Thermal multi-electron transfer catalysis by polyoxometalates. Application to the practical problem of sustained, selective oxidation of hydrogen sulfide to sulfur

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Abstract

Novel polyoxometalate-based catalytic systems for the effective and selective aerobic oxidation of H_2S to $S(0)$ are reported. The base stable catalysts $TMA_9[Nb_3P_2W_{15}O_{62}]$, **1**, $Li_{33}[H_7P_8W_{48}O_{184}]$, **2**, $K_{10}[Zn_4P_2W_{18}O_{68}]$, **3**, and $K_4[Nb_2W_4O_{19}]$ produce 17, 135, 5.7 and 8.8 turnovers of S_8, respectively (23°C; 1.0 atm O_2; 4 h; sealed vessel). The stability of these catalysts during sulfide oxidation are evaluated. The redox potentials of these polyoxometalates and the primary fragmentation products pertinent to sulfide oxidation are given. Early time kinetics of the reduction of **1** by sulfide proceeds according to the rate law $+d[Nb_3P_2W_{15}O_{62}^{10-}]/dt = k[1][HS^-]$, with a complex pH dependence. The buffering agent is shown to be non-innocent and at parity of reaction conditions, the reduction of $K_{14}[NaP_5W_{30}O_{110}]$, **4**, by sulfide in media buffered with PO_4^{3-}, CO_3^{2-}, $B_4O_{10}^{2-}$, and OH^- (a blank) results in 40, 9.0, 49, and 10 turnovers of S_8, respectively.

Keywords: Electron transfer; Thermal catalysis; Polyoxometalates; Oxidation; Hydrogen sulphide; Sulphur

1. Introduction

The selective oxidation of H_2S to elemental sulfur is an industrially significant processes for two major reasons. First, much of the natural gas reserves in the world are 'sour gas', that is they contain H_2S as an undesirable contaminant which must be removed before utilization [1]. Second, selective removal of H_2S as elemental sulfur affords the opportunity to transform a toxic by-product into a safe, salable commodity. The desired overall reaction is shown in Eq. 1.

$$\text{H}_2\text{S} + 1/2\text{O}_2 \xrightarrow{\text{Catalyst}} \text{H}_2\text{O} + 1/8\text{S}_8 \qquad (1)$$
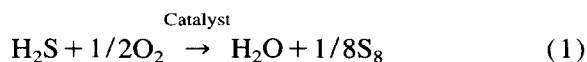
To execute this oxidation selectively and efficiently, the catalyst utilized must be capable of performing three tasks simultaneously. First, the two-electron oxidation of the sulfide to molecular sulfur must dominate over oxidation to higher thio-oxy anions, primarily thiosulfate ($S_2O_3^{2-}$), dithionate ($S_2O_6^{2-}$) and sulfate (SO_4^{2-}) (four-, seven-, and eight-electron oxidations of sulfide respectively). Second, the efficient four-electron reduction of O_2 to H_2O is required. Third, the conditions of this reaction demand that the catalyst exhibits a very high degree of resistance to oxidative and hydrolytic degradation.

At the present time, chelated iron complexes such as $Fe^{III}(NTA)^-$ and $Fe^{III}(EDTA)^-$ which exploit the iron $2^+/3^+$ redox couple, are used as

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the primary catalysts for the oxidative removal of H_2S from flue gas streams [2–6]. The principal shortcoming of the current processes is short catalyst lifetimes under operating conditions due to irreversible oxidative degradation of the chelating ligands. The generation of peroxide and hydroxyl radical intermediates at the metal center during reoxidation of the catalyst leads to rapid and irreversible degradation of these organic ligands.

While polyoxometalates (early transition metal oxygen anion clusters) [7–11], are extremely resistant to oxidative degradation; they are, in general, susceptible to degradation in basic, aqueous solutions. One promising solution strategy is to substitute other early transition metals for tungsten in the polyoxometalate framework. Since niobium substitution for tungsten as an addenda atom is known to impart base stability to these complexes [12,13], one logical effort is to study Nb-substituted polyoxometalates in the search for more efficient catalysts. Several of these compounds are known and more are in preparation [1].

