collectively indicate that the radical chain component of these reactions is small, if it exists at all, and/or that the propagation steps in the chain are significantly faster than the quenching reactions (hydroquinone + freely diffusing radical intermediates). Table 1 indicates that H**1** and **2** differ significantly in both their catalytic oxidation and their peroxide disproportionation activity, with H**1** being more reactive than **2** for both reactions. The rate of H_2O_2 decomposition in the absence of thioether is about 2–3 orders of magnitude lower than the rate of H_2O_2 consumption in the presence of thioether. At 20 °C, $[\mathrm{H}\mathbf{1}] = 5 \times 10^{-3}$ M and $[H_2O_2] = 0.1$ M; 44% of H_2O_2 is decomposed in 8 days. The catalytic activity of the TBA titanopolytungstophosphates, H**1** and **2**, for thioether oxidation by H_2O_2 also correlates with the rate of each transformation into the active peroxo complexes (vide infra).

A systematic study of H**1** or **2** in the absence of the substrate (i.e., the full catalytic system without the substrate) reveals key features of these oxidations and the presence of two peroxotitanium complexes. Several lines of evidence establish the nature of these two peroxotitanium complexes and, to some extent, their role in substrate oxidation. First, treatment of an 0.005 M MeCN solution of **2** with a 30-fold molar excess of H_2O_2 results in a slow (about 24 h) formation of an orange peroxo complex (**II**) (^{31}P NMR singlet at −12.98 ppm), whereas treatment of H**1** under the same conditions results in the more rapid formation (about few hours) of a second peroxo complex (**I**; ^{31}P NMR singlet at −12.43 ppm). Second, both **I** and **II** have very similar UV–vis spectra, with maxima at $\lambda = 400$ and 395 nm, respectively, which in turn are very similar to the spectrum for the peroxo complex $P(TiO_2)W_{11}O_{39}{}^{5-}$ known in aqueous solution (392 nm, $\epsilon = 1600$ M^{-1} cm^{-1}),[46,47] consistent with peroxo groups in all three compounds. Third, both FAB-MS and infrared spectra show the disappearance of the dimeric structure on treatment of H**1** with H_2O_2. Dinuclear titanium μ-oxo/μ-peroxo complexes are precedented,[32,80,81] and the cleavage of μ-oxo linkages in dimeric POMs by H_2O_2 is also well precedented.[55a]

Fourth, as in the case of the reactant POMs H**1** and **2**, the peroxo complexes **I** and **II** can be converted into each other by the addition of 1 equiv of H^+ or OH^- (Figure 8). The stepwise addition of H^+ to **II** results in the downfield shift and narrowing of the ^{31}P resonance (δ ($\Delta\nu_{1/2}$, Hz) −12.88 (12), 12.77 (16), 12.66 (10), and 12.43 (4) at 0.2, 0.4, 0.6, and 1.0 equiv of H^+, respectively). This confirms that **I** and **II** differ in their proton content and are in the fast exchange on the NMR time scale. The higher acidity and consequently higher electrophilicity of **I** versus **II** is consistent with their relative reactivities toward the nucleophilic thioether substrates.

Fifth, **I** is more reactive and less stable than **II**. Thioether oxidation proceeds rapidly when ^{31}P NMR reveals the presence of **I** but very slowly when ^{31}P NMR reveals the presence of only **II**. This is in accordance with our preliminary data.[24] It is well known that acid additives (Brønsted and Lewis) enhance the catalytic activity of peroxotitanium porphyrin complexes[82] and titanium silicalites.[34–37] Clearly, protons are needed to generate the active forms of the peroxo species in these systems. The ambiguity here is that acids of all kinds also directly activate

