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A new synthetic method for MS_4^{2-} (M = Mo, W). Evidence for catalysis of aqueous MO_4^{2-}/MS_4^{2-} interconversion by thiols

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Abstract

The reaction of aqueous molybdate with sulfide leading to $[MoO_{4-x}S_x]^{2-}$ (x = 1–4, hereafter referred to as S_1–S_4) in basic solution is greatly accelerated by thiols, as are the reverse hydrolyses. In aqueous solution buffered at pH 9, a 50-fold molar excess of 2-mercaptoethanol over molybdenum increased the rate of formation of S_1 from molybdate and sulfide by at least a factor of 10^4 and also substantially increased the rates of $S_2 \rightarrow S_3 \rightarrow S_4$ conversion. Dithiols behaved similarly to 2-mercaptoethanol in accelerating the formation of S_1–S_4 from molybdate and sulfide. The same molar excess of 2-mercaptoethanol over molybdenum was found to increase the rates of hydrolyses of S_2 and S_3 by $\approx 10^2$ and $\approx 10^1$, respectively, at pH 9. Thus, in basic aqueous solution, thiols appear to function as catalysts of oxo/sulfido ligand substitution on $[MoO_{4-x}S_x]^{2-}$. Similar accelerating effects of thiol were observed on reactions of aqueous tungstate with sulfide. Based on these results a new method for the preparation of $(NH_4)_2[MS_4]$ (M = Mo, W) was developed; this method combines aqueous MO_4^{2-} and lithium sulfide in the presence of 2-mercaptoethanol in NH_3/NH_4^+ buffer at pH 9.6. These results may be relevant to the biological chemistry of molybdate and tungstate.

Introduction

The reactions between aqueous molybdate or tungstate and sulfide leading to $[MO_{4-x}S_x]^{2-}$ (M = Mo, W; x = 1–4) were studied as long ago as 1826 [1], and the biological importance of this reaction in the case of M = Mo has become increasingly evident in recent years. Molybdenum–sulfido species are known to exist at the active sites of enzymes such as nitrogenase and xanthine oxidase from organisms in which molybdate is the only known biological uptake and transport form of molybdenum [2–4]. Molybdate has been used to activate nitrogenase *in vitro* in the presence of a specific combination of bacterial extracts [5]. $[MoS_4]^{2-}$, believed to be generated from molybdate and sulfide in the rumen, has been implicated in the copper–molybdenum antagonism in ruminants [1, 2].

Oxo/sulfido ligand substitutions on $[MO_{4-x}S_x]^{2-}$ (M = Mo, W; x = 0–4) are conceptually simple reactions. However, both the rate and extent of the reaction of aqueous molybdate with sulfide leading to $[MoO_{4-x}S_x]^{2-}$ (x = 1–4, hereafter referred to as S_1–S_4)** are highly dependent on conditions such as pH, ionic strength, and the presence of nucleophiles or counterions [1, 6]. For example, procedures for preparations of S_2, S_3 and S_4 from molybdate and sulfide invariably call for high concentrations of ammonia [1, 6, 7]. Although the rates of oxo → sulfido ligand substitutions on $[MoO_{4-x}S_x]^{2-}$ decrease with increasing pH [6], the strongly basic preparative conditions dissolve enough additional sulfide so that the oxo → sulfido ligand substitutions can proceed at appreciable rates and to appreciable extents, after which the ammonium salts of S_2, S_3 or S_4 can be isolated. The rate constants for these ligand substitutions decrease with increasing numbers of sulfido ligands on $[MoO_{4-x}S_x]^{2-}$ [1, 6], and these successive decreases allow isolation of the intermediate substitution products, S_2 and S_3. Several previous studies have demonstrated that S_1–S_4 have distinctive Vis/near-UV absorption spectra and that, therefore, the oxo/sulfido ligand substitution reactions can be conveniently followed and quan-

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**Abbreviations used: S_1, $[MoO_3S]^{2-}$; S_2, $[MoO_2S_2]^{2-}$; S_3, $[MoOS_3]^{2-}$; S_4, $[MoS_4]^{2-}$; TAPS, sodium 3-[[tris(hydroxymethyl)methyl]amino]propane-sulfonate; 2-ME, 2-mercaptoethanol.