In previous work [14], we reported that particular d^0 polyoxometalates can catalyze the sustained and selective aerobic two-electron oxidation of sulfide to sulfur. The focus of this paper is to find base-stable polyoxometalates that exhibit this same catalytic activity and selectivity. In addition to the niobium-substituted compounds, there are several other base-stable polyoxometalates in the literature [11,15–19]. The catalytic activity for aerobic oxidation of sulfide to sulfur of these complexes is also evaluated in this study. The potential of this chemistry, an investigation of the rate behavior of one representative niobium-substituted polyoxometalate, $[Nb_3P_2W_{15}O_{62}]^{9-}$ [16], 1, (Fig. 1) and other features of sulfide oxidation catalyzed by these compounds is presented.
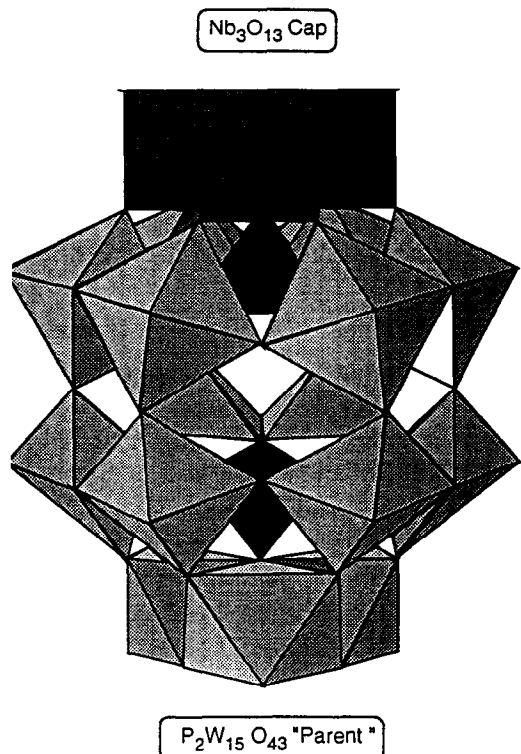
2. Experimental section

2.1. General methods and materials

All commercially available chemicals used were reagent grade, oxygen was u.s.p. grade, argon was prepurified grade and all were used as received. The catalysts used, $TMA_9[Nb_3P_2W_{15}O_{62}] \cdot nH_2O$ [16], 1, (TMA = tetramethylammonium) $Li_{33}[H_7P_8W_{48}O_{184}] \cdot nH_2O$ [17], 2, $K_{10}[Zn_4P_2W_{18}O_{68}] \cdot nH_2O$ [18], 3, $K_{14}[NaP_5W_{30}O_{110}] \cdot nH_2O$ [11], 4, $Na_9[PW_9O_{34}] \cdot nH_2O$ [18], $K_4[Nb_2W_4O_{19}] \cdot nH_2O$ [19], and $Na_{12}[P_2W_{12}O_{68}] \cdot nH_2O$ [20] were synthesized and purified according to literature procedures. The Versene Photochelate, a gift from Dr. Stephen A. Bedell of Dow Chemical Co., was used as received. Deionized water from a Barnstead single

Fig. 1. Polyhedral illustration of the triniobium substituted Dawson polyanion, $[Nb_3P_2W_{15}O_{62}]^{9-}$, 1, first prepared by Finke and coworkers, derived from crystallographic coordinates. Each octahedron represents one MO_6 unit, the niobium octahedra being more shaded than those representing tungsten.

Nb₃O₁₃ Cap

P₂W₁₅O₄₃ "Parent"

[1] Niobium has been successfully incorporated into several different polytungstate frameworks. Work continues in our group to develop new compounds of this type.

stage de-ionizer (mixed bed type) was used in all syntheses. Burdick and Jackson distilled-in-glass grade water was used for the catalytic reactions without further purification. The NaHS was synthesized from H_2S and stored in a sealed vessel under dry Ar to prevent hydration and oxidation [21]. Infrared spectra were obtained as KBr pellets (2–5 wt.%) on a Nicolet 510M FTIR Spectrophotometer. UV–Vis spectra were obtained using a HP 8451 Diode Array Spectrophotometer. Cyclic voltammetry was performed on a PAR model 173 potentiostat and a PAR model 175 universal programmer. Elemental analyses were conducted by E + R Microanalytical Laboratories. ^{31}P NMR spectra were recorded with an IBM WP-200SY FT spectrometer at 81.015 MHz. The ^{31}P NMR chemical shifts are referenced to 85% H_3PO_4 in D_2O, referenced by the substitution method. Chemical shifts downfield from the reference are reported as positive ($+\delta$). The spectral parameters for ^{31}P NMR were acquisition time = 0.512 s, relaxation delay = 1.00 s, pulse width = 14.8 μs, spectral window = 4000 Hz, digital resolution = 1.95 Hz/point. The probe temperature was 295 K in all NMR experiments.

While 1 is known to dimerize through Nb–O–Nb linkages in acidic media [12], all of the reactions in this work were conducted in media several pH units more basic than that for the onset of dimerization with the exception of the final phase of the oxidative titrations. Oxidative titrations of the reduced form of 1 were performed with a standardized solution of Ce^{4+} [22]. In a Schlenk flask was placed 379 mg (80.0 μmol) of the catalyst, 1, 44.8 mg (0.80 mmol; 10.0 equivalents) of dry NaHS, and 20.0 ml of degassed water (final pH $\approx$ 8.5) under one atmosphere of argon. The vessel was placed in a thermostated bath at 23°C for 1 h. The excess unreacted sulfide was then removed as H_2S by the addition of 1.1 equivalents of acid (as 2.0 M HCl) followed by careful evacuation on a vacuum line. The actual titrations were carried out in triplicate on 5.0-ml aliquots of the

reduced 1 solution using the Ce^{4+} standard to colorless and clear end points [2].

