

# Polyoxometalate Catalysis of the Aerobic Oxidation of Hydrogen Sulfide to Sulfur

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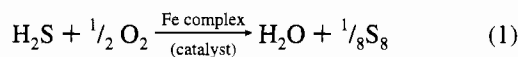
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Polyoxometalate-based catalytic systems for the effective and selective aerobic oxidation of H<sub>2</sub>S to S(0) (H<sub>2</sub>S + 1/2 O<sub>2</sub> → H<sub>2</sub>O + 1/8 S<sub>8</sub>, eq 1) are reported. K<sub>5</sub>[ZnPW<sub>11</sub>O<sub>39</sub>], α-K<sub>8</sub>[SiW<sub>11</sub>O<sub>39</sub>], α-K<sub>6</sub>[ZnSiW<sub>11</sub>O<sub>39</sub>], and K<sub>14</sub>[NaP<sub>5</sub>W<sub>30</sub>O<sub>110</sub>] (**1**) are effective catalysts for eq 1 exhibiting 40, 29, 21, and 7.4 turnovers, respectively at 60 °C with 1.1 atm of O<sub>2</sub> for 24 h in a sealed, constant pressure system. Under these same conditions, K<sub>7</sub>[PW<sub>11</sub>O<sub>39</sub>] produces 50 turnovers and partially decomposes while sulfide quantitatively demetallates many substituted Keggin complexes: H<sub>2</sub>S + [(TM)X<sup>n+</sup>W<sub>11</sub>O<sub>39</sub>]<sup>(10-n)-</sup> → (TM)S + [X<sup>n+</sup>W<sub>11</sub>O<sub>39</sub>]<sup>(12-n)-</sup> + 2H<sup>+</sup>, TM = Fe<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, or Cu<sup>II</sup> and X<sup>n+</sup> = P<sup>V</sup> or Si<sup>IV</sup>. An evaluation of the redox potentials of water compatible and redox active polyoxometalates and all sulfur species pertinent to eq 1 at pH 0 and pH 8.5, the practically optimal pH for eq 1, indicates that many polyoxometalates should selectively facilitate eq 1, including **1**. The rates for the reduction of **1** by HS<sup>-</sup>, the likely sulfur redox intermediates, polysulfide (S<sub>n</sub><sup>2-</sup>), S<sub>2</sub>O<sub>6</sub><sup>2-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, and the product, S<sub>8</sub>, (pH 8.5, borax buffer, [**1**] = 2.0 mM, [substrate] = 2.6 mM, 298K) are V<sub>0</sub> = 0.96, 22.2, 159, 0, and 0, μM s<sup>-1</sup> respectively. The experimental rate law for oxidation of HS<sup>-</sup> by **1** is first order in HS<sup>-</sup> and second order in **1**, with a complex pH dependence. A comparison of eq 1 catalyzed by **1** versus the chelated Fe compounds used industrially indicates that, for **1**, the reaction is slower initially, lasts far longer since the catalyst is not degraded, and produces higher purity S<sub>8</sub> (>99.5% for **1** versus 89.8% for Fe<sup>III</sup>(EDTA)<sup>-</sup>). The success limiting factor for eq 1 catalyzed by **1** derives from appreciable undesirable uncatalyzed background oxidations, particularly the production of sulfate (HS<sup>-</sup> + 2O<sub>2</sub> → HSO<sub>4</sub><sup>-</sup>).

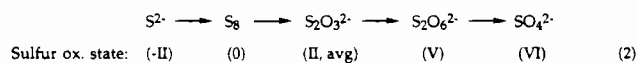
## Introduction

H<sub>2</sub>S is deleterious not only to a variety of life forms but also to industrially significant processes. It is a major source of sulfur poisoning in heterogeneous catalysts, particularly those containing copper, including the Cu/ZnO methanol synthesis and water gas shift reaction catalysts.<sup>1-3</sup> In addition, H<sub>2</sub>S or its conjugate base, the hydrosulfide ion, HS<sup>-</sup>, are toxic waste products in several large scale chemical reactions.<sup>4</sup> Consequently, the selective aerobic oxidation of H<sub>2</sub>S to S(0), eq 1, is



a process of considerable fundamental and practical significance. At present, chelated iron complexes including Fe<sup>III</sup>(EDTA)<sup>-</sup> and Fe<sup>III</sup>(NTA) are used as catalysts for the oxidative removal of H<sub>2</sub>S.<sup>4-8</sup> The usual net process is given in eq 1. The existing processes suffer from short catalyst lifetimes under operating conditions, irreversible oxidative degradation of the chelating

organic ligands, and other problems. The fundamental interest lies in the redox complexity and demands inherent in catalyzed aerobic oxidation of H<sub>2</sub>S to S<sub>8</sub>. First, the two-electron oxidation of the substrate, sulfide, to molecular sulfur, must dominate over the four-, seven-, and eight-electron oxidations to thiosulfate (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>), dithionate (S<sub>2</sub>O<sub>6</sub><sup>2-</sup>), and sulfate (SO<sub>4</sub><sup>2-</sup>), eq 2, which



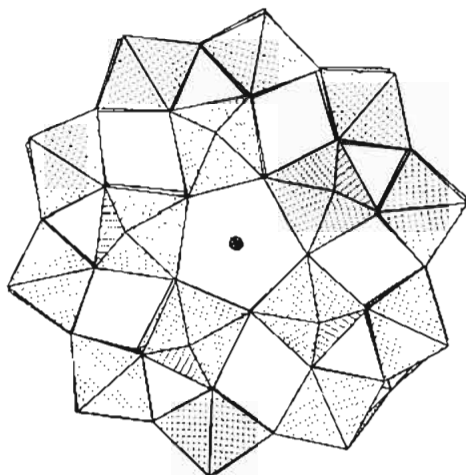
are all thermodynamically allowed and experimentally observed in the commercial catalyzed process, eq 1. Second, the efficient four-electron reduction of O<sub>2</sub> to H<sub>2</sub>O is required. A substantive generation of peroxide or hydroxyl radical intermediates will lead to more rapid irreversible degradation of the organic ligands of the catalyst and other deleterious consequences. Third, the conditions of this reaction demand that the catalyst exhibits a very high degree of resistance not only to oxidative degradation but also to hydrolytic and solvolytic degradation.

In this paper we report that particular d<sup>0</sup> polyoxometalates (early transition metal oxygen anion clusters),<sup>9-12</sup> can catalyze the sustained and selective aerobic two-electron oxidation of sulfide to sulfur. One promising catalyst upon consideration of several features is the Pope–Jeannin–Preyssler (or PJP) ion, [NaP<sub>5</sub>W<sub>30</sub>O<sub>110</sub>]<sup>14-</sup>, **1** (Figure 1).<sup>13,14</sup> The scope of this

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**Figure 1.** Polyhedral illustration of the PJP polyoxoanion,  $[\text{Na}_5\text{W}_{30}\text{O}_{110}]^{14-}$ , **1**, derived from the literature coordinates,<sup>13</sup> looking down the 5-fold axis. Each octahedron represents one  $\text{WO}_6$  unit.

chemistry, and an evaluation of the mechanism and features of sulfide oxidation catalyzed by **1** are presented.