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titated spectrophotometrically [1, 6, 7]. These statements all apply qualitatively to the corresponding thiotungstates, which form more slowly than the thiomolybdates [1].

Despite the long history of the reaction between aqueous molybdate and sulfide and its biological relevance, the effects of thiols on this reaction have apparently never been examined. In the present study we have examined the effect of thiols on the reactions of aqueous molybdate and tungstate with sulfide leading to $[MO_{4-x}S_x]^{2-}$ (M = Mo, W; $x = 1$–4) and on the hydrolyses of thiomolybdates in basic solution.

Experimental

Reagents were of the highest purity commercially available and were used without further purification. All manipulations were carried out at room temperature under a purified Ar atmosphere in either Schlenk-type glassware or septum-capped vials attached to a vacuum manifold. Stainless steel tubing and gas-tight syringes were used to transfer reagents and samples. Aqueous solutions were prepared from distilled, deionized water. Unless otherwise specified the buffer was 0.3 M TAPS/KOH pH 9.05. Elemental analyses were performed by either the Department of Inorganic and Metallo-Organic Chemistry, University of Milan or by the Pascher Mikroanalitisches Laboratorium, Bonn, FRG.

$(NH_4)_2[MoO_2S_2]$ and $Cs_2[MoOS_3]$ were prepared by previously described methods [7]. D, L-Dihydrolipoate was prepared as previously described [8], and the concentration of its buffered solution was determined iodometrically. Buffered stock solutions of 2–3 M sodium sulfide were prepared no less often than weekly from washed crystals of the nonahydrate; the sulfide concentrations were determined either iodometrically or with Ellman's reagent [9] at least every other day.

$(NH_4)_2[MoS_4]$

Forty milliliters of a saturated solution of ammonium chloride in water at 50 °C were filtered while hot and diluted with half the volume of concentrated ammonium hydroxide. The resulting ammonia buffer had a pH of ≈9.6. All subsequent steps were performed anaerobically. Ammoniun molybdate (2.0 g, 11 mmol) and 2.0 ml (28 mmol) of 2-mercaptoethanol were dissolved in 10 ml of the ammonia buffer at 50 °C. Lithium sulfide (1.8 g, 39 mmol) was dissolved separately in 10 ml of ammonia buffer at room temperature. After 30 min the two solutions were combined and stirred overnight at 50 °C. Upon cooling to −18 °C (at which temperature the mixture did not freeze), orange–brown crystals separated from the deep yellow solution in 24–72 h. The large needle-like crystals were collected by filtration, washed with 5 ml of ice-cold water and dried *in vacuo*. The yield was 1.6 g (64%). *Anal.* Calc. for $H_8N_2MoS_4$: H, 3.08; N, 10.8. Found: H, 3.11; N, 10.9%. A similar yield of analytically pure material was obtained when the cheaper but extremely deliquescent sodium sulfide nonahydrate was substituted for lithium sulfide. The compound prepared with either sulfide salt gave an identical absorption spectrum (water) λ_{max} (nm) (ϵ ($M^{-1}cm^{-1}$)): 467 (12 100), 317 (15 100), 241 (19 800) (literature values [7]: 467 (11 850), 316 (16 750), 241 (24 700)).