The molar extinction coefficient of 1 (at $\lambda_{max} = 700$ nm) was determined in the following manner. A Schlenk vessel, sealed with a septum stopper and wired shut, containing 59.8 mg (12.7 μmol) of 1 and 222.7 mg of sodium dithionite, (1.27 mmol, 100.0 equivalents) was rigorously degassed and placed under an atmosphere of Ar. Likewise, an aqueous solution of 0.01 mM KOH was degassed and placed under argon [3]. Using a gas-tight syringe, 11.8 ml of the base solution was added to the former vessel and it was left to stir at room temperature for 15 min. Triplicate aliquots were subsequently drawn from the reaction vessel and placed in a Schlenk cuvette with an affixed glass top (argon filled) and absorbance measurements were repeated each minute until a stable maximum value was obtained, and the molar extinction coefficient was calculated using Beer's law. ^{31}P NMR was utilized to confirm that the analyte remained $\approx$ 100% intact.

2.2. Comparison of polyoxometalate activity (Table 2)

Reactions were carried out in a 100-ml round bottomed flask with a glass stopcock side-arm. In a typical reaction, the catalyst was weighed and added to a dry vessel which was then flushed with oxygen. In a separate vessel, the substrate solution was prepared by saturating water with H_2S, then adding the appropriate amount of buffer (as the solid) and adjusting the pH to the desired value [4]. A 15-ml aliquot of this solution was subsequently placed in a dry reaction vessel with the catalyst and a magnetic stir bar, quickly sealed with a septum stopper and wired shut. The vessel was then

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[2] The pH drops in two stages during the experiment. During the removal of the H_2S, the five equivalents of acid reduce the pH to $\sim$ 4. During the actual titrations, the pH dropped to below 1 as the Ce^{4+} was dissolved in 10% H_2SO_4.

[3] The solution was maintained at a slightly basic pH throughout the experiment. See Results and Discussion for details.

[4] The temperature of saturation was recorded and Henry's Law was used to calculate the initial concentration of sulfide. The water was saturated with H_2S before the buffer was added.

placed into a thermostated bath at 23°C and allowed to react for 4.0 h with constant stirring at 750 RPM. The reaction was analyzed in the following manner. After removal from the bath, the solid products were filtered off utilizing a 0.20 μm nylon-66 membrane. These products were washed, dried, weighed and sent for elemental analysis. To the remaining solution was added 1.2 equivalents (based on charge-moles of catalyst) of CsBr [5], precipitating the polyoxometalate catalyst as the Cs$^+$ salt. This was filtered off with a 0.2 μm nylon membrane. These products were dried, weighed and analyzed by FTIR and NMR. Before obtaining NMR spectra, the sample was submitted to a Cs$^+$–Li$^+$ cation exchange by treating the Cs$^+$ salt with a slight excess of Li$^+$ (LiClO$_4$ in D$_2$O) to solubilize the polyanion.

Effect of buffer on catalytic activity (Table 3). Reactions were carried out in a 100-ml round bottomed flask with a Teflon stopcock side-arm at ambient temperature. In a typical reaction, the catalyst was weighed and added to a clean, dry vessel which was then flushed with oxygen. The reaction solution was prepared by first placing the appropriate amount (0.01 mole) of the desired buffer in a flask and adding 50.0 ml of water, freshly saturated with H$_2$S [6]. The pH was quickly adjusted to 7.2 and 15.0 ml aliquots of this substrate/buffer solution were transferred to the catalyst containing vessel. A magnetic stir bar was added to this vessel and it was then sealed with a suba-seal septum stopper and wired shut. The reaction was stirred at 750 RPM for four hours in a bath thermostated at 23°C. The solid sulfur product was collected and washed on 0.20 μm nylon-66 filter membranes, dried and weighed. Catalyst stability was assayed by adding fresh sulfide substrate to the spent reaction solution and observing the renewed catalytic activity. ^{31}P NMR was utilized to assess the integrity of the catalyst.

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[5] Equivalents used are calculated as moles of catalyst times charge on the anion. The amount necessary varied with the polyanion used.

[6] The temperature of saturation was recorded and Henry's Law was used to calculate the initial concentration of sulfide. The water was saturated with H$_2$S before the buffer was added.

2.3. Cyclic voltammetry of 1 and 3

A working concentration of 1.00 mM in catalyst (0.10 mM NaCl aqueous solution) was used with a scan rate of 50 mV/s. Measurements were taken at ambient temperature. The reference electrode was Ag/AgCl, the counter electrode was a coil of platinum wire, and the working electrode was glassy carbon. Between experiments the working electrode was polished with 0.05 μm alumina. For 1, the cyclic voltammetry was performed in basic aqueous solution to insure that the analyte remained exclusively in the monomer form, and this was confirmed by IR spectroscopy after the electrochemical measurement. The potentials reported are the reversible voltammetric half-wave potentials; they are assumed to differ negligibly from the formal potentials of the redox couples.