### Experimental Section

**General Methods and Materials.** All chemicals were commercially available reagent grade, argon was prepurified grade, oxygen was USP grade, and all were used as received. NaHS was synthesized from  $\text{H}_2\text{S}$  and stored in a sealed vessel under dry Ar to prevent hydration and oxidation.<sup>15</sup>  $\text{Pb}(\text{NO}_3)_2$  (ACS reagent grade from Aldrich) used as an analytical reagent for quantifying sulfide concentration, had to be purified (recrystallization followed by two filtrations through 0.45  $\mu\text{m}$  nylon membranes) before satisfactory results were obtained. The catalysts  $\text{K}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]\cdot n\text{H}_2\text{O}$  (**1**),<sup>13</sup>  $\text{K}_7[\text{PW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ ,<sup>16</sup>  $\alpha\text{-K}_6[\text{SiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ ,<sup>17</sup>  $\text{K}_3[\text{MnPW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ ,<sup>18</sup>  $\text{K}_5[\text{FePW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ ,<sup>18</sup>  $\text{K}_3[\text{CoPW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ ,<sup>18</sup>  $\text{K}_5[\text{NiPW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ ,<sup>18</sup>  $\text{K}_5[\text{CuPW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ ,<sup>18</sup>  $\text{K}_3[\text{ZnPW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ ,<sup>18</sup>  $\alpha\text{-K}_6[\text{MnSiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ ,<sup>18</sup>  $\alpha\text{-K}_6[\text{FeSiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ ,<sup>18</sup>  $\alpha\text{-K}_6[\text{CoSiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ ,<sup>18</sup>  $\alpha\text{-K}_6[\text{NiSiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ ,<sup>18</sup>  $\alpha\text{-K}_6[\text{CuSiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ ,<sup>18</sup> and  $\alpha\text{-K}_6[\text{ZnSiW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$ <sup>18</sup> were synthesized and purified according to literature procedures. The equivalents of water present as waters of hydration were considered in all analyses. Deionized water from a Barnstead single stage deionizer (mixed bed type) was used in all syntheses. Water for the reactions was Burdick and Jackson distilled-in-glass grade and used without further purification. Infrared spectra were obtained as KBr pellets (2–5 wt % of the sample) on a Nicolet 510M FTIR spectrophotometer. Electronic spectra were obtained using a Hewlett-Packard 8451 diode array spectrophotometer. Elemental analyses were conducted by E + R Microanalytical Laboratories. <sup>31</sup>P NMR spectra were recorded with an IBM WP-200SY FT spectrometer at 81.015 MHz. The <sup>31</sup>P NMR chemical shifts were referenced to 85%  $\text{H}_3\text{PO}_4$  in water; referencing was achieved by the substitution method. Chemical shifts downfield from the reference are reported as positive (+ $\delta$ ). In reporting NMR data, multiplicity, numbers of the nuclei, and coupling constants (in Hz), as applicable, are given in parentheses. The probe temperature was 295 K in all NMR experiments. The spectral parameters for <sup>31</sup>P NMR were acquisition time = 0.512 s, relaxation delay = 1.00 s, pulse width = 14.8  $\mu\text{s}$ , spectral window = 4000 Hz, and digital resolution = 1.95 Hz/point.

**Oxidative Titration of 1.** The oxidative titration of the reduced form of **1** was performed with a standardized solution of  $\text{Ce}^{4+}$ .<sup>19</sup> To 52.8 mg (6.21  $\mu\text{mol}$ ) of the catalyst, **1**, and 32.7 mg (0.584 mmol; 94.0 equiv) of dry NaHS in a Schlenk flask under argon was added 17.0 mL of degassed water (final pH = 10). Although the characteristic

heteropoly blue color was evident immediately, the vessel was placed in a sand bath at 60 °C for 24 h. The excess sulfide was then removed as  $\text{H}_2\text{S}$  by treatment of the contents of the reaction vessel with 5 equiv of acid (3.00 mL of 2.0 M HCl) followed by evacuation on a vacuum line. All of the  $\text{H}_2\text{S}$  was removed from the residual solution of the reduced complex as determined by an independent titration of aliquots with  $\text{Pb}^{2+}$ . Some of the water was also removed, but the change in volume was quantified and the appropriate correction made in the titrations. The actual titrations were carried out in triplicate on 5.0-mL aliquots of the reduced **1** solution using the  $\text{Ce}^{4+}$  standard to colorless and clear end points.<sup>20</sup>

**Comparison of Polyoxometalate Activity at Low pH (Table 1).** Reactions were carried out in a 25-mL round-bottomed flask with a glass stopcock side arm. The reaction temperature was kept constant by placing the vessel in a thermostated sand bath at 60 °C. The importance of temperature on the solubility of the gases  $\text{H}_2\text{S}$  and  $\text{O}_2$  is apparent from the plots in Figure S1 (supplementary material) relating to Henry's law. In a typical reaction, the catalyst was weighed and added to a clean, dry vessel which was then placed under vacuum to remove any residual moisture from the system. The complete experimental assembly was then weighed and flushed with oxygen. Reaction was initiated by addition of 10 mL of water freshly saturated with  $\text{H}_2\text{S}$ , (by bubbling the gas through a flask of water), and the initial pH is 4–5. The vessel was quickly sealed with a septum stopper and placed into the sand bath. The oxygen pressure (1.1 atm) was maintained at a constant value through the side arm. After a reaction time of 24 h, a needle connected to an  $\text{H}_2\text{S}$  trap was inserted through the septum stopper, and the unreacted sulfide was removed as  $\text{H}_2\text{S}$  to terminate the reaction. A small amount of acid was added to ensure removal of all  $\text{H}_2\text{S}$ . The  $\text{H}_2\text{S}$  trap was a bubbler containing saturated aqueous  $\text{Pb}(\text{NO}_3)_2$ .<sup>21</sup> The  $\text{H}_2\text{S}$ -derived solid oxidation products were analyzed by filtration using a 0.2  $\mu\text{m}$  nylon membrane and subsequent gravimetric analysis. The amount of unreacted sulfide substrate was determined by weighing the amount of PbS collected in the trap. Other specifics are given in the Table 1 footnotes.

**Kinetic Measurements for Reduction of 1 by Sulfur Species (Table 3 and Figure 4).** These rate determinations involved reduction of **1**, and in all cases initial rate methods were used. All measurements were conducted under an atmosphere of Ar at pH 8.5 (borax buffer) using a quartz cuvette with an affixed glass stopcock at 25 °C. The reaction was initiated by the addition of 1.0 mL of a 9.1 mM (2.6 mM final concentration) aqueous solution of the sulfur-containing substrate to the cuvette containing 2.5 mL of a 2.8 mM aqueous solution of **1** (2.0 mM final concentration). Both **1** and substrate were introduced into the cuvette as previously degassed solutions with a Hamilton gastight syringe except elemental sulfur and polysulfide, which were added as the solids. The reaction progress was monitored by the appearance of the characteristic absorption peak of the d<sup>1</sup> reduced catalyst ( $\lambda_{\text{max}} = 696 \text{ nm}$ ;  $\epsilon = 4400 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>13</sup> The values for the two highly reactive substrates in Table 3 and Figure 4,  $\text{S}_2\text{O}_4^{2-}$  and  $\text{S}_2\text{O}_6^{2-}$ , were determined using 0.26 mM substrate with all other concentrations being the same.

**Rate Law and Reaction Rates.** The rate law and rates for oxidation of  $\text{HS}^-$  by **1** were evaluated using integrated rate expressions, computational curve fitting and initial rate methods. The experimental apparatus, conditions, reactant concentrations, and methodology were similar to those given in the section above. Again, a borax buffer (0.025 M) was used as the solvent for all reactions, providing a constant pH (8.5) and ionic strength ( $I = 0.310$ ). Given the known stoichiometry for the reaction ( $1 \text{ HS}^- + 2 \text{ 1}$ , and the rate law,  $-d[\text{1}]/dt = k[\text{1}]^2[\text{HS}^-]$ ), determined as described below, the appropriate integrated third-order

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(20) The pH drops in two stages during the experiment. During the removal of the  $\text{H}_2\text{S}$ , the 5 equiv of acid reduce the pH to ~4. During the actual titrations, the pH dropped to below 1 as the  $\text{Ce}^{4+}$  was dissolved in 10%  $\text{H}_2\text{SO}_4$ .