$(NH_4)_2[WS_4]$

In 30 ml of the same ammonia buffer used for the synthesis of $(NH_4)_2[MoS_4]$, 2.5 g (10 mmol) of tungstic acid were dissolved at 70 °C followed by 6 ml (85 mmol) of 2-mercaptoethanol. Separately, 7.2 g (150 mmol) of Li_2S were suspended in 10 ml of ammonia buffer. After 30 min at 70 °C, the two solutions were combined and stirred at 70 °C for 48 h. A white–yellow cloudiness was removed by filtration of the hot solution through a Celite pad, and the clear filtrate was left at −18 °C for 2 days. Dark yellow crystals formed, which were collected by filtration of the cold solution, washed with 2-propanol and ether and dried under dynamic vacuum. Yield 1.6 g (46.3%). *Anal.* Calc. for $WN_2S_4H_8$: H, 2.30, N, 8.07; S, 36.89. Found: H, 2.32; N, 8.00; S, 35.71%. Absorption spectrum (water) λ_{max} (nm) ($\epsilon(M^{-1}cm^{-1})$): 397 (19 800); 278 (25 400); 217 (41 400) (literature values [7]: 397 (19 600); 277 (24 500)).

Physical measurements

All measurements were made at room temperature. Electronic absorption spectra were obtained on a Perkin-Elmer model 544 double-beam scanning spectrophotometer or a 3840 diode array spectrophotometer using 0.5 mm pathlength cylindrical quartz cuvettes. These cuvettes were fitted with tight-fitting rubber septa, and the samples therein were maintained under an Ar atmosphere during recording of spectral time courses. The total molybdenum concentration in the reaction mixtures was normally fixed at ≈4 mM. Concentrations of S_1–S_4 in reaction mixtures at various times were calculated from absorption spectra using either our own or published extinction coefficients [6, 7] and sets of simultaneous equations. Observed first order rate constants were calculated from standard semi-log plots of fractional completion of reaction (assuming complete conversion to S_4 at infinite time) versus time. These plots were linear to at least 75% completion. The sets of simultaneous equations referred to above were used to determine concentrations.

Results

The addition of 100 mM sodium sulfide to a solution of 4 mM sodium molybdate buffered at pH 9 did not produce absorbance changes indicative of S_1–S_4 formation for at least 23 days at room temperature under an Ar atmosphere. Only a very faint yellow color due to a broad absorption at ≈300 nm developed over this time period. This absorption, which was observed in a previous study [6], is possibly due to some oxidation of sulfide and formation of polysulfides [10, 11]. Similarly, when excess 2-mercaptoethanol (2-ME) was mixed with sodium molybdate at pH 9, no changes in the absorption spectrum were observed for at least several days. However, addition of excess sulfide to the molybdate/2-ME solution resulted in the spectral changes shown in Fig. 1. These spectral changes are indicative of successive formation of S_1–S_4 [1, 6]. For example, the 2 min spectrum is due predominantly to S_1 (λ_{max} 292 nm) with some contribution from S_2 (λ_{max} 288, 393 and 320 nm), whereas the 24 h spectrum is due to a mixture of S_3 and S_4. S_3 has its most prominent absorption maximum at 393 nm, whereas the buildup of S_4 is most readily observed as the increase in absorbance of the peak at 467 nm [1, 6]. The appearance of S_1 after just 2 min in the spectrum of Fig. 1 and its failure to appear after 23 days in the absence of 2-ME means that this thiol accelerates the reaction of molybdate with sulfide leading to S_1 by a factor of at least 10^4 under the conditions of Fig. 1. Substitution of dithiothreitol or D, L-dihydrolipoate for 2-ME at the same total RSH concentration resulted in the formation of $S_1 \rightarrow S_4$ on time-scales similar to that shown in Fig. 1. Experiments conducted at 50, 200 and 400 mM 2-ME showed that the observed first order rate constant for S_4 formation increased with increasing 2-ME concentration, but the reaction appeared to be less than first order in thiol. This behavior may be due to the fact that the pK_a of 2-ME (9.45 [12]) is near pH 9. Increasing the sulfide concentration from 100 to 200 mM did not affect the rate of S_4 formation.