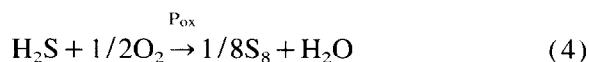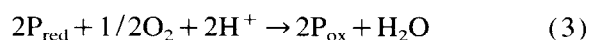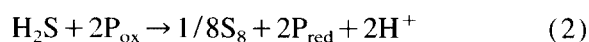### 2.4. Kinetic measurements and determination of rate law

These rate determinations involved reduction of 1, and in all cases initial rate methods were used as facile oxidation of initial products precluded the use of integrated rate laws and high conversions. As the species of primary interest, 1, was also the analytic chromophore in the UV–Vis experiments, this constrained the concentration regime to one narrower than would be more typical with investigations of this nature. Similarly, the problems of solubility and the rapid rate of reduction at higher concentrations further restricted the reliable working range of the experiment. All measurements were made anaerobically under an atmosphere of Ar using a quartz cuvette with an affixed glass stopcock top. The reaction progress was monitored by the appearance of the characteristic absorption peak of the d^1 reduced catalyst ($\lambda_{max} = 700$ nm; $\epsilon = 1075$ M^{-1} cm^{-1}). The reaction was initiated by the addition of 1.0 ml of substrate to the cuvette containing 2.5 ml of an aqueous solution of 1. Both 1 and substrate were introduced into the cuvette as previously degassed solutions with a Hamilton Gastight

syringe. In all these reactions the buffer was $Na_2B_4O_7 \cdot 10H_2O$ and the temperature was 23°C. The rate dependence in **1** was determined by varying the concentration of **1** with a constant concentration of HS^-. The rate dependence in HS^- was determined in a similar manner. For experiments on the pH dependence, the concentration of **1** was 4.0 mM and the concentration of HS^- was 50 mM. The pH of the borax buffer was varied from 7.2 to 8.7, but the strength of the buffer solution was corrected so as to maintain a constant total ionic strength.

3. Results and discussion

3.1. General features

Most polyoxotungstates have the requisite redox potentials [7,23,24] to readily oxidize H_2S to molecular sulfur in water, Eq. 2. The introduction of an O_2 atmosphere results in re-oxidation of the reduced polyoxometalate, P_{red}, Eq. 3, completing the catalytic cycle, Eq. 4. Re-oxidation of reduced polyoxometalates by O_2 has been documented for a number of reversibly reduced complexes in both aqueous and non-aqueous media [25–30].

$$H_2S + 2P_{ox} \rightarrow 1/8S_8 + 2P_{red} + 2H^+ \qquad (2)$$

$$2P_{red} + 1/2O_2 + 2H^+ \rightarrow 2P_{ox} + H_2O \qquad (3)$$

$$H_2S + 1/2O_2 \xrightarrow{P_{ox}} 1/8S_8 + H_2O \qquad (4)$$

There are four lines of evidence consistent with Eqs. 2 and 3. First, the characteristic heteropoly blue color of the reduced species is evident immediately upon introduction of sulfide to the catalyst solution. This color disappears when titrated with Ce^{4+} or, more slowly, upon exposure to air. Second, UV–Vis spectra taken during reaction shows a peak consistent with reduction of the catalyst. ($\lambda_{max} = 700$ nm, $\epsilon = 1075$ M^{-1} cm^{-1}) Third, ^{31}P NMR spectra taken before and after reaction with sulfide show the catalyst remains intact throughout the reaction. Fourth, FTIR spectra taken before

and after reaction with sulfide also support this conclusion.

For most of the polyoxotungstate catalysts studied, the re-oxidation step is rate-limiting for the overall process. An accumulation of reduced catalyst, easily identified by the characteristic d^1 absorption band, (heteropoly blue) was observed throughout the reaction with sulfide, even under one atmosphere of pure oxygen. Increasing total catalytic speed is one key to a more efficient system since the uncatalyzed direct oxidation of sulfide by O_2 (Eq. 5) is an undesirable background reaction (and unavoidable in a one-vessel reactor) [31]. To accomplish this goal,

$$2O_2 + 2HS^- \rightarrow S_2O_3^{2-} + H_2O \qquad (5)$$
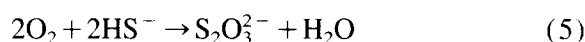
new catalyst candidates should have redox potentials as negative as possible, while retaining excellent stability under mildly basic conditions.

Replacement of one or more tungsten atoms in the polyoxometalate framework with niobium atoms has the above mentioned beneficial effects on the catalytic properties. First, it is known that incorporation of niobium into the polyoxometalate framework lends increased base stability over the parent tungsten compounds [7,19]. This increased stability allows access to structural classes not normally stable at basic pH. Second, substitution of Nb^V for W^{VI} increases the negative charge carried on the polyanion and shifts the redox potentials to more negative (cathodic) values accordingly. The hydrosulfide ion (HS^-) is easily oxidized thermodynamically (See Table 1) and kinetically which allows polyoxometalates to posses quite negative potentials and still be effective oxidation catalysts.