(21) The solubility of  $\text{Pb}(\text{NO}_3)_2$  is 1.27 g/mL at 100 °C and the  $K_{\text{sp}}$  of PbS =  $9.04 \times 10^{-29}$  (*CRC Handbook of Chemistry and Physics*, 70th ed.; Weast, R. C., Editor-in-Chief; CRC Press, Inc.: Boca Raton, FL, 1990). It was experimentally determined that one bubbler was sufficient to trap ~100% of the  $\text{H}_2\text{S}$  (see text).

rate expression is eq 3,<sup>22</sup>

$$\frac{2}{(2Y_0 - X_0)} \left( \frac{1}{X} - \frac{1}{X_0} \right) + \frac{2}{(2Y_0 - X_0)^2} \ln \left( \frac{Y_0 X}{X_0 Y} \right) = kt \quad (3)$$

$$X = X_0 - [(A_t - A_0)/\epsilon l] \quad Y = Y_0 - [(A_t - A_0)/2\epsilon l]$$

where  $A_t$  is the absorbance (at 696 nm) at time  $t$ ,  $A_0$  is the initial absorbance, and  $X_0$  and  $Y_0$  are the initial concentrations of **1** and sulfide, respectively. The time-dependent concentrations for both **1** and sulfide were calculated from the absorbances recorded, and nonlinear least-squares fits of the absorbance-time kinetic traces were performed using the program CoStat.<sup>22b</sup> As suspected from the chemistry, and particularly from the far higher rates for reaction of some intermediate sulfur oxidation products, including polysulfide, than for  $\text{HS}^-$  itself, the reaction of  $\text{HS}^-$  by **1** had to be confined to low conversions. For this reason, substantial conversions and curve fitting coupled with the use of eq 3 were clearly less appropriate than low conversions and initial rate methods. The rate dependence in **1** was determined by varying the concentration of **1** with a constant concentration of  $\text{HS}^-$ . The concentration of  $\text{HS}^-$  was 2.6 mM, and the concentration of **1** was varied (by 0.5 mM increments) from 1.0 to 3.0 mM. A larger concentration range would have been desirable here, but solubility limits (for **1**) and absorbance limitations confined experiments to this range. The rate dependence in  $\text{HS}^-$  was determined in a similar manner using 2.0 mM **1**, and the concentration of  $\text{HS}^-$  varied from 0.7 to 10.4 mM. High rates of reaction and other limitations constrained these measurements to the indicated range. For experiments on the pH dependence, the pH of the borax buffer was varied, but the strength of the buffer solution was corrected so as to maintain the total ionic strength at a constant value. For all reactions in the pH dependence experiments, the concentration of **1** was 2.0 mM and the concentration of  $\text{HS}^-$  was 2.6 mM. In all rate law measurements, the temperature was maintained at 25 °C.

**High Turnover Study.** A solution of **1** (2.19 g in 250 mL, 1.03 mM) was placed in a vessel of the same design as described above but with a capacity of 500 mL. The vessel was placed in a sand bath at 60 °C and a continuous supply of oxygen was fed into the system through the side arm. Fresh NaHS was introduced into the flask daily for several days. During this time the pH was also monitored and maintained at approximately 8.5 with the appropriate amount of HCl. This addition and acidification was performed through the septum stopper to prevent loss of substrate (as  $\text{H}_2\text{S}$ ). The catalyst stability was periodically monitored by  $^{31}\text{P}$  NMR, replacing the sample after each experiment so as not to continually reduce the amount of catalyst in the system. After several days, the reaction solution was filtered to remove all solid  $\text{S}_8$  products. These were dried, weighed, and then sent out for elemental analysis. The supernatant was subsequently treated with 1.4 g of CsBr precipitating the  $\text{Cs}^+$  salt of **1** as a white amorphous powder, which was collected, dried, and weighed. It was characterized by elemental analysis, FTIR, and  $^{31}\text{P}$  NMR. The NMR sample was submitted to a  $\text{Cs}^+ - \text{Li}^+$  cation exchange by treating the Cs salt of **1** with 15 equiv of  $\text{Li}^+$  ( $\text{LiClO}_4$  in  $\text{D}_2\text{O}$ ) to solubilize the polyanion. To the remaining reaction solution was added 10.0 g of  $\text{Pb}(\text{NO}_3)_2$ , precipitating a white amorphous solid. This was collected, dried, and weighed. The solid was characterized by both FTIR and elemental analysis. The total weight of products was used to determine the minimum turnovers of catalyst.

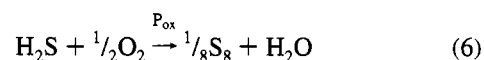
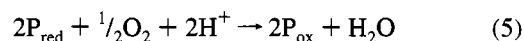
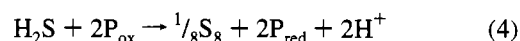
**High pH Comparison With Fe(EDTA).** A solution of  $[\text{Fe}(\text{EDTA})]^{+}$  (Versene Photochelat, Dow Chemical Co., used as received) was prepared identically to the solution of **1** described in the high turnover section above (1.03 mM, 250 mL). The reaction was run in a 500 mL vessel with an affixed glass stopcock through which oxygen was fed continuously. Fresh NaHS was introduced into the flask daily for several days, and the pH was maintained at approximately 8.5 with the appropriate amount of HCl. After several days, when no further reaction was observed, the reaction solution was filtered to remove all

solid products.<sup>23</sup> These were dried, weighed, analyzed by FTIR, and then sent for elemental analysis. A blank containing no catalyst, identical to the above reactions in all respects, was also run. The products were analyzed in the manner described above.

## Results and Discussion

### Polyoxometalate-Catalyzed Aerobic Oxidation of Sulfide.

**General Features.** Some polyoxometalates have the requisite redox potentials, hydrolytic stability, and other features to readily oxidize  $\text{H}_2\text{S}$  to molecular sulfur,  $\text{S}_8$ , in water (eq 4). While many polyoxometalates have been demonstrated to have reversible redox chemistry under chemical or electrochemical conditions, it is primarily those complexes constituted principally by type I  $\text{MO}_6$  octahedra (octahedra with only one terminal M = O group) that display this behavior (the Pope criterion).<sup>9</sup> The rate of eq 4, monitored by the appearance of the blue chromophore resulting from d-d and intervalence charge transfer bands, is rapid even for the polyoxometalates with the most negative redox potentials. Introduction of an  $\text{O}_2$  atmosphere results in reoxidation of the reduced polyoxometalate,  $\text{P}_{\text{red}}$ , eq 5, completing a catalytic cycle, eq 6. Reoxidation of reduced polyoxometalates by  $\text{O}_2$  has been documented for a number of reversibly reduced complexes in both aqueous and nonaqueous media and in conjunction with several catalytic processes,<sup>24–26</sup> but it has been studied in detail only to a limited degree.<sup>27,28</sup> The ratio  $k_4/k_5$  varies considerably between polyoxometalates. No polyoxomolybdate or polyoxovanadate examined successfully catalyzed eq 6 under these mild conditions because the reoxidation, eq 5, was too slow or nonexistent. In contrast, eqs 4 and 5 both proceeded readily for several polyoxotungstates.



Fifteen polyoxometalates, all with documented reversible or quasi-reversible redox chemistry, were prepared, purified, and evaluated as catalysts for the aerobic oxidation of  $\text{H}_2\text{S}$  in water (eqs 4–6). The natural pH of  $\text{H}_2\text{S}$ -saturated water,  $\text{pH} \sim 4.5$ , was used. Table 1 lists the complexes that were the most successful or most illustrative of key points. The data indicate that the lower charged phosphorus-containing polyoxometalates are more effective. Under steady-state turnover conditions (see Experimental Section and Table 1 caption), for most of the polyoxometalates, the reduced form ( $\text{P}_{\text{red}}$ ) is the dominant species in solution. The Zn-substituted polyoxometalates  $[\text{ZnX}^{n+}\text{W}_{11}\text{O}_{39}]^{(10-n)-}$  ( $\text{X} = \text{P}^{5+}, \text{Si}^{4+}$ ) are somewhat slower than the lacunary Keggin species  $[\text{X}^{n+}\text{W}_{11}\text{O}_{39}]^{(12-n)-}$ . This is counterintuitive inasmuch as the Zn complexes have both a lower charge density and a potential coordination site for sulfide

(23) The complex  $\{\text{Fe}[\text{EDTA}]\text{S}(\text{H})\}^{2-}$ , referred to as “complex Y” by Negaglov et al. (Neyaglov, A. A.; Digurov, N. G.; Bukharkina, T. V.; Mazgarov, A. M.; Fakhriev, A. M. *Kinet. Catal. (Engl. Transl.)* **1991**, *32*, 485) was no longer detected after the second day. The reaction was allowed to continue for the same length of time as the reaction with **1**, however, to keep the comparison of long-term reactivity valid.