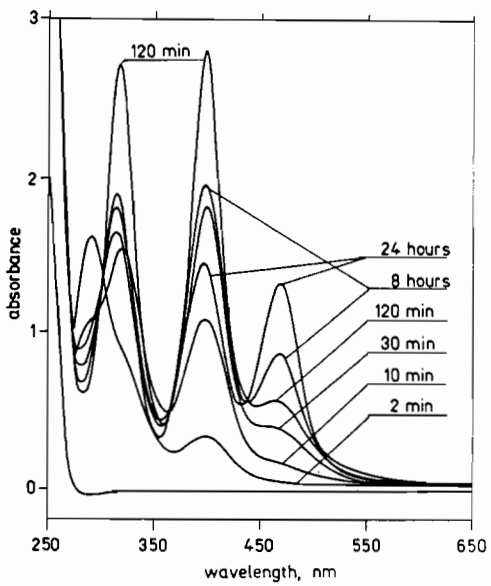

Fig. 1. Absorption spectral time courses of buffered (0.3 M TAPS pH 9.0) aqueous solutions containing 4 mM sodium molybdate and 200 mM 2-mercaptoethanol. The times listed in the Figure are those after addition of sodium sulfide to a concentration of 100 mM. The spectrum of lowest intensity is of the mixture prior to addition of sulfide.

Starting with the 120 min spectrum in Fig. 1, isosbestic points are observable at ≈430, 360 and 300 nm. These isosbestic points are indicative of $S_3 \rightarrow S_4$ interconversion [1, 6]. From absorption spectral time courses such as those of Fig. 1 and a set of simultaneous equations, the time courses for formation of S_2, S_3 and S_4 were calculated. Figure 2 shows representative results of such calculations. As implied by the isosbestic points referred to above, the concentration time course shows that after about 30 min nearly all of the molybdate has been converted to S_3, and the remaining time course involves only $S_3 \rightarrow S_4$ conversion.

Use of the same concentrations of reagents as for Fig. 1, but substituting $Cs_2[MoOS_3]$ for sodium molybdate, resulted in a spectral time course for S_4 formation very similar to the latter stages of the time course in Fig. 1. Similarly, substitution of $(NH_4)_2[MoO_2S_2]$ for sodium molybdate under the conditions of Fig. 1 resulted in rapid formation of S_3 (0.05 min^{-1}) followed by much slower formation of S_4 (0.02 h^{-1}), the latter rate being very similar to that starting with $Cs_2[MoOS_3]$ (spectra not shown). In the absence of thiol, addition of excess sulfide to aqueous solutions of preformed S_2 or S_3 at pH 9 resulted only in gradual decreases in absorbance throughout the visible region,

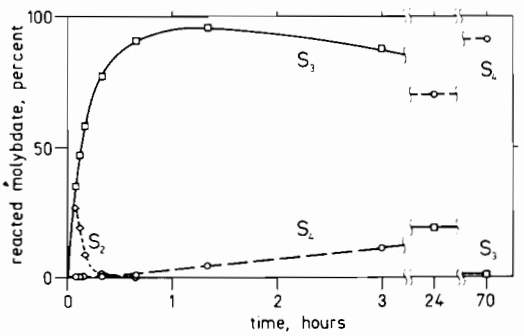

Fig. 2. Concentration time courses for formation of $[MoO_2S_2]^{2-}$ (S_2), $[MoOS_3]^{2-}$ (S_3) and $[MoS_4]^{2-}$ (S_4). Spectra of buffered (0.3 M TAPS pH 9.0) aqueous solutions containing 4 mM sodium molybdate and 200 mM 2-mercaptoethanol were recorded at the times indicated by the data points after addition of sodium sulfide to a concentration of 100 mM. Concentrations of S_2 (◇), S_3 (□) and S_4 (○) were calculated from absorbance data and a set of simultaneous equations.

which we attribute to reduction of S_2 or S_3. These absorbance decreases occurred on a slower time-scale than did the $S_2 \rightarrow S_3$ and $S_3 \rightarrow S_4$ conversions, respectively, in the presence of 2-ME and sulfide. Thus, in the reaction system with thiols described here, the behaviors of preformed S_2 and S_3 are fully consistent with their being intermediates on the pathway to S_4 starting from molybdate.