The redox potentials of some representative catalysts as well as other pertinent sulfur species are given in Table 1. There are three important features to be noted here. The first is the difference in the reduction potential of hydrosulfide and elemental sulfur. An effective and selective catalyst must have a sufficiently negative potential to fall within this range so as to be capable of oxidizing hydrosulfide cleanly without oxidation of the primary product, sulfur. The second point is the dif-

Table 1
Potentials of selected species [a]

Species	E/V
$[Nb_3P_2W_{15}O_{62}]^{9-}$ **1**	−0.170
$[P_2W_{18}O_{62}]^{6-}$	+0.141 [b]
$[NaP_5W_{30}O_{110}]^{14-}$ **4**	−0.149 [c]
$[H_7P_8W_{48}O_{184}]^{33-}$ **2**	−0.629 [d]
$[Nb_2W_4O_{19}]^{4-}$	−1.01 [e]
$[PW_9O_{34}]^{9-}$	−0.559 [f]
$[P_2W_{12}O_{46}]^{12-}$	−0.149 [f]
Hydrosulfide (S/HS^-)	−0.316
Polysulfide (nS/S_n^{2-}) [g]	−0.428
Sulfur $(S_2O_3^{2-}/S_8)$	+0.234

[a] Standard reduction potentials vs. SHE; values for the sulfide species taken from [32]; values calculated for pH 8.5 from standard potential given.
[b] Value taken from [footnote 5, see text]; pH = 5.
[c] Taken from ref. [11]; pH = 10.
[d] Taken from ref. [23].
[e] Taken from ref. [19].
[f] Taken from ref. [35].
[g] Reported value is for S^{2-}.

ference in the potential of **1** and hydrosulfide. The potential of **1** was measured by cyclic voltammetry at pH 8.5 (see Fig. 2) and it exhibited a voltammagram very similar to the one reported for the parent species $[P_2W_{18}O_{62}]^{6-}$ [33] with three one-electron, waves. It is evident from the values reported for **1** that the potential could be negatively shifted by as much as 150 mV and the catalyst would still be capable of sulfide oxidation. Since the catalyst is accumulating in the reduced state [7], shifting the potential to a more negative value would favor the re-oxidation of reduced catalyst and speed the rate of production of sulfur. The third point is the magnitude of the shift in the redox potential between **1** and the parent Dawson compound. The substitution of three niobium atoms for tungsten atoms in the Dawson structure yields a 5:1 W:Nb ratio. This ratio resulted in a redox shift of −0.311 V. This imparts some predictive power for the effect of niobium substitution on the redox potential for other classes of mixed addenda polyoxometalates.

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[7] Accumulation of catalyst in the reduced state is evidenced by the persistence of the characteristic heteropoly blue color throughout the reaction with sulfide.

Table 2
Aerobic oxidation of hydrogen sulfide catalyzed by base-stable polyoxometalates [a]

Catalyst [b]	Turnovers [c]	Notes [d]
$[Nb_3P_2W_{15}O_{62}]^{9-}$	17	Catalyst ≈95% intact after reaction
$[Nb_2W_4O_{19}]^{4-}$	8.8	Stability not assayed
$[H_7P_8W_{48}O_{184}]^{33-}$	135 [e]	Catalyst completely destroyed
$[Zn_4P_2W_{18}O_{68}]^{10-}$	5.7	Zinc demetalates rapidly (as ZnS)
Versene	68	Catalyst mostly degraded

[a] Reaction conditions: 23°C, 1.0 atm O_2, 4 h. reaction time in a sealed system. Substrate: catalyst ratio ~ 110:1, phosphate buffer = 0.20 M, pH = 7.2. See Experimental section for other details.
[b] 15 μmol catalyst per reaction.
[c] Defined as 1/8 mole S_8/mole catalyst.
[d] State of catalyst after reaction assayed by FTIR and/or NMR spectroscopy; product purity assayed by elemental analysis.
[e] Reaction run with 0.1 mM catalyst due to solubility problems and catalyst precipitation.

3.2. Catalytic activity of base-stable polyoxometalates

Table 2 compares the activity of four structurally distinct polyoxometalates known to be stable in slightly basic aqueous media and gives the effect of the concentrated basic aqueous sulfide on the physical integrity of each complex; while
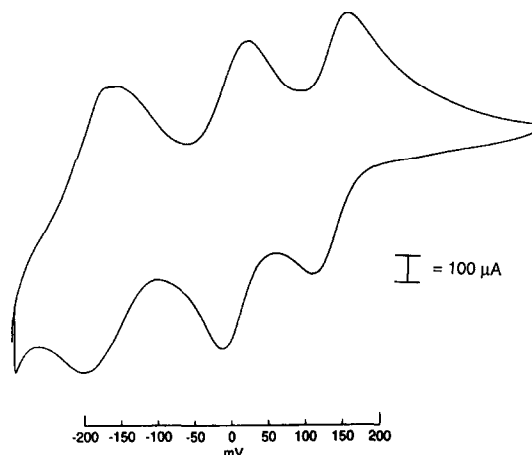