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(22) (a) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*; Wiley: New York, 1981; p 28. (b) CoStat software, version 4.02. CoHort Software, Berkeley, CA, 1990.

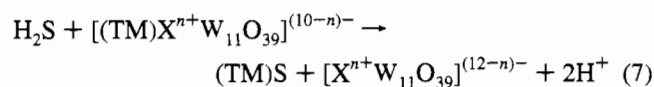
**Table 1.** Aerobic Oxidation of Hydrogen Sulfide Catalyzed by Polyoxometalates<sup>a</sup>

catalyst <sup>b</sup>	turn-overs <sup>c</sup>	yield, % <sup>d</sup>	notes
blank		1.6	no catalyst added
K <sub>14</sub> [NaP <sub>5</sub> W <sub>30</sub> O <sub>110</sub> ] (1)	7.4	6.3	catalyst still >99% intact <sup>e</sup>
K <sub>7</sub> [PW <sub>11</sub> O <sub>39</sub> ]	50	47	partial catalyst destruction <sup>e</sup>
K <sub>5</sub> [ZnPW <sub>11</sub> O <sub>39</sub> ]	40	37	Zn remains in P <sub>ox</sub> framework <sup>e</sup>
α-K <sub>8</sub> [SiW <sub>11</sub> O <sub>39</sub> ]	29	25	
α-K <sub>6</sub> [ZnSiW <sub>11</sub> O <sub>39</sub> ]	21	19	Zn remains in P <sub>ox</sub> framework <sup>e</sup>
Na <sub>2</sub> WO <sub>4</sub>	3.1	2.9	[WS <sub>x</sub> O <sub>4-x</sub> ] <sup>2-</sup> formed <sup>e</sup>

<sup>a</sup> Reaction conditions: 60 °C, 1.1 atm of O<sub>2</sub>, and 24 h reaction time in a sealed, constant pressure system. All other specifics are given in the Experimental Section. <sup>b</sup> 10 mmol of catalyst per reaction; substrate: catalyst ratio ~100:1. <sup>c</sup> mol of S<sub>8</sub>/mol of catalyst. <sup>d</sup> (mol of S<sub>8</sub>/initial mol of H<sub>2</sub>S) × 100. <sup>e</sup> State of catalyst after reaction determined by FTIR and NMR spectroscopies. See text (and supplementary material) for details.

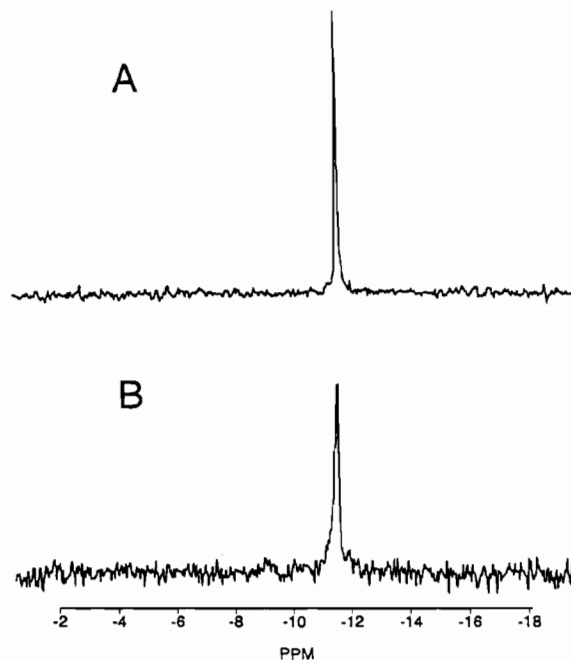
that the lacunary species do not. The higher negative charge density of the lacunary species should facilitate a greater preassociation via hydrogen-bonding with the H<sub>2</sub>S substrate than for the corresponding Zn complexes, however. It is also noted that the reaction with **1** is slower than with any of the Keggin species. This is consistent with the redox potentials and the protonation states of sulfide (vide infra).

Although all of the compounds evaluated catalyze the aerobic oxidation of sulfide, the sulfide substrate itself effects rapid and clean demetalation of the monotransition-metal-substituted polyoxometalate (TMSP) complexes of the Keggin structural class, [(TM)X<sup>n+</sup>W<sub>11</sub>O<sub>39</sub>]<sup>(10-n)-</sup>, where TM is Fe<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, and Cu<sup>II</sup>, forming the corresponding insoluble sulfide, (TM)S, and the lacunary polyoxometalate complex (eq 7). The undamaged



lacunary ion, [X<sup>n+</sup>W<sub>11</sub>O<sub>39</sub>]<sup>(12-x)-</sup> resulting from demetalation continues to catalyze the aerobic oxidation of sulfide. In contrast to the Fe<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, and Cu<sup>II</sup> complexes, the Zn<sup>II</sup> and Mn<sup>II</sup> complexes are not subject to demetalation, even after multiple catalytic turnovers (evaluation of demetalation was conducted after approximately 20 turnovers). Figure 2 shows an exemplary <sup>31</sup>P NMR study establishing the physical integrity of K<sub>5</sub>-[ZnPW<sub>11</sub>O<sub>39</sub>]<sub>n</sub>H<sub>2</sub>O in aqueous solution after reaction with 100 equiv of sulfide. The chemical shift remains at -11.6 ppm. Just as significantly, no other polytungstophosphates including K<sub>7</sub>[PW<sub>11</sub>O<sub>39</sub>]<sub>n</sub>H<sub>2</sub>O (δ = -10.3 ppm) are generated. The presence of the Zn stabilizes the parent lacunary polyoxometalate. <sup>31</sup>P and <sup>29</sup>Si NMR spectroscopy establish that some degradation of the lacunary catalysts occurs after only a few turnovers. A final point from Table 1 and other experiments is that the green mononuclear ([WS<sub>x</sub>O<sub>4-x</sub>]<sup>2-</sup>) and polynuclear sulfidotungstates which are known to form in acidic sulfide solutions of tungstates<sup>29,30</sup> are readily detected in the case of monomeric tungstate and most of the polytungstates, but not in the case of **1**.

The natural pH of H<sub>2</sub>S-saturated water (~4.5) is an attractive one in which to conduct this study as most polyoxotungstates, including derivatives of the well-developed Keggin and Wells-Dawson structural classes, are most stable at acidic and neutral pH. The remaining studies have been conducted in aqueous



**Figure 2.** <sup>31</sup>P NMR spectra of [ZnPW<sub>11</sub>O<sub>39</sub>]<sup>5-</sup>: (A) before reaction and (B) after reaction with H<sub>2</sub>S (40 turnovers at the time the reaction was terminated). The chemical shift of the single phosphorus resonance remains at -11.6 ppm indicating that the Zn remains in the polyoxometalate framework. See Table 1 for reaction details.

solutions buffered at pH = 8.5 for four reasons, however. First, a slightly basic pH, one above the first pK<sub>a</sub> of sulfide (pK<sub>a1</sub> = 7.04 in 0.1–0.01 N solution at 18 °C)<sup>31</sup> would result in conversion of nearly all the sulfide to the nonvolatile salt form, hydrosulfide, HS<sup>-</sup>, preventing loss of sulfide from H<sub>2</sub>S volatilization. Second, at basic pH the rate of oxidation is faster as HS<sup>-</sup> is a stronger base, nucleophile, and reducing agent than H<sub>2</sub>S. Third, a pH of ca. 8, maintained by addition of bicarbonate, is used in the industrial aerobic oxidations of sulfide catalyzed by chelated Fe.<sup>4</sup> Fourth, basic conditions facilitate the most reproducible kinetics measurements.

