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Kinetics of the Interconversion of Sulfido- and Oxomolybdate(VI) Species $MoO_xS_{4-x}^{2-}$ in Aqueous Solutions

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Kinetic studies are reported for the formation and aquation of tetrahedral molybdate(VI) species, $MoO_xS_{4-x}^{2-}$, at 25 °C, $I = 0.50$ M (NaCl), and pH 8.2–10.2 (NH_3/NH_4^+ buffer). Rate constants ($M^{-2}\ s^{-1}$) obtained for the formation reactions by reacting the appropriate molybdate $MoO_xS_{4-x}^{2-}$ species with H_2S, rate law $k[MoO_xS_{4-x}^{2-}][HS^-][H^+]$, are in the range $k_{01} = 4 \times 10^9$ to $k_{34} = <1.6 \times 10^6$, where subscripts indicate the number (initial and final, respectively) of coordinated sulfides. Rate constants for aquation (s^{-1}), $k_{10} = 6.5 \times 10^{-3}$, $k_{32} = (3–6) \times 10^{-5}$, and $k_{43} = 1.6 \times 10^{-6}$, indicate a trend to smaller values the more sulfide ligands present. The aquation of $MoOS_3^{2-}$ was also studied at pH 3.6–5.6 (acetate buffer). The presence of sulfide ligands does not in these reactions give rise to a labilization effect. Results are explained in terms of the larger S^{2-} crowding the reaction site and making associative substitution more difficult. Information has also been obtained concerning the magnitude of stepwise (formation) equilibrium constants.

Although tetrahedral sulfido- (i.e., thiolato-) molybdenum(VI) complexes MoS_4^{2-}, $MoOS_3^{2-}$, $MoO_2S_2^{2-}$, and MoO_3S^{2-} have been known for some time[1,2] kinetic and mechanistic aspects of their formation (from MoO_4^{2-}) and interconversion have not been studied. All except MoO_3S^{2-}, which is difficult to isolate in the pure state,[3] are well characterized as crystalline solids. X-ray crystal studies of $(NH_4)_2[MoS_4]$[4] and $Cs_2[MoOS_3]$,[5] as well as K_2MoO_4,[6] have been reported. Surprisingly few quantitative aqueous solution studies with H_2S as a reactant are to be found in the literature, and at the outset we experienced some difficulty in defining and implementing conditions appropriate to this study. Under acid conditions the reactions of $Ru(NH_3)_5H_2O^{2+}$ (substitution)[7] and CrO_4^{2-} (redox)[8] with H_2S have been reported. Aquation and anation (NCS^-) studies on $Cr(H_2O)_5SH^{2+}$ have also been described.[9]

Experimental Section

Preparations of Complexes. These were essentially as described previously in the literature.[10] Thus for preparation of the MoS_4^{2-} complex H_2S was bubbled through a solution of ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (5 g), H_2O (15 mL), and concentrated NH_3 (50 mL) for ca. 10 min. During this time the solution became yellow and then dark red. Brown-red crystals formed which were filtered off, washed with H_2O (0 °C) and alcohol, and then dried in vacuo. This and other samples were stored under N_2. Anal. Calcd for $(NH_4)_2[MoS_4]$: H, 3.1; N, 10.7; S, 49.8. Found: H, 3.1; N, 10.8; S, 49.3. A sample of $MoO_2S_2^{2-}$ was obtained by bubbling H_2S for 15 min through a solution of ammonium molybdate (5 g), H_2O (5 mL) and concentrated NH_3 (30 mL) at ca. 5 °C. A yellow solid was obtained. This was washed with H_2O (0 °C), alcohol, and diethyl ether. Anal. Calcd for $(NH_4)_2[MoO_2S_2]$: H, 3.6; N, 12.4; S, 27.8. Found: H, 3.5; N, 12.3; S, 28.1. The procedure for formation of the $MoOS_3^{2-}$ complex was to bubble H_2S through a solution containing $(NH_4)_2[MoO_2S_2]$ (ca. 5 g) and CsCl (1:4 mole ratio) in 100 mL of H_2O at 5 °C. After 5 min, the solution became an orange color, and a solid was obtained. This was filtered off, washed with H_2O (0 °C) and alcohol, and dried in vacuo. Details of the UV–visible spectrum (in H_2O) were in agreement with published values. Spectra of $MoO_xS_{4-x}^{2-}$ species are shown in Figure 1. The complex MoO_3S^{2-} is difficult to isolate in the pure state, and the spectrum given was deduced from absorbance measurements on equilibrated MoO_4^{2-}/H_2S solutions as described below.