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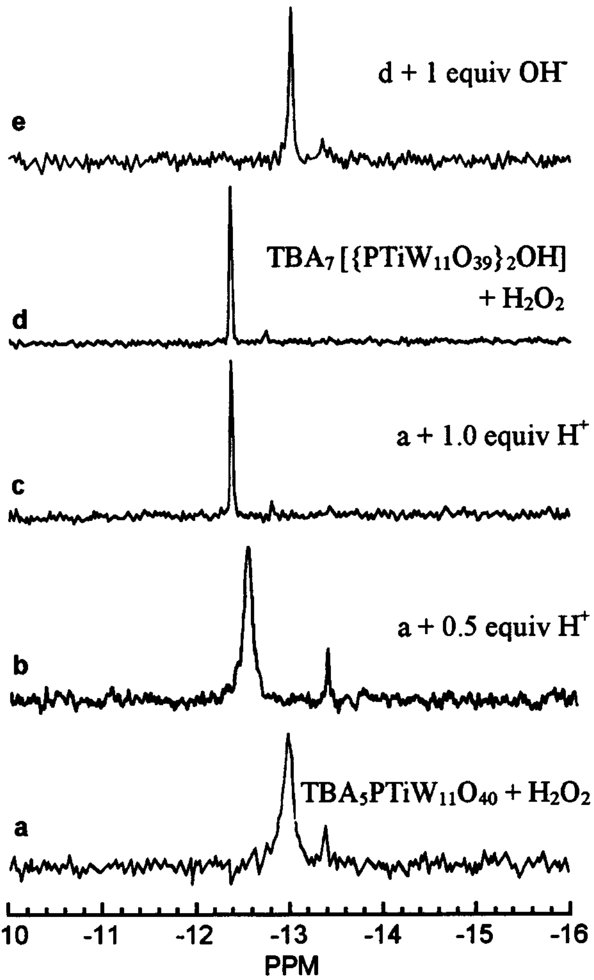

Figure 8. ^{31}P NMR spectra of **2** (0.005 M) 36 h after the addition of (a) 20 μL of 77% H_2O_2 with no added H^+, (b) 0.5 equiv of H^+, and (c) 1.0 equiv of H^+, showing the formation of some η^2-peroxotitanium complex (**II**). ^{31}P NMR spectra of H**1** (0.005 M) 4.5 h after addition of (d) 20 μL of 77% H_2O_2 and (e) 1 equiv of OH^- (TBAOH in MeOH).

H_2O_2 for oxidations of nucleophilic substrates, including thioethers.[83,84] The argument in favor of thioether oxidation via a peroxotitanium complex is that the rate of the thioether oxidation increases with the increase of water concentration (Table 1), whereas the opposite effect would be expected if the reaction were catalyzed by H^+. In the latter case, water and thioether would compete for protons, and the concentration of the $RR'SH^+$ species (mechanism via nucleophilic oxygen transfer) would decrease.

Sixth, the rate of the peroxo complex formation correlates with the catalytic reactivity of different Ti POMs; both the rate of peroxo formation and substrate oxidation are significantly higher for H**1** than for **2**. This is not surprising, given that the Ti═O group in Ti(IV) porphyrins has long been known to be inert toward numerous reagents.[85] Importantly, the rate of the peroxotitanium complex formation is higher for the protonated monomer (H**2**) than for H**1**. Specifically, when H_2O_2 is added to solutions containing mixtures of either H**2** and **1** or H**2** and **2**, H**2** (δ −13.44) readily transforms into the active peroxo complex, **I** (δ −12.43), whereas the peaks for **2** (δ −13.34) or **1** plus H**1** (δ −12.8 to −13.2) remain unchanged (Figure 9). These relative rates of peroxotitanium formation (H**2** > **1** > **2**) suggest that all peroxotitanium species form via H**2**. This is also consistent with eq 2 and the observation that the rate of catalytic thioether oxidation increases with increasing water concentration.

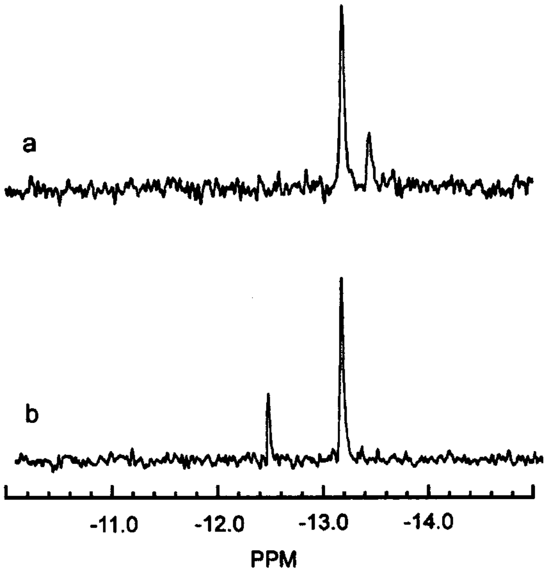

Figure 9. ^{31}P NMR spectra of **2** containing 1 equiv of H^+ (a mixture of **2** and H**2**) (a) before and (b) 10 min after addition of H_2O_2. The −13.34 and −13.44 ppm peaks in (a) are assigned to **2** and H**2**, respectively, and the −12.43 and −13.34 ppm peaks in (b) are assigned to the peroxo complex **I** and **2**, respectively.