The PJP polyanion, **1**, was chosen for most of the subsequent measurements as a consequence of its remarkable stability, redox potentials, and spectroscopic characteristics. Many polyoxometalates, including those in Table 2, are capable of being reduced by more than one electron,<sup>9,12,32</sup> and **1** is capable of being reversibly reduced in aqueous media by at least eight electrons.<sup>13</sup> Oxidative titrations were performed on the reduced form of **1** generated under varying conditions (see Experimental Section). Under the reaction conditions at pH = 8.5, HS<sup>-</sup> reduces **1** by 1.07 ± 0.05 electron. The stoichiometry in eqs 4 and 5 (the coefficient of 2 for the polyoxometalate) is derived from titrations of reduced **1**. The stability of **1** is easily monitored by <sup>31</sup>P NMR as the five phosphorus atoms are equivalent by symmetry, and any perturbation in the polyoxometalate framework produces multiple <sup>31</sup>P NMR resonances. The stability of **1** was evaluated under conditions pertinent to the title reaction. First, the pH range of stability reported by Pope, Jeannin and co-workers (pH 0–11 at 25 °C)<sup>13</sup> was confirmed and quantified: no decomposition of **1** was observed in solutions at pH = (a) 2.0, (b) 6.5, and (c) 10.2 for 72 h at this temperature (for example, see supplementary material, Figure S3). Second, the stability of the reduced compound, [NaP<sub>5</sub>W<sub>30</sub>O<sub>110</sub>]<sup>15-</sup>, was evaluated. Compound **1** was reduced

(29) Müller, A. *Polyhedron*, **1986**, *5*, 323–340 and references cited.

(30) Fedin, V. P.; Sokolov, M. N.; Geras'ko, O. A.; Kolesov, B. A.; Fedorov, V. Ye.; Mironov, A. V.; Yufit, D. S.; Slovohotov, Yu. L.; Struchkov, Yu. T. *Inorg. Chim. Acta* **1990**, *175*, 217–229 and references cited.

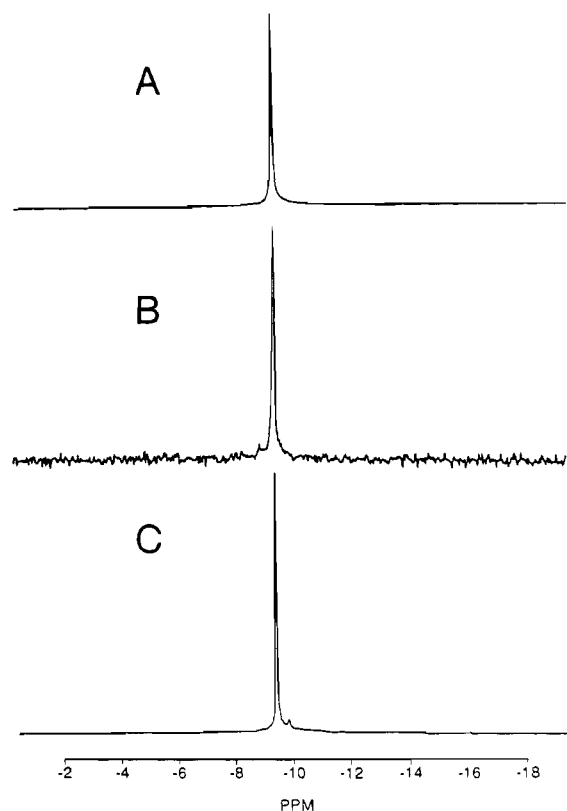
(31) *CRC Handbook of Chemistry and Physics*, 71st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1990; p 8–37.

(32) Launay, J.-P. *J. Inorg. Nucl. Chem.* **1976**, *38*, 807–816.

**Table 2.** Thermodynamic Potentials of **1** and Selected Sulfide Species<sup>a</sup>

species	$E^{\circ}$ , V	$E_{8.5}$ , V <sup>b</sup>
$K_{14}[NaP_5W_{30}O_{110}]$ ( <b>1</b> )	-0.149 <sup>c</sup>	-0.149 <sup>c</sup>
hydrogen sulfide (S/H <sub>2</sub> S)	0.142 <sup>d</sup>	<i>e</i>
hydrosulfide (S/S <sup>2-</sup> )	-0.478	-0.316
polysulfide ( $nS/S_n^{2-}$ ) <sup>f</sup>	-0.428	-0.428
sulfite (SO <sub>4</sub> <sup>2-</sup> /SO <sub>3</sub> <sup>2-</sup> )	-0.93	-0.605
dithionite (SO <sub>3</sub> <sup>2-</sup> /S <sub>2</sub> O <sub>4</sub> <sup>2-</sup> )	-1.12	-0.471
dithionate (SO <sub>4</sub> <sup>2-</sup> /S <sub>2</sub> O <sub>6</sub> <sup>2-</sup> )	-0.22 <sup>d</sup>	-0.723
sulfur (S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> /S <sub>8</sub> )	-0.74 <sup>g</sup>	0.234
thiosulfate (SO <sub>3</sub> <sup>2-</sup> /S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> )	-0.571	-0.084
sulfate (S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> /SO <sub>4</sub> <sup>2-</sup> )	2.01	2.01

<sup>a</sup> Standard reduction potentials vs. SHE in basic media; all values taken, except as otherwise noted, from: *CRC Handbook of Chemistry and Physics*, 70th ed.; Weast, R. C., Editor-in-Chief; CRC Press, Inc.: Boca Raton, FL, 1990. <sup>b</sup> Values calculated for pH 8.5 from standard potential given. <sup>c</sup> Taken from ref 2a; pH = 10. <sup>d</sup> Acidic standard potential. <sup>e</sup> Species does not exist at pH 8.5 in appreciable quantities. <sup>f</sup> Reported value is for S<sub>2</sub><sup>2-</sup>. <sup>g</sup> Taken from: Milazzo, G.; Caroli, S. *Tables of Standard Electrode Potentials*; Wiley-Interscience: New York, 1978.



**Figure 3.** <sup>31</sup>P NMR spectra of  $[NaP_5W_{30}O_{110}]^{14-}$  (A) before reaction in a reaction with HS<sup>-</sup>, (B) after 9 days, and (C) after 14 days. After 14 days (225 turnovers), the catalyst shows very little decomposition. See text for details.

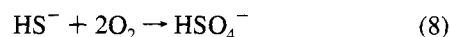
with a slight excess of HS<sup>-</sup> under anaerobic conditions. The <sup>31</sup>P NMR spectrum of this solution displayed a single line at -0.51 ppm (in D<sub>2</sub>O vs 85% H<sub>3</sub>PO<sub>4</sub>). After 4 days the vessel was opened to the air and the complex allowed to reoxidize (eq 5). The <sup>31</sup>P NMR of this reoxidized solution again indicated the presence of **1** and no detectable decomposition products derived from **1**. Third, the stability under actual turnover conditions was assayed. Figure 3 illustrates the impressive stability of **1** (see the high turnover section for reaction conditions). After 9 days no detectable decomposition was observed, and after 14 days only minimal decomposition was noted.

**Table 3.** Relative Rates of Reduction of **1** by Various Sulfur Species<sup>a</sup>

substrate	$V_0^b$	$V_{0,rel}^c$
hydrosulfide (SH <sup>-</sup> )	0.955	1.00
sulfur (S <sub>8</sub> ) <sup>d</sup>	0.0	0.0 <sup>e</sup>
polysulfide (K <sub>2</sub> S <sub>n</sub> ) <sup>d,f</sup>	22.3	23.3
thiosulfate (S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> )	0.0	0.0 <sup>e</sup>
dithionite (S <sub>2</sub> O <sub>4</sub> <sup>2-</sup> )	192	201
dithionate (S <sub>2</sub> O <sub>6</sub> <sup>2-</sup> )	159	167
sulfate (SO <sub>4</sub> <sup>2-</sup> )	0.0	0.0 <sup>e</sup>
sulfite (SO <sub>3</sub> <sup>2-</sup> )	$3.18 \times 10^{-6}$	$3.33 \times 10^{-6}$

<sup>a</sup> Reaction conditions: [**1**] = 2.0 mM, [substrate] = 2.6 mM, pH = 8.5 (0.025 M borax buffer), 298 K. All other conditions are described in the Experimental Section. <sup>b</sup> Absolute initial rate in  $\mu$ M/s. <sup>c</sup> All rates are given relative to the initial rate of the reduction of **1** with HS<sup>-</sup>, which was given an arbitrary value of 1.00 units. <sup>d</sup> Solid ground to a very fine powder with an agate mortar and pestle and dried before use. Added to the reaction as a solid, not completely dissolved. <sup>e</sup> After several days at 298 K, no reduction of **1** was observed. <sup>f</sup> Fused potassium sulfide (Fisher) used as received.