Other Materials. AnalaR grade sodium molybdate (Na_2MoO_4) and sodium chloride were used without further purification. Buffers were made up from commercially available AnalaR NH_4Cl and NH_3 (acid dissociation pK_a of NH_4^+ ca. 9.3, where NH_3 was added to NH_4Cl (0.25 M) to give the required pH (8.0–10.5)) and from sodium acetate/acetic acid (pK_a of acetic acid ca. 4.8 (pH range 3.5–6.0)). Cylinder hydrogen sulfide (Air Products) was used without further purification.

Measurement of pH. A Radiometer (PHM 4) meter fitted with a combined electrode (GK2322C) was calibrated at pH 9.2 and 7.0 by using appropriate buffer tablets.

Procedure. All solutions were deoxygenated by using N_2, serum caps, and 2-mm gauge Teflon tubing techniques (use of steel needles resulted in brown precipitates on introducing H_2S). Without this precaution solutions of H_2S and buffer gave absorbance changes at ca. 300 nm within a few minutes. Saturated solutions of H_2S in H_2O were prepared fresh each day, and the concentration (0.095 M at 25 °C) was determined by iodometric methods. The H_2S stock solution was diluted (microsyringes) into already air-free solutions as required. For studies on the formation of MoS_4^{2-} from $MoOS_3^{2-}$ higher H_2S concentrations were obtained by using a stock solution of NH_3 (0.65 M), NH_4^+ (0.25 M), and NaOH (0.50 M) saturated with H_2S (ca. 1.1 M by titration). A pale yellow coloration (λ_{max} ca. 300 nm) which slowly forms did not effect the magnitude of rate constants in runs commenced during a 4-h period following preparation of this stock solution. Tris, cacodylate, and collidine buffers were found to be unsatisfactory presumably due to side reactions. With a 0.25 M NH_3/NH_4^+ buffer, pH's in the range 9.2–10.2 were found to be constant (±0.02) throughout the runs. The complexes $MoO_2S_2^{2-}$, $MoOS_3^{2-}$, and MoS_4^{2-} gave precipitates of MoS_2 on treatment with 0.1 M HCl. Anal. Calcd: S, 40. Found: S, 43.5. The liberated H_2S functions as a mild reducing agent for Mo(VI) under these conditions of acidity. Because of the distinctive UV–visible spectra, interconversion could be monitored by conventional spectrophotometry on Unicam SP500 and Perkin-Elmer 554 instruments. The absorptions of H_2S, MoO_4^{2-}, and NH_3/NH_4^+ are small at wavelengths >275 nm. First and second acid dissociation constants of H_2S give pK_a's of 7 and 14 (the latter possibly as low as 13), respectively.[11,12] The first protonation constant of MoO_4^{2-} is $3 \times 10^3\ M^{-1}$ at 25 °C and $I = 1.0$ M (NaCl).[13] Ionic strengths of reaction solutions were made up with $I = 0.50$ M (NaCl) except for studies on the formation of MoS_4^{2-}, when a value $I = 2.0$ M (NaCl) was required. The Mo(VI) reactant was in at least 10-fold excess, and plots of absorbance (A) changes $\log |A_\infty - A_t|$ against time were linear to >80% completion unless otherwise stated. First-order rate constants were obtained from the slope (×2.303).

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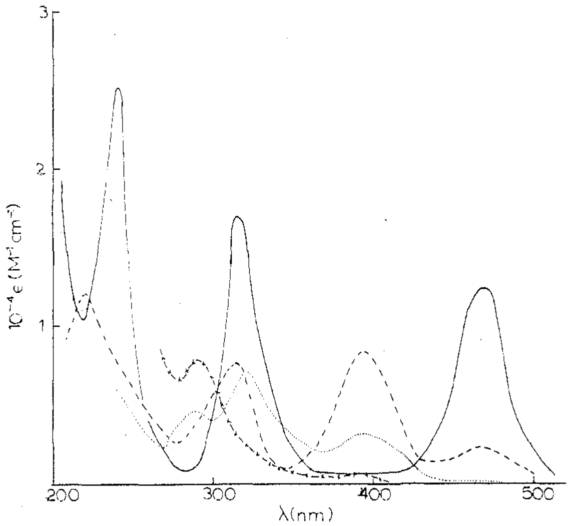

Figure 1. UV-visible spectra of MoO_3S^{2-} (-×-), $MoO_2S_2^{2-}$ (···), $MoOS_3^{2-}$ (---), and MoS_4^{2-} (—) in aqueous solution.