Stability of the Titanopolytungstophosphate Catalysts. As indicated above, many Keggin POMs rapidly degrade in the presence of aqueous H_2O_2. If a second chlorocarbon phase containing a phase transfer catalyst (PTC), usually a quaternary ammonium cation, is also present, then the polyperoxometalates formed in situ are extracted into the organic layer where they function as effective catalysts for epoxidation with H_2O_2.[79,86,87] In contrast, the Keggin titanopolytungstophosphates in MeCN with H_2O_2, the focus of this study, do not degrade under same conditions of time and temperature. Interestingly, while this titanopolytungstophosphate/MeCN/H_2O_2 system does not epoxidize alkenes, these same POMs in H_2O/chlorocarbon two-phase systems do.[17,19]

To understand this difference, we examined H**1** by ^{31}P NMR in both homogeneous MeCN and biphasic CH_2ClCH_2Cl/H_2O in the presence of a 100-fold molar excess of H_2O_2 over H**1**. One can see from Figure 10a that the only signal observable in homogeneous MeCN is that of the active peroxo complex **I** (δ −12.43); no products derived from degradation of the Keggin POM unit are detectable in the range of +7 to −22 ppm even after storing the solution at 100 °C for 24 h or increasing the peroxide molar excess to 500 ($[H_2O_2]/[H\mathbf{1}] = 500$). Significantly, the Keggin unit is largely destroyed in aqueous solution under identical conditions (Figure 10b). Under the conditions for alkene epoxidation in the two-phase system (60 °C, $[H_2O_2]/[\text{catalyst}] = 500$, PTC = tetrahexylammonium chloride),[17,19] the Keggin POM is degraded. H_2O clearly results in the breakdown of titanium-containing POMs, like many other

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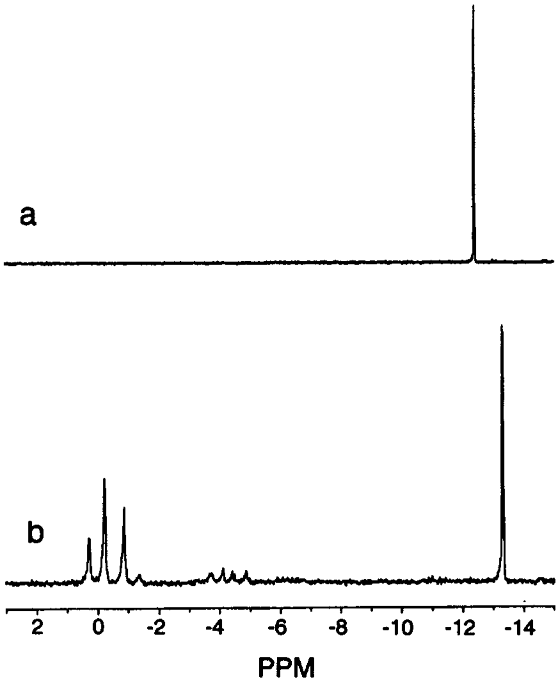

Figure 10. ^{31}P NMR spectrum of (a) H**1** (0.01 M) in MeCN and (b) $H_5PW_{11}TiO_{40}$ in H_2O (pH 1.8), both 24 h after the addition of a 100-fold molar excess of H_2O_2.

POMs, in two-phase catalytic H_2O_2-based oxidation systems and, thus, facilitates generation of the lower nuclearity species, which are the actual catalysts. Another group has reported that the alkene oxidation by H_2O_2 occurs in MeCN in the presence of **2**.[21,22] In light of these results and the ^{31}P NMR data reported earlier,[22] however, it is quite likely that the observed activity might be due to impurities in the catalyst and/or species derived from the degradation of **2**.

With the above data in hand, we now turn to the final fate of the catalyst. The active peroxotitanium species, **I**, persists from its initial high-yield generation from H**1** until all the H_2O_2 has been consumed. At this point, its characteristic yellow color and ^{31}P NMR signal (δ −12.43) disappear, and H**2** or a mixture of H**2**, **1**, and H**1** is formed. The ^{31}P NMR for H**1** shifts slightly in the latter stages of reaction because deprotonation of H**1** by the increasing sulfoxide product and the H_2O byproduct (derived from the consumed H_2O_2) is building up. Both sulfoxide and H_2O are known to deprotonate the highly acidic unsubstituted heteropoly acid POMs (i.e., those with only Mo(VI) or W(VI) addenda atoms). The situation is less clear (pK_a values not yet adequately established) for heteropoly acids substituted with one or more lower valent metal ions, including Ti(IV) or Nb(V). In one case, the actual sulfoxonium (protonated sulfoxide) salts of the POMs were isolated and shown to be stable under very similar reaction conditions (peroxide oxidations of thioethers catalyzed by vanadopolymolybdophosphates in MeCN).[76] In a control experiment, we added some product sulfoxide (MPSO) to the substrate-free system (H**1**/H_2O_2/MeCN), and the same shifts as those in the spent catalytic reactions were seen (upfield shifts of the ^{31}P NMR resonance of H**1**). In confirmation of this deprotonation effect, the same shifts in the ^{31}P NMR peaks were also seen when small quantities of H_2O or MeOH were added to the substrate-free system. The ^{31}P NMR signals remain relatively sharp throughout in all these reactions because the proton transfer (POM protonation/deprotonation) reactions are considerably faster than the NMR time scale (i.e., the fast exchange limit is operational).