A problem in the aerobic oxidation of sulfide to sulfur for both the Fe-catalyzed industrial process, eq 1, and the polyoxometalate catalyzed processes, is the background oxidation of sulfide to sulfate, eq 8. While the principal S<sub>8</sub> product was



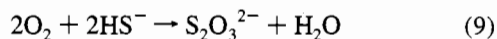
readily isolated in the polyoxometalate systems and its purity checked (vide infra), it was not possible to gravimetrically quantitate the SO<sub>4</sub><sup>2-</sup> product as the Pb<sup>2+</sup> reagent nonselectively precipitated all other sulfur species remaining in solution after reaction including residual S<sup>2-</sup> reactant and various sulfur oxyanion products along with SO<sub>4</sub><sup>2-</sup>. For **1**, however, the quantity of all Pb<sup>2+</sup>-precipitated sulfur salts (based on the average composition of the precipitate to be PbS<sub>2</sub>O<sub>3</sub>) accounted for ca. 30% of the initial sulfide; highly pure S<sub>8</sub> product accounted for the remaining ca. 70%.

**Thermodynamic and Kinetic Factors in Aerobic Oxidation of Sulfide Catalyzed by **1**. Origins of Selectivity.** Tables 2 and 3 and Figure 4 provide key data. Table 2 lists the potentials at pH = 14 (standard potentials,  $E^{\circ}$ ) and at pH = 8.5 of both **1** and several sulfur species potentially derivable from sulfide. Table 3 gives the relative rates of reduction of **1** by the sulfide-derived species, including sulfur oxyanions pertinent to the title reaction. HS<sup>-</sup> substrate was assigned an arbitrary rate of 1.00 which corresponds to an absolute initial rate,  $v_0$ , of  $0.96 \mu$ M s<sup>-1</sup> ([HS<sup>-</sup>]<sub>0</sub> = 2.6 mM, [**1**]<sub>0</sub> = 2.0 mM, pH = 8.5,  $T = 25$  °C). From the data presented, several points regarding selectivity in the aerobic oxidation of sulfide to elemental sulfur can be inferred. First, reduction of **1** by HS<sup>-</sup> proceeds readily at room temperature. Note that HS<sup>-</sup> is present only in minute quantities ( $\leq 1.0$  mM) under the conditions in Table 1. Second, polysulfide (S<sub>n</sub><sup>2-</sup>,  $n \geq 2$ ), is more reactive than the monomeric sulfide. This is not surprising given that S<sub>n</sub><sup>2-</sup> contains atoms adjacent to the terminal anionic nucleophilic sulfur atoms that have lone pairs (the nucleophilic  $\alpha$  effect).<sup>33,34</sup> Polysulfide results not only from the incomplete oxidation of HS<sup>-</sup> but also from the reaction of HS<sup>-</sup> with the initially produced elemental

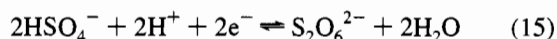
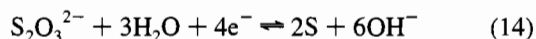
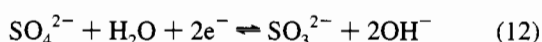
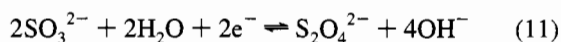
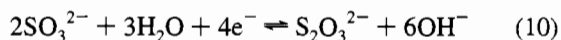
(33) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry. Part A: Structure and Mechanisms*, 3rd ed.; Plenum Press: New York, 1990; p 288.

(34) Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, 1969; pp 107-111.

sulfur species ( $S^0_x$ ).<sup>35</sup> Facile oxidation of polysulfide militates against the accumulation of soluble oligomeric sulfides and aids in the formation of elemental sulfur ( $S_8$ ), which quickly precipitates from the reaction solution and begins to flocculate into macroscopic particles. The physical removal of the sulfur product from solution also limits its overoxidation to less desirable products since upon precipitation, the effective concentration of the substrate decreases by orders of magnitude. Third, **1** is thermodynamically incapable of oxidizing  $S_8$ . This allows the catalyzed reaction to stop cleanly at the desired product. Fourth, the rate of oxidation of  $S_2O_3^{2-}$  and  $SO_3^{2-}$  are zero and nearly zero, respectively. In the industrial oxidation catalyzed by chelated Fe, background oxidation to  $S_2O_3^{2-}$  (eq 9) contributes to the undesirable overoxidation of sulfur.



A comparison of the standard potentials in Table 2 and the initial rates of reduction in Table 3 defines a nonlinear relationship between the two parameters. The experimental behavior can be explained by considering several factors. First, some of the pertinent half-reactions, eqs 10–15, are highly



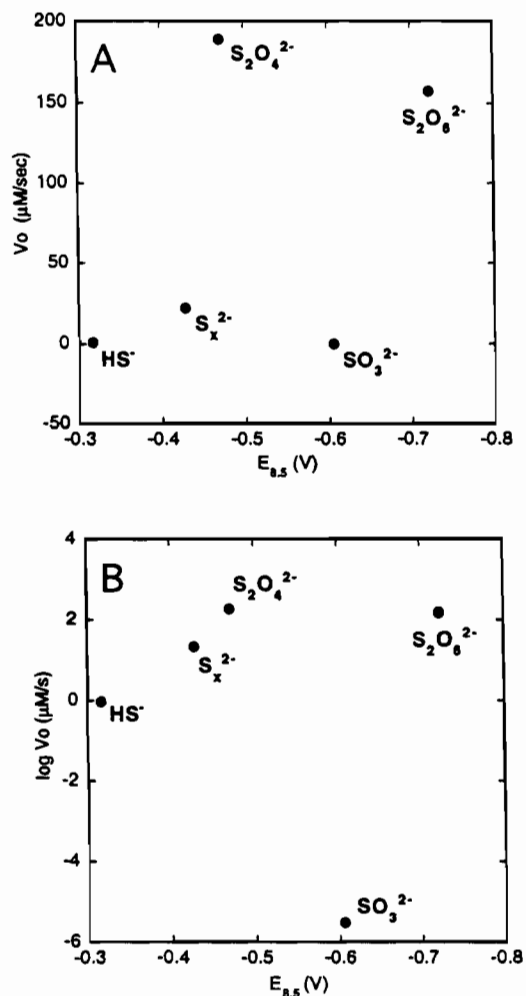
pH dependent. Upon correction of the potentials to the pH of the catalytic reaction conditions (pH 8.5), the relationship between these two parameters becomes clearer.<sup>36</sup> The three species that effect no reduction of **1** all possess  $E_{8.5}$  values too positive for reaction to occur (see Table 3). The remaining species all possess sufficiently negative potentials and varying rates of reduction are observed. Figure 4 gives the initial rate of reduction of **1**,  $v_0$ , and  $\log v_0$ , as a function of the corrected potential. The rate of reduction of **1** generally increases with decreasing potential, with the exception of dithionite ( $S_2O_4^{2-}$ , also called hydrosulfite) and sulfite ( $SO_3^{2-}$ ) which fall above and below the expected values, respectively. The anomalously high rate for reduction by dithionite, more than likely, is due to the presence of the sulfoxylate radical anion  $SO_2^{\bullet-}$ . While  $SO_2^{\bullet-}$  is present only in small quantities (the dissociation constant,  $K$ , for eq 16 under similar conditions to these has been



estimated to be ca.  $6 \times 10^{-10}$ ), its doublet ground state dictates

(35) The reaction of sulfide ( $HS^-$ ) with itself and with  $S^0_x$  species is well documented: *Inorganic Sulphur Chemistry*; Nickless, G., Ed.; Elsevier Publishing Co.: New York, 1968; Chapters 10 and 19 and references therein.

(36) The actual potential of several pertinent sulfur oxyanions deviates from the calculated value obtained through use of the Nernst equation. For an exemplary treatment see: Teder, A., *Acta Chem. Scand.* **1973**, 27, 705.