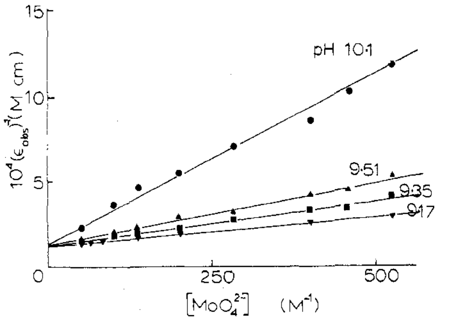

Figure 2. Determination of the equilibrium constant for formation of MoO_3S^{2-} from MoO_4^{2-} and H_2S in NH_3/NH_4^+ buffer (0.25 M) (I = 0.50 M (NaCl) at 25 °C). The reciprocal plot, eq 2, of absorption coefficient is against molybdate (in large excess).

Results

Equilibrium Constant for the Formation of MoO_3S^{2-}. The complex MoO_3S^{2-} is known to have an absorption maximum at ca. 289 nm, but the precise absorption coefficient has not been determined, a complicating feature being that $MoO_2S_2^{2-}$ has an absorption maximum at this same wavelength. Our experiments indicated an absorption maximum at 292 nm for MoO_3S^{2-}. Conditions were T = 25 °C, pH 9.2–10.2 (0.25 M NH_3/NH_4^+), I = 0.5 M (NaCl), $[H_2S] = 1.9 \times 10^{-4}$ M, and $[MoO_4^{2-}] = (0.25–2.0) \times 10^{-2}$ M. Absorbance changes were monitored during the equilibration process, and the maximum absorbance (yielding ϵ_{obsd}) was recorded at 292 nm. A subsequent decrease in absorbance corresponds to the formation of amounts of $MoO_2S_2^{2-}$. For equilibrium 1, expression 2 can

$$MoO_4^{2-} + H^+ + HS^- \overset{K_{01}}{\rightleftharpoons} MoO_3S^{2-} + H_2O \qquad (1)$$

$$\frac{1}{\epsilon_{obsd}} = \frac{1}{K_{01}[H^+]\epsilon_1} \frac{1}{[MoO_4^{2-}]} + \frac{1}{\epsilon_1} \qquad (2)$$

be derived, where ϵ_{obsd} and ϵ_1 are absorption coefficients (M^{-1} cm^{-1}) for equilibrated solutions and for MoO_3S^{2-}, respectively, and $MoO_4^{2-}/NH_3/H_2O$ solutions have negligible absorbances. From linear plots of $(\epsilon_{obsd})^{-1}$ against $[MoO_4^{2-}]^{-1}$, Figure 2, the ratio of intercept/slope gave $K_{01}[H^+]$ values. The slope of a plot of $K_{01}[H^+]$ against $[H^+]$ gave $K_{01} = (5.8 \pm 0.3) \times 10^{11}$ M^{-2}. This can be expressed alternatively as (3), in which case

$$MoO_4^{2-} + H_2S \rightleftharpoons MoO_3S^{2-} + H_2O \qquad (3)$$

$K'_{01} = 6 \times 10^4$ M^{-1} (with the use of 10^7 M^{-1} for the protonation constant for HS^-). The latter gives a value of 3.3×10^6 (no units!) with $[H_2O]$ = 55 M. Alternatively the equilibrium can be expressed as (4) when $K''_{01} = 1.9 \times 10^8$ M^{-1} (with the use

$$MoO_4H^- + HS^- \rightleftharpoons MoO_3S^{2-} + H_2O \qquad (4)$$

of 3×10^3 M^{-1} for the first protonation constant of MoO_4^{2-}). Because oxo protonation constants for other $MoO_xS_{4-x}^{2-}$ species are not known, constants expressed in this manner are less useful for comparative purposes. At the 292-nm peak MoO_3S^{2-} gives ϵ 7400 M^{-1} cm^{-1} which compares with a value for $MoO_2S_2^{2-}$ of 4600 M^{-1} cm^{-1}. The full spectrum of MoO_3S^{2-} in Figure 1 was obtained from spectra of equilibrated MoO_4^{2-}/H_2S solutions prior to $MoO_2S_2^{2-}$ formation.