Figures 3 and 4 show that 2-ME at pH 9 also accelerated the hydrolysis of S_2 and its subsequent equilibration to a mixture of S_1–S_4. The isosbestic points in Figs. 3(a) and (b) at ≈306 nm (indicated by the upward arrows) agree with the published isosbestic point for S_2 and S_1 [5], and comparison of the two time courses indicates that hydrolysis of S_2 to S_1 is ≈160 times faster in the presence of 2-ME. Note, for example, that the 15 s spectrum in Fig. 3(b) (with thiol) most closely resembles the 40 min spectrum in Fig. 3(a) (without thiol). Figure 4 plots the concentration time course for S_2 equilibration in the presence of 2-ME. Solutions of $(NH_4)_2[MoO_2S_2]$ or $(Et_4N)_2[MoO_2S_2]$ invariably show contamination by S_1 and S_3 when examined by ^{95}Mo NMR spectroscopy [13–15]. The plot in Fig. 4 is consistent with contamination of our solution of S_2 by S_1 prior to addition of thiol, but such contamination would not affect our conclusion that 2-ME accelerates the hydrolysis of S_2.

Figure 4 shows that, in the presence of 2-ME, a decrease in S_1 concentration occurs after its initial increase. This decrease in $[S_1]$ is presumably due to the buildup of sulfide in the solution resulting from the initial $S_2 \rightarrow S_1$ conversion. This buildup leads to some $S_2 \rightarrow S_3$ conversion and $S_1 \rightarrow S_2$ back reaction. At about 20 min in Fig. 3(b) a second isosbestic point at ≈296 nm (indicated by the downward arrow) becomes visible; this isosbestic point agrees with that published for $S_2 \rightarrow S_3$ conversion [6]. Analogous experiments to those described in Figs. 3 and 4 showed that 2-ME also accelerates hydrolysis of S_3. Thus, starting from ≈3.5 mM S_3 and 200 mM 2-ME, approximately half of the S_3 was converted to a mixture of S_1, S_2 and S_4 in 1 h, whereas, in the absence of thiol the half-time for conversion of the same starting concentration of S_3 was ≈24 h. We have observed no hydrolysis of S_4 under our conditions in either the presence or absence of thiol for at least several hours. Thus, in the presence of 2-ME the hydrolysis rates decreased in the order $S_2 > S_3 > S_4$.

The results described above led us to develop a new method for preparation of $(NH_4)_2[MoS_4]$ which uses 2-ME to accelerate the formation of S_4 from aqueous molybdate. This preparative scale reaction, described in 'Experimental', yielded little or no S_4 if thiol was omitted. The analogous statements apply to the synthesis of $(NH_4)_2[WS_4]$ from aqueous tungstate except that