**Figure 4.** Oxidation of various sulfur species by **1** showing (A) initial rates and (B) log initial rates, as a function of potential. All potentials are corrected to pH = 8.5. See Experimental Section for conditions and text for further details.

a significantly faster rate in one-electron reductions.<sup>37,38</sup> Again, **1** acts primarily as a one-electron acceptor in the oxidation of sulfur species, data consistent with the voltammetric behavior at high pH first reported by Pope and co-workers.<sup>13</sup> The anomalously low rate for reduction by  $SO_3^{2-}$  defensibly derives from the absence of facile one-electron pathways (note the thermodynamic data, including the potentials for one- and two-electron oxidations).<sup>39–41</sup>

**Mechanism for Aerobic Oxidation of Sulfide Catalyzed by 1.** We now examine one of the most versatile and stable polyoxometalate systems for catalysis of aerobic sulfide oxidation, that based on **1**. We focus on the sulfide oxidation itself, eq 4. (The mechanism for the reoxidation of reduced polytungstophosphates in aqueous media by  $O_2$ , eq 5, the effective second step in the two-step catalytic process, cf. eqs 4–6, has recently been studied.<sup>27,28</sup>) Equation 17 gives the basic stoichiometry for eq 4 in the case of **1** from quantification of the loss

(37) *Inorganic Sulphur Chemistry*; Nickless, G., Ed.; Elsevier Publishing Co.: New York, 1968; Chapter 14 and references therein.

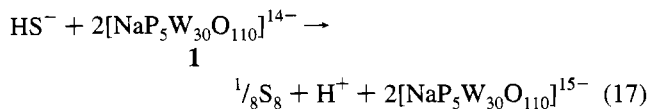
(38) Lynn, S.; Rinker, R. G.; Corcoran, W. H. *J. Phys. Chem.* **1964**, 68, 2363.

(39) The speciation of the sulfite is complex at high pH were the predominant state is the fully deprotonated  $SO_3^{2-}$ . For a more complete discussion on the solution form of  $SO_3^{2-}$  see: (a) *Comprehensive Inorganic Chemistry*, Brasted, R., Ed.; D. Van Nostrand and Co.: Princeton, NJ, 1961; Vol. VIII, Chapters 1 and 2, and references therein. (b) Reference 36, Chapter 6.

(40) Huie, R. E.; Neta, P. *J. Phys. Chem.* **1984**, 88, 5665.

(41) Huie, R. E.; Neta, P. *J. Phys. Chem.* **1985**, 89, 3918.





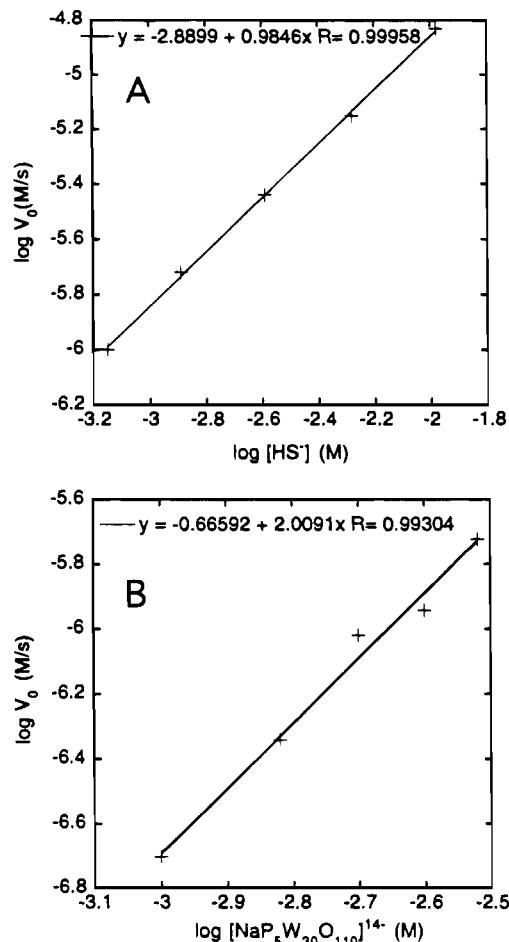
of both substrate and production of  $\text{S}_8$  product. While integrated rate laws and computational curve fitting techniques were used to assess the kinetics data, the characteristics of sulfide oxidation by  $\mathbf{1}$ , (e.g. sulfur catenation with both itself and sulfide species) and, in particular, the very high reactivities of initial products (e.g. polysulfide reduces  $\mathbf{1}$  23 times faster than sulfide itself) demanded that reaction conversions be kept quite low (see Experimental Section). As a consequence, initial rate methods gave more reliable data. Indeed fits of the data using CoStat<sup>23</sup> indicated that all simple standard integrated rate laws were unsatisfactory with the appropriate third-order one giving the best fit. Figure 5 shows log–log plots for the initial rate of eq 17 with respect to both sulfide and catalyst. In part A, five reactions were run at varying concentrations of sulfide establishing a first order dependence in this substrate. In part B, five reactions were run at varying concentrations of  $\mathbf{1}$ , establishing a second-order dependence in this complex. While larger substrate concentration ranges would have been desirable, solubility, high speed of reaction, and other experimental limitations necessitated the use of the indicated ranges (see Experimental Section). Both the close-to-integral value for the slopes and the high quality of the data (5-point fits with 99+% correlation coefficients) provided validation for the reaction orders determined by this method. A second-order dependence in  $\mathbf{1}$  demands that two molecules of  $\mathbf{1}$  are involved in or prior to formation of the rate-limiting transition state complex. These results are understandable given the stoichiometry of eq 17. The oxidation of sulfide to elemental sulfur requires the transfer of two electrons. Since the oxidative titration data presented previously indicate that  $\mathbf{1}$  is only reduced by one electron, two catalyst molecules are required to effect the complete oxidation.

Two methods were employed to determine the value for  $k_{\text{obs}}$ , the rate constant for the reduction of  $\mathbf{1}$  by sulfide. The initial rate method led to eq 18 and  $k_{\text{obs}} = 79.3 \pm 7.1 \text{ M}^{-2} \text{ s}^{-1}$ . The

$$V_0 = k_{\text{obs}}[\mathbf{1}]_0^2[\text{HS}^-]_0 \quad (18)$$

appropriate integrated rate expression, eq 3, again, gave less satisfactory results:  $k_{\text{obs}} = 96 \pm 43 \text{ M}^{-2} \text{ s}^{-1}$  and a systematic deviation in the value for  $k_{\text{obs}}$  was found as the time of reaction increased.<sup>42</sup> This large experimental error results, again, from the very complex nature of aqueous sulfide solutions and the relative reactivities of several partially oxidized sulfur species toward  $\mathbf{1}$ .

The pH dependence of eq 17 given in Figure 6A, not surprisingly, is complex. The most dominant factor in this dependence is the protonation state of  $\mathbf{1}$ . Repeated acid–base titrations of  $\mathbf{1}$  under the experimental conditions going in both acidic and basic directions failed to exhibit clear endpoints although there appears to be a change in protonation state. The kinetics implicate that the complex is undergoing deprotonation over the indicated pH range (7.4–9.5) resulting in a form of the complex at the basic end of the range that is more negatively charged, less oxidizing, and less reactive toward sulfide.<sup>43</sup> A more protonated  $\mathbf{1}$  is also more able to associate, via hydrogen



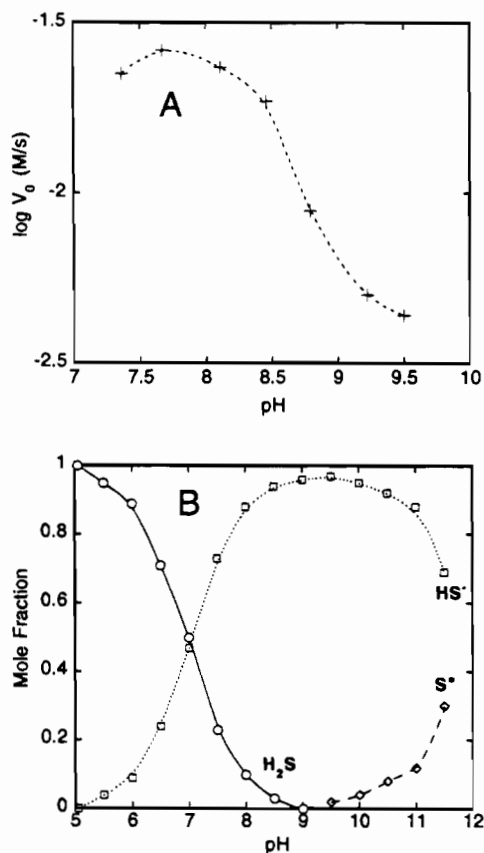
**Figure 5.** Plots (log–log) for the initial rates of reaction of  $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$  with  $\text{HS}^-$ : (A) dependence on concentration of  $\text{HS}^-$ ; (B) dependence on concentration of  $\mathbf{1}$ . The equations in each box are the best fit lines through the experimental points with their correlation coefficients. All conditions are described in the Experimental Section.