Fig. 2. Cyclic voltammagram of the *monomer* $TMA_{9-x}H_x[Nb_3P_2W_{15}O_{62}] \cdot nH_2O$. Conditions: 1.00 mM **1** in 0.10 M NaCl, reference electrode, Ag/AgCl, working electrode, glassy carbon, working solution was maintained at a slightly basic pH to insure no dimerization of the polyoxometalate.
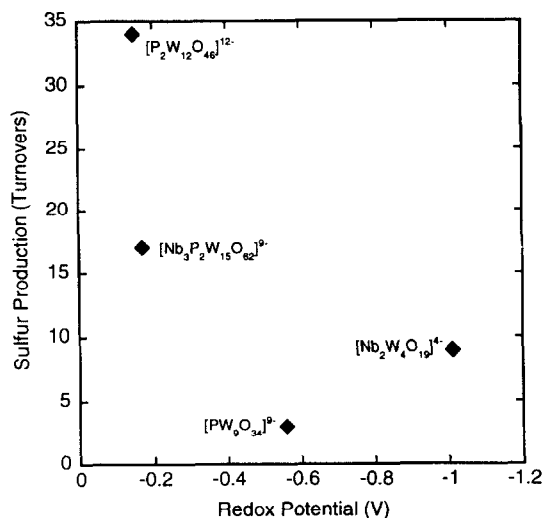
Fig. 3. Plot of the observed rate of turnover in reaction with sulfide as a function of the first-wave reduction potentials of selected polyoxometalates. All conditions are described in Table 2.

Fig. 3 plots the activity of a similar select ensemble of polyoxometalates. The results illuminate some salient points. The hexametalate, $[Nb_2W_4O_{19}]^{4-}$, consistent with the redox potentials (Table 1), exhibits little activity.

The selectivity for elemental sulfur in Eq. 1 catalyzed by 1 is 88% ± 4%. The remaining product was a mixture of higher thio-oxy anions (exact ratios were impossible to obtain). One possible explanation for this is that the more labile niobium-based oxygens could be involved in this overoxidation of the sulfide despite the lack of redox chemistry of the Nb^V centers themselves [13,34]. As Fig. 4 shows, there is minimal decomposition of 1 at early times under typical reaction conditions (approximately 10% after 50 turnovers).

A comparison of the activity of the remaining species also yields some interesting points. The highest activity encountered was exhibited by $[H_7P_8W_{48}O_{184}]^{33-}$, 2, while $[Zn_4P_2W_{18}O_{68}]^{10-}$, 3, exhibited the lowest. Both catalysts were completely destroyed over the course of the reaction. The initial activity exhibited by 3 was approximately two orders of magnitude below that for 2. This is understandable in view of the potentials of the most likely immediate degradation products. The fragmentation of 2, a cyclic tetramer, into its

subunits yields four equivalents of the lacunary polyanion $[P_2W_{12}O_{68}]^{12-}$. Under the catalytic aerobic oxidation conditions, 3 is cleanly demetalated to form ZnS producing the trivalent species $[PW_9O_{34}]^{9-}$. This species possesses a potential too negative for the facile oxidation of sulfide leading to the low production of elemental sulfur. The sulfur production values for $[P_2W_{12}O_{68}]^{12-}$ and $[PW_9O_{34}]^{9-}$ were obtained from the parent species.

3.3. Effect of buffer on catalysis

Table 3 shows the effect of differing buffer systems on the total production of sulfur as catalyzed by both chelated iron and polyoxometalates. The polyoxometalate catalyst employed, $K_{14}[NaP_5W_{30}O_{110}]$, 4, was used because of its high stability under the reaction conditions. The first point of note is the profound effect the buffering medium has on the reaction. Under otherwise identical reaction conditions, the rate of catalytic sulfide oxidation (S_8 production) is 5.4 times faster in borate buffer than in carbonate buffer at parity of buffer concentration and pH. As anticipated, the buffer ions are likely non-innocent. Buffer species could, in principal, participate in the catalysis. It is also noted that none of the buffers employed, however, have redox potentials
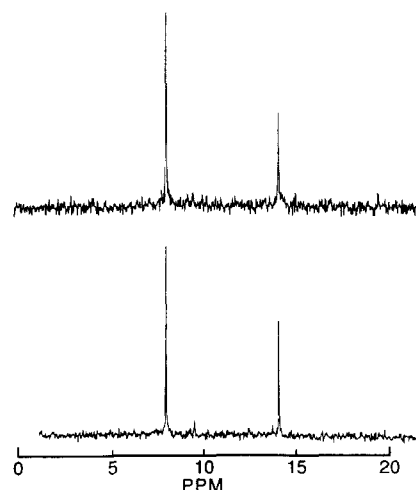

Fig. 4. ^{31}P NMR spectra of 1 (top spectrum) before reaction and (bottom spectrum) after approximately 20 turnovers. All conditions are described in the Experimental section.