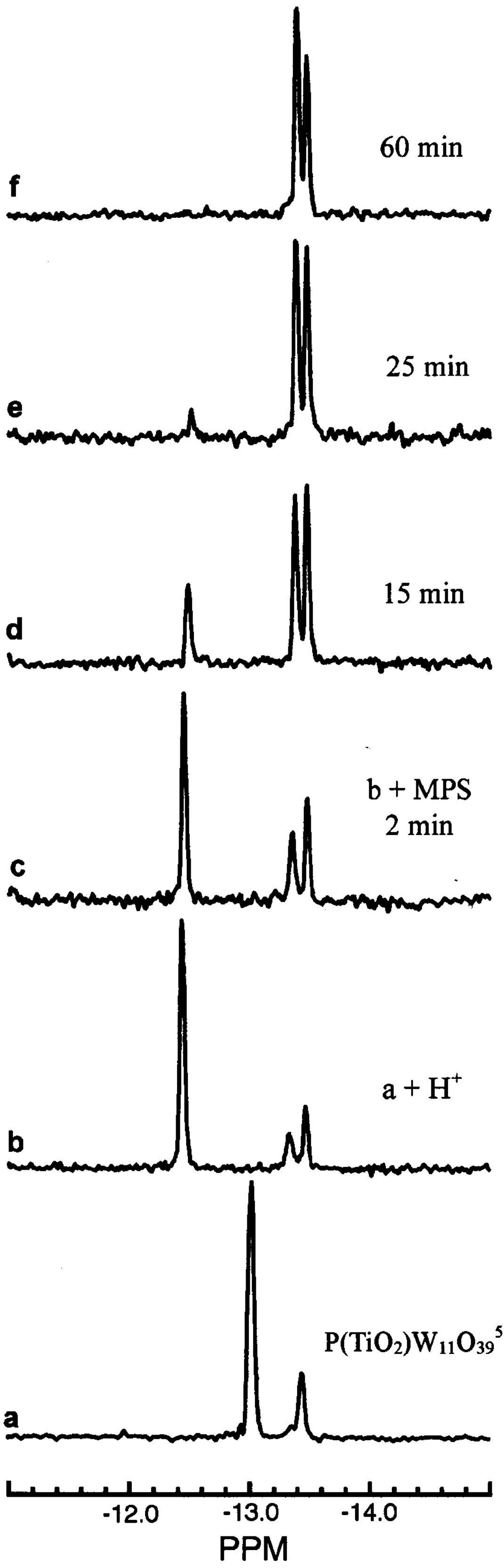

Figure 11. ^{31}P NMR spectra of **II** (a) before the addition of H^+, (b) after the addition of 1 equiv of H^+, and after the addition of MPS recorded after (c) 2, (d) 15, (e) 25, and (f) 60 min. All spectra were run in MeCN at 20 °C. [**II**] = 0.02 M, and [MPS] = 0.1 M.

Stoichiometric Oxidation of Thioether Substrate by the Reactive Peroxotitanium Complex. The best evidence for a particular step (elementary process) in a mechanism derives from finding experimental conditions where that step only is experimentally operable. Under such conditions, the step can be directly observed and studied. In this catalytic thioether oxidation chemistry (thioether/H**1**/H_2O_2/MeCN), we sought final confirmation that the peroxotitanium complex, **I**, was the active oxidant under turnover conditions. Thus, we sought to generate it cleanly and examine its direct interaction (oxidation) with one molecule of thioether substrate, in this case, MPS. While **I** is not sufficiently stable for satisfactory isolation and independent study, it can be generated from **II** in very high yield by protonation. Again, **II** is generated directly by reaction with H_2O_2 and **2**, and it is unreactive to thioether at ambient temperature in MeCN solution. The TBA salt of **II** has actually been known since 1985,[46] and its diisopropylammonium salt was characterized by X-ray crystallography, which confirms it contains a "side-on" or η^2-peroxometal group.[89] η^2-Peroxometal groups, like that in **II**, are typically minimally reactive and electrophilic;[21,82,90,91] they exhibit weak O−O stretching bands in the IR (no dipole moment change is possible for such symmetrically bound ligands), and they are activated by protons and Lewis acids, as is **II**, which converts to **I**.