bonding, with the substrate  $\text{HS}^-$ . Whether the role of protonation of  $\mathbf{1}$  in enhancing the rate is an electronic effect and/or an association effect can not be determined from these studies. The protonation state of sulfide over a similar pH range, Figure 6B, runs in the opposite direction to the observed overall rate, namely, as the more reducing and reactive  $\text{HS}^-$  is formed from the less reducing and reactive  $\text{H}_2\text{S}$ , the rate decreases. The decrease in rate at low pH values, below where  $\mathbf{1}$  is protonated (below pH 7.5), results from the declining mole fraction of  $\text{HS}^-$ .

A mechanism consistent with the data is given in eqs 19–22 and the rate law derived from this mechanism, eq 24, is reducible to the experimentally determined rate law. A protonated molecule of the PJP polyanion,  $\mathbf{1H}$ , associates, most likely via hydrogen bonding, with  $\text{HS}^-$  (eq 20), and this complex then reacts in a subsequent slow step with  $\mathbf{1}$  (eq 21). Such a preassociation mechanism is much more likely than one involving a termolecular process between two molecules of  $\mathbf{1}$  (protonated or unprotonated), and one molecule of  $\text{HS}^-$ . The products of the rate limiting step, eq 21, lead, after many steps involving redox and sulfur catenation processes, to the observed products, reduced  $\mathbf{1}$  and  $\text{S}_8$ , eq 22. Processes analogous to eqs 20 and 21 can be written involving preassociation with  $\mathbf{1}$  in place of  $\mathbf{1H}$ , but all the rate constants should be significantly slower. Inclusion of such elementary processes would not change the general form of the derived rate law. Simple bimolecular reactions such as eq 23 can be ruled out from the experimental rate law, particularly given the quality of the order

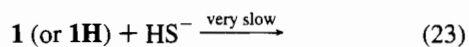
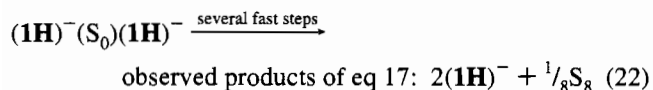
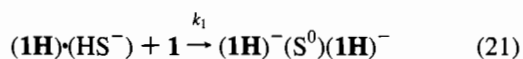
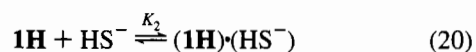
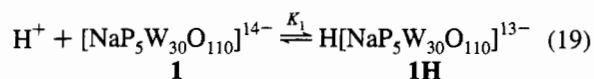
(42) The point value for  $k_{\text{obs}}$  steadily decreases with time in the first 5–8% conversion.

(43) It is well established that protonated polyoxometalates are kinetically more potent oxidizing agents than their deprotonated analogues. For example, see: Renneke, R. F.; Kadkhodayan, M.; Pasquali, M.; Hill, C. L. *J. Am. Chem. Soc.* **1991**, *113*, 8357.



**Figure 6.** (A) pH dependence of the initial rate for the reduction of  $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$  with  $\text{HS}^-$  (eq 17) from pH 7.4 to 9.5. (B) Acid–base speciation of sulfide over a similar range. All conditions are described in the Experimental Section.

determination in  $1-2.009$  order with an  $R$  value of 99.3% for a five-point fit.



$$v_0 = k_1[(\mathbf{1H})\cdot(\text{HS}^-)][\mathbf{1}] \quad (24)$$

The complete rate expression would generate separate terms for  $\text{H}_2\text{S}$  and  $\text{HS}^-$  and even one to account for the trace of  $\text{S}^{2-}$  present. However, such an expression would lead to a highly complex and unwieldy rate law that would probably not provide significant further insight into the mechanism in reference to

eqs 19–24. Two features of significance in the kinetics are not covered in these equations. The first is the likely reduction of  $\mathbf{1}$  by  $\text{S}^{2-}$  ( $\text{p}K_{a2}$  for sulfide = 11.96 in 0.1–0.01 N solution at 18 °C).<sup>31</sup> While there is very little  $\text{S}^{2-}$  even at pH 9.5, the most basic pH in Figure 6A (0.3% of the sulfide present), this species is significantly more reactive than  $\text{HS}^-$ . The second is the possibility of ion pairing between  $\mathbf{1}$  and its associated counterions, and/or the alkali metal cations present in the buffer systems.<sup>44</sup>

**High Turnover Study and Comparison of  $\mathbf{1}$  with the Commercial Catalyst.** A high turnover study was performed on the reaction between  $\mathbf{1}$  and  $\text{HS}^-$ . The pH was maintained at 8.5 throughout the reaction and readjusted each time additional sulfide was added. Three separate reactions were run, all under identical conditions, each for a total of 14 days. The first reaction contained  $\mathbf{1}$  as the catalyst, the second, an equimolar amount of  $\text{NH}_4[\text{Fe}^{\text{III}}(\text{EDTA})]$  (Versene Photochelatate), the commercially used catalyst for this process, and the third, no catalyst. In the control reaction (no catalyst), 0.136 g of solid material was collected and the sulfur content was determined to be 98.3% by elemental analysis. This was used as a correction to the gross weight of solid products in the analysis of the other two reactions. The solid collected from the  $\text{NH}_4[\text{Fe}^{\text{III}}(\text{EDTA})]$  reaction weighed 0.888 g and was determined to be 89.8% sulfur by elemental analysis. This corresponds to a product to catalyst ratio of 99:1 or 198 turnovers. The low purity of the sulfur collected is due to the presence of degraded catalyst in the precipitate. Approximately 100% of the iron introduced into the reaction as the catalyst was recovered, primarily as  $\text{FeS}$ , in the sulfur solid. The solid collected from the reaction with  $\mathbf{1}$  weighed 0.931 g and was >99.5% sulfur, which corresponds to 225 turnovers. Figure 3 shows the  $^{31}\text{P}$  NMR spectra for  $\mathbf{1}$  before, during, and after this reaction. Only in the final spectrum is any decomposition of the catalyst noted. Upon redissolving the recovered catalyst in water and adding fresh sulfide, immediate reduction of  $\mathbf{1}$  was observed.

The principal factor favoring  $\text{NH}_4[\text{Fe}^{\text{III}}(\text{EDTA})]$  versus  $\mathbf{1}$  as an industrial catalyst is the faster rate of reoxidation for the Fe complex, which minimizes the undesirable uncatalyzed background oxidation of sulfide to sulfate, eq 8. In the future, however, it should be possible to prepare polyoxometalates that exhibit the desirable attributes of  $\mathbf{1}$  pertinent to sulfide oxidation, namely selectivity for  $\text{S}_8$  coupled with extraordinary catalyst stability, and also react with complete turnover rates comparable to the catalysts in present use.

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**Supplementary Material Available:** Plots for the solubility of both  $\text{H}_2\text{S}$  and  $\text{O}_2$  in  $\text{H}_2\text{O}$  as a function of temperature (Figure S1),  $^{31}\text{P}$  NMR spectra of  $\mathbf{1}$  before and after reaction with  $\text{H}_2\text{S}$  at low pH (Figure S2), and  $^{31}\text{P}$  NMR spectra exhibiting the stability of  $\mathbf{1}$  at various pH values (Figure S3) (3 pages). Ordering information is given on any current masthead page.

(44) The possibility of rate acceleration due to ion-pairing between  $\mathbf{1}$  and the cations present (in the buffer solution) is currently under investigation.