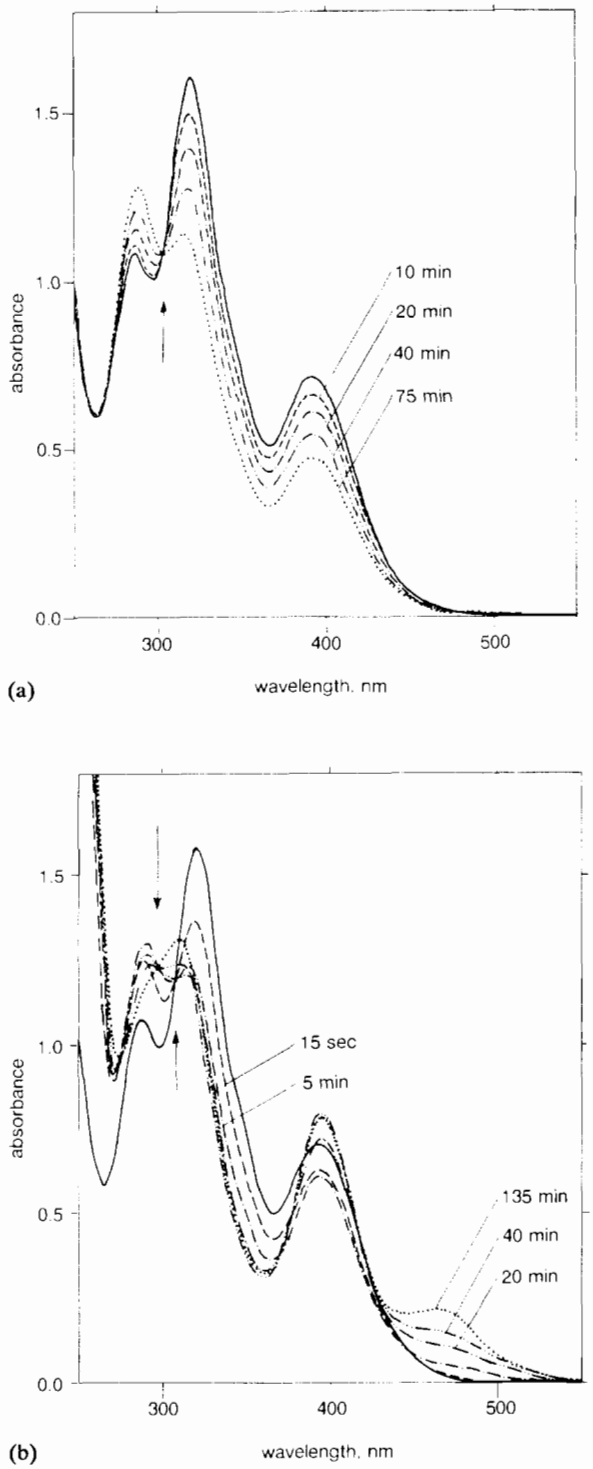

Fig. 3. Absorption spectral time courses for formation of $[MoO_{4-x}S_x]^{2-}$ ($x = 1$–4) starting from a buffered (0.3 M TAPS pH 9.0) aqueous solution of 4.25 mM $(NH_4)_2[MoO_2S_2]$ in the absence (a) and presence (b) of 200 mM 2-mercaptoethanol. Solid curves represent spectra obtained within 2 min of dissolution of $(NH_4)_2[MoO_2S_2]$, and in (b) prior to addition of 2-mercaptoethanol, which was added within 3 min of dissolution of $(NH_4)_2[MoO_2S_2]$. Times of spectral acquisition are indicated after dissolution of $(NH_4)_2[MoO_2S_2]$ in (a) and after addition of thiol in (b). Arrows indicate positions of isosbestic points.

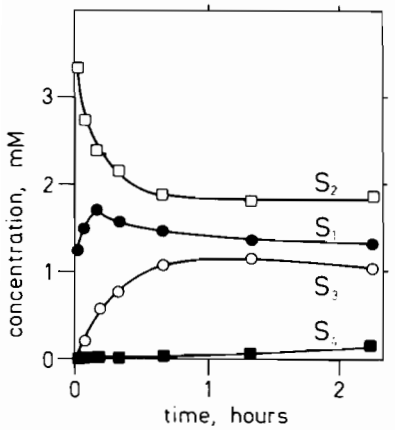

Fig. 4. Concentration time course for formation of $[MoO_{4-x}S_x]^{2-}$ ($x=1$–4 labelled as S_1–S_4) from $(NH_4)_2[MoO_2S_2]$ and 2-mercaptoethanol calculated from the absorption spectra of Fig. 3(b) and a set of simultaneous equations. Concentrations of S_1 (●), S_2 (□), S_3 (○) and S_4 (■) are plotted as a function of time elapsed after addition of 2-mercaptoethanol. The apparent zero time points were derived from the 15 s spectrum in Fig. 3(b). Some time points were calculated from spectra not shown in Fig. 3(b) for clarity.

longer reaction times and an excess rather than stoichiometric sulfide were required. When stoichiometric concentrations were used (i.e. 4 mol sulfide/mol tungstate) in an otherwise identical synthetic procedure, the distinctive absorption spectrum of WOS_3^{2-} [7] rather than WS_4^{2-} was evident in an acetonitrile solution of the isolated product.