Table 3
Effect of buffer on catalytic activity [a]

Catalyst [b]	Buffer	Turnovers [c]	Notes [d]
Versene	PO_4^{3-}	68	Catalyst decomposed in all reactions
Versene	CO_3^{2-}	56	Sulfur purity $\approx 95\%$
Versene	$B_4O_{10}^{2-}$	34	
Versene	OH^-	35	$pH > 9$ after reaction
$[NaP_5W_{30}O_{110}]^{14-}$	PO_4^{3-}	40	Catalyst 100% intact in all reactions
$[NaP_5W_{30}O_{110}]^{14-}$	CO_3^{2-}	9.0	Sulfur purity $> 99.5\%$
$[NaP_5W_{30}O_{110}]^{14-}$	$B_4O_{10}^{2-}$	49	
$[NaP_5W_{30}O_{110}]^{14-}$	OH^-	10	$pH > 9$ after reaction

[a] Reaction conditions: 23°C, 1.0 atm O_2, 4 h reaction time in a sealed system. Substrate: catalyst ratio $\sim 110{:}1$, buffer concentration = 0.20 M, pH = 7.2.
[b] 15 μmol catalyst per reaction.
[c] mole $1/8$ S_8/mole catalyst.
[d] State of catalyst after reaction assayed by FTIR and/or NMR spectroscopy; product purity assayed by elemental analysis. See text for details.

in the region of study. The nature of the buffer could also affect the rate of the background reaction between sulfide and oxygen itself. Finally, the buffer may affect the rate and mechanism of association of the elemental sulfur being generated. If the sulfur product flocculates and precipitates faster, it is less likely to undergo subsequent reaction to a mix of undesirable overoxidation products.

3.4. Rate behavior and mechanism of the reduction of 1 by sulfide

The rate behavior of the oxidation of sulfide by a representative base-stable polyoxometalate, 1, was examined in detail. We focus on the sulfide oxidation itself, Eq. 2, as the mechanism for the re-oxidation of reduced polytungstophosphates in aqueous media by O_2, Eq. 3, the second step in the two-step catalytic process, has recently been studied [28,29]. Eq. 6 gives the overall stoichiometry for the reduction of 1 by sulfide.

$$HS^- + 2[Nb_3P_2W_{15}O_{62}]^{9-}$$
$$\underset{(1)}{}$$

$$\rightarrow 1/8S_8 + H^+ + 2[Nb_3P_2W_{15}O_{62}]^{10-} \quad (6)$$
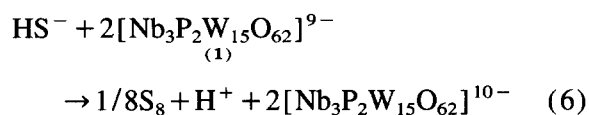
The highly complex nature of the reaction enforced some physical strictures on the collection of this rate data. The higher reactivities of the initial products [14], e.g. polysulfides, as well as

problems related to the precipitation of sulfur product demanded that conversions be kept low. As a consequence, initial rate methods gave the most reliable data. Fig. 5 gives Van't Hoff log–log plots for the initial rate of Eq. 6 with respect to both substrate (A) and catalyst (B). In A, five reactions were run at varying concentrations of sulfide establishing a first order dependence in this substrate. In B, five reactions were run at varying concentrations of 1 establishing a first order dependence in catalyst as well. Both plots give near integral values for the order with a high goodness-of-fit correlation providing validation for these reaction orders utilizing this methodology. The first order dependence in substrate was expected, but the first order dependence in 1 was mildly surprising in light of the known second order dependence found for reaction with $K_{14}[NaP_5W_{30}O_{110}]$ [14]. Oxidative titration data indicates that only one electron is being transferred per catalyst molecule [8] (1.14 ± 0.22 e$^-$/molecule) lending credence to a simple bimolecular reaction between catalyst and substrate. Fig. 6 shows the complex dependence on pH (A) and the speciation of sulfide (B) as a function of pH. Sixteen individual experiments were run over the