Figure 11 shows through ^{31}P NMR the generation of **I** from the addition of 1 equiv of H^+ to **II** and the disappearance of **I** upon the addition of the thioether MPS. The direct reaction between **I** and MPS was also monitored by UV−vis spectroscopy. Note that **I** slowly decomposes in MeCN; however, the rate of its decomposition estimated from UV−vis and NMR data is about 20 times slower than the rate of its consumption in the presence of MPS. The splitting of the ^{31}P NMR signal of the parent Ti−POM into two lines is most likely due to its protonation upon the addition of the acid (see Figure 6). The disappearance of **I** directly parallels the formation of sulfoxide from the thioether, as detected by GC. Since **I** is the only active oxo transfer species in the reaction, it is reasonable to infer that it is reacting directly with the thioether substrate to generate the sulfoxide product. To the best of our knowledge, this is the first demonstration of a direct stoichiometric reaction between a peroxotitanium complex and an organic substrate.

At this stage of research, the exact structure of the active peroxo complex, **I**, and the site of the activating proton remain uncertain. The proton may be on a peroxo oxygen atom (η^1-hydroperoxo complexes **A** and **B**, respectively, or η^2-hydroperoxo complex **C**), or it may be on the Ti−O−W bridge (η^2-peroxo complex **D**) (Figure 12). The fact that the chemical shift of **I** is not affected by added H_2O argues against structure **D** because bases should result in the upfield shift of its ^{31}P resonance, as in the case of H**1**. Hydroperoxotitanium species types **A**, **B**, and **C** have been proposed as the active intermediates in the commercially useful H_2O_2-based oxidations catalyzed by TS-1 and related systems;[34−37,92−95] however, compelling spectroscopic evidence in favor of one of these structures has yet to be obtained. In the present study the active hydroperoxotitanium complex was detected spectroscopically for the first time. Further spectroscopic and kinetic studies are in progress to clarify the structure of this active species and the precise mechanism of its interaction with the thioether substrates.

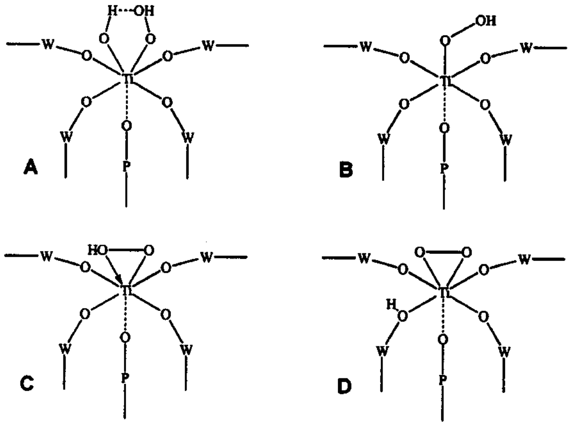

Figure 12. Possible structures for the active peroxotitanium complex.

Conclusions

Three main conclusions can be drawn from the present work. First, four forms of the monosubstituted Ti(IV)-containing Keggin POMs have been generated and investigated in MeCN solution, namely, the μ-hydroxo dimer $[(PTiW_{11}O_{39})_2OH]^{7-}$ (H**1**) and its conjugate base $[(PTiW_{11}O_{39})_2O]^{8-}$ (**1**) and two monomers $PTiW_{11}O_{40}^{5-}$ (**2**) and its conjugate acid $P(TiOH)W_{11}O_{39}^{4-}$ (H**2**). The relative concentrations of these four species depend on the concentrations of both H^+ and H_2O. Acetonitrile-soluble TBA salts of H**1** and **2** can be easily isolated in pure form. Second, the catalytic activity of these titanium-containing POMs in thioether oxidation by H_2O_2 correlates with their activity in H_2O_2 decomposition and with the rates at which they form the peroxotitanium complexes. Rates for peroxotitanium formation and thioether oxidation are H**2** > H**1** > **2**. Third, protons are needed to form the active peroxo species, which is most probably a hydroperoxotitanium complex, $P(TiOOH)W_{11}O_{39}^{5-}$. This complex reacts directly with thioether substrates under both stoichiometric and catalytic conditions.

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