Discussion

The purpose of the present study was to investigate the possibility that thiols can accelerate oxo/sulfido ligand substitutions on $[MO_{4-x}S_x]^{2-}$ (M=Mo, W) at a pH as near as possible to physiological but without interference from H^+, which is also known to accelerate these substitutions [6]. Our results show that at room temperature in aqueous solution buffered at pH 9, 2-ME in a 50-fold molar excess over molybdenum increases the rate of formation of S_1 from molybdate and excess sulfide by at least a factor of 10^4 and also substantially increases the rates of $S_2 \rightarrow S_3 \rightarrow S_4$ conversion. The contrast to the situation in the absence of thiols is striking: at pH 9 under anaerobic conditions, no formation of S_1–S_4 from molybdate and excess sulfide could be detected for at least 23 days at room temperature. Dithiols behave similarly to 2-ME in accelerating formation of S_1–S_4 from molybdate and sulfide. The same excess of 2-ME increases the rates of hydrolyses of S_2 and S_3 by $\approx 10^2$ and $\approx 10^1$, respectively, at pH 9. Thus, thiols appear to function as catalysts of oxo/sulfido ligand substitutions on $[MoO_{4-x}S_x]^{2-}$. The rates of both formation and hydrolysis of $[MoO_{4-x}S_x]^{2-}$ in the presence of 2-ME were found to generally decrease with increasing numbers of sulfido ligands, in agreement with previous studies conducted in the absence of thiols [1, 6]. Our observation of significantly slower oxo→sulfido ligand substitution on WO_4^{2-} than on MoO_4^{2-} also agrees with previous observations in the absence of thiols [1]. These same trends suggest that thiol does not dramatically change the mechanism of oxo/sulfido ligand substitutions on $[MO_{4-x}S_x]^{2-}$. In the case of M=Mo, tetrahedral-to-octahedral transformation of the coordination sphere, perhaps induced by protonation of an oxo ligand, followed by associative substitution of HS^- or H_2O has been suggested [6]. It is possible that thiols promote such a tetrahedral-to-octahedral transformation via formation of transient thiolate–Mo(VI) complexes. Low formation constants for these complexes would explain our failure to detect them in this work and why excess thiol is required to observe appreciable rate accelerations. We also cannot rule out a mechanism involving transient reduction of Mo(VI) by thiol [16, 17].

A kinetic study by Harmer and Sykes [6] found that, near pH 9, high concentrations of NH_3/NH_4^+ (>0.5 M) were required to achieve appreciable formation of S_4 from S_3 even with a large excess of sulfide. We have confirmed that NH_3/NH_4^+ at pH 9 (0.3 M TAPS) does accelerate the formation of S_1–S_4 from molybdate and sulfide, but less efficiently than does 2-ME [18]. Therefore, ammonia could play the same role as thiolate in accelerating oxo/sulfido ligand substitutions on $[MO_{4-x}S_x]^{2-}$. We have combined the accelerating effects of NH_3/NH_4^+ and 2-ME at pH 9.6 in a new method for preparation of $(NH_4)_2[MS_4]$ (M=Mo, W) from MO_4^{2-} and sulfide which avoids use of the highly toxic H_2S called for in all previous preparative methods [1, 6, 7].

In light of the results discussed above, it is noteworthy that the active site of xanthine oxidase contains a six-coordinate Mo(VI) with a terminal sulfido and two thiolate ligands, and that the ultimate source of this molybdenum is presumably molybdate [2]. Three enzymes are now known to contain six-coordinate W(VI) with at least two thiolate and two oxo but no sulfido ligands [19]. This lack of sulfido ligands is consistent with the lower rates and extents of sulfido ligand substitution on WO_4^{2-} observed in the present work. In any case our results clearly indicate that thiols can accelerate oxo/sulfido ligand substitutions on Mo(VI) and W(VI). Therefore, the possible occurrence of this effect of thiols at the active sites of molybdenum and tungsten enzymes must be considered.

Supplementary material

A listing of extinction coefficients and sets of simultaneous equations used to calculate concentrations of $[MoO_{4-x}S_x]^{2-}$ ($x=1$–4) from absorbance data (2 pages) may be obtained upon request from the corresponding author.

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