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[8] As an unavoidable consequence of the conditions of the oxidative titration the pH of the catalyst containing solution was lowered to a regime where dimerization of 1 typically occurs. This could affect the reliability of the data obtained.
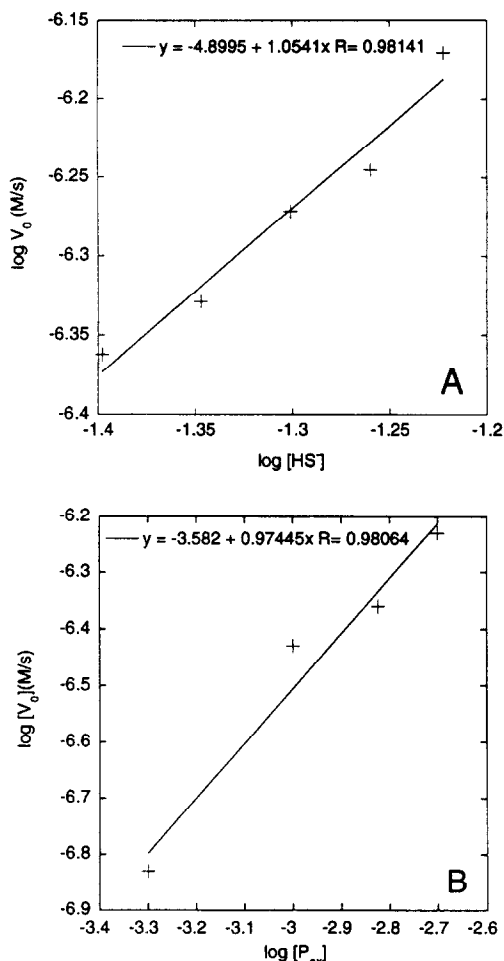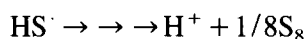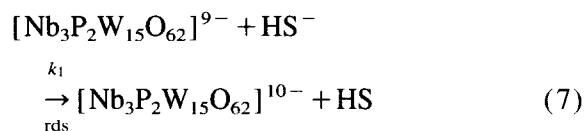
Fig. 5. Log–log plots for the initial rates of reaction of $[Nb_3P_2W_{15}O_{62}]^{9-}$ with HS^-: (A) dependence on concentration of HS^- and (B) dependence on concentration of 1. The equations in each box are the best fit lines with their correlation coefficients. All conditions are described in the Experimental section.

indicated pH range and the points, as shown, were very reproducible. The magnitude of the slope, however, 0.4, indicates that the role of protons in the reaction is complex, with protons most likely being involved in the reaction at more than one juncture. One general consideration of this behavior is that the rate is changing in a direction opposite to that expected based on substrate protonation considerations alone. That is, as pH increases so does the concentration of the more reducing deprotonated sulfide species, but the overall rate decreases.

A mechanism consistent with the data is given in Eqs. 7 and 8 and the rate law derived from this

mechanism is given as Eq. 9. While the possibility of simultaneous two-electron reduction exists, this is quite unlikely considering the oxidative titration data and the redox potentials involved.

$$[Nb_3P_2W_{15}O_{62}]^{9-} + HS^-$$

$$\xrightarrow[\text{rds}]{k_1} [Nb_3P_2W_{15}O_{62}]^{10-} + HS \qquad (7)$$

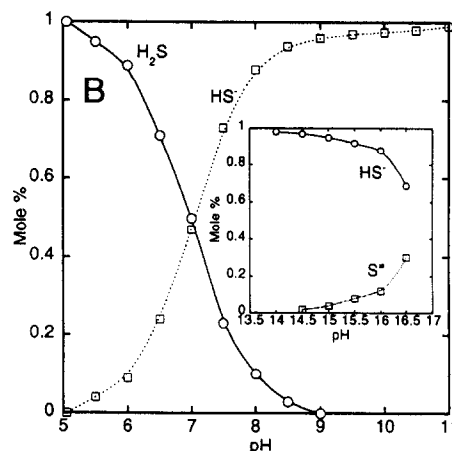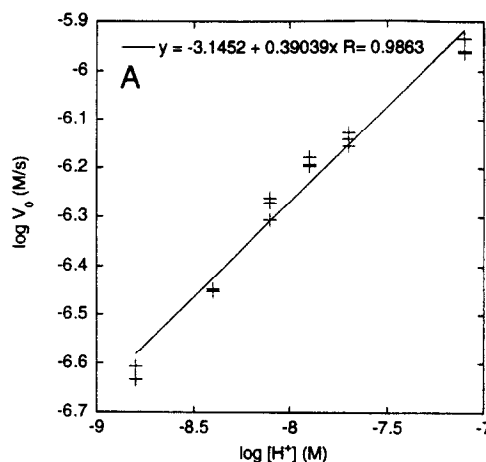$$HS^\cdot \rightarrow \rightarrow \rightarrow H^+ + 1/8 S_8$$

(Many fast redox and catenation reactions)

$$(8)$$

Fig. 6. (A) The pH dependence of the initial rate for the reduction of $[Nb_3P_2W_{15}O_{62}]^{9-}$, 1, with HS^- (Eq. 17) from pH 7.0 to 9.0; (B) acid–base speciation of sulfide from pH 5 to 17. pK_{a2} value taken to be 17 ± 1 [36]. All conditions are described in the Experimental section.

$$+ d[S_8] / dt = k_1 [Nb_3P_2W_{15}O_{62}]^{9-} [HS^-] \quad (9)$$

A more complete rate expression would account for both protonation state (for both catalyst and substrate) and the fate of the initial oxidation product, HS^-, but it is doubtful if such an unwieldy expression would reveal more insight into the reaction than this simplified version offers.

Acknowledgements

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