Table I. Rate Constants k_{eq} (25 °C) for the Equilibration of MoO_4^{2-} with H_2S (1.9×10^{-4} M) at pH 9.24–10.20 (0.25 M NH_3/NH_4^+ Buffer) and I = 0.50 M (NaCl)

$10^3 \times [MoO_4^{2-}]$, M	10^2k_{eq}, s^{-1}				
	pH 9.24	pH 9.40	pH 9.51	pH 9.73	pH 10.20
3.0	1.25	1.12 (2)	0.98 (3)	0.78 (2)	
4.0				0.82	
5.0	1.86 (2)	1.50	1.24	0.87	0.75
6.5	2.13				
7.5	2.45 (2)	1.75	1.48 (3)	1.05	0.73
8.5	2.63				
10.0	3.00	2.18	1.85	1.15	0.80
11.5				1.30	
12.5	3.55	2.60	2.35	1.40	0.88
15.0	4.00	3.02	2.60	1.60	0.98
16.5	4.38				
17.5		3.40	2.85		0.98
20.0		4.15	3.23		1.05

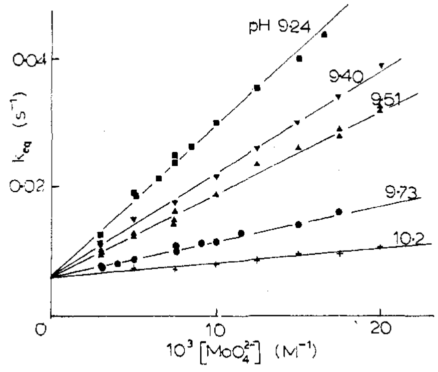

Figure 3. The dependence of rate constants, k_{eq}, for the equilibration of MoO_4^{2-} and H_2S to give MoO_3S^{2-} in NH_3/NH_4^+ buffer (0.25 M) (I = 0.50 M (NaCl) at 25 °C) on MoO_4^{2-} (in large excess).

Kinetics of the 1:1 Equilibration of H_2S and MoO_4^{2-}. The reaction can be expressed as in (5), with rate constants k_{01} and

$$MoO_4^{2-} + H^+ + HS^- \underset{k_{10}}{\overset{k_{01}}{\rightleftharpoons}} MoO_3S^{2-} + H_2O \qquad (5)$$

k_{10} as defined. Conditions were T = 25 °C, pH 9.2–10.2 (0.25 M NH_3/NH_4^+ buffer), and I = 0.50 M (NaCl). The increase in absorbance was monitored at 292 nm ($t_{1/2}$ in the range 15–70 s), and equilibration rate constants k_{eq}, Table I, were obtained from first-order plots, where A_∞ was the experimentally observed value prior to $MoO_2S_2^{2-}$ formation. Rate constants were the same (±5%) whether MoO_4^{2-} or H_2S was in excess, pH 9.67. Rate constants were also independent of the buffer, 0.02–0.25 M, at pH 9.2 (±8%). On varying the $[MoO_4^{2-}]$ in the range 0.0030–0.0225 M with $[H_2S] = 1.9 \times 10^{-4}$ M, linear plots of k_{eq} against $[MoO_4^{2-}]$ were obtained at each pH, Figure 3. These gave a common intercept, with slopes dependent on $[H^+]$. Thus the equilibration process may be summarized by (6), where k_b is for the back-reaction and

$$k_{eq} = k_f[MoO_4^{2-}] + k_b \qquad (6)$$

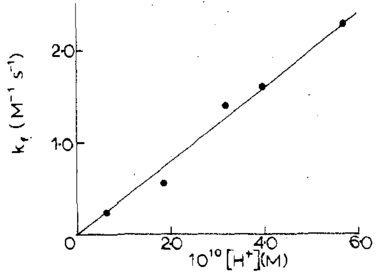

Figure 4. The dependence of the rate constant k_f for formation of MoO_3S^{2-} on $[H^+]$ in NH_3/NH_4^+ buffer (pH 9.24–10.2, $I = 0.50$ M (NaCl) at 25 °C).

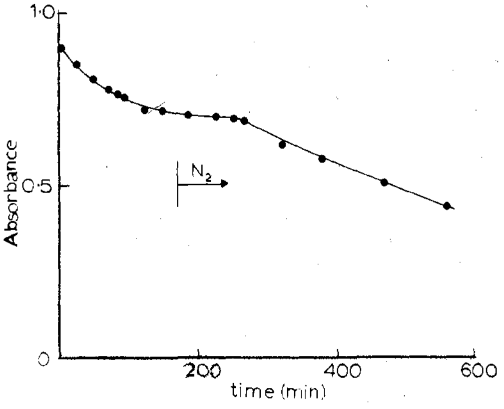

Figure 5. Plot of absorbance changes (λ 393 nm) with time for aquation of $MoOS_3^{2-}$ (ca. 10^{-4} M) in 0.25 M NH_3/NH_4^+ buffer (pH 8.45, $I = 0.50$ M (NaCl) at 25 °C). Approach to equilibrium and further progress of reaction were accomplished on removal of H_2S by bubbling a stream of N_2 through the solution.

corresponds to k_{10}. A value of (6.5 ± 0.5) × 10^{-3} s^{-1} was obtained. The formation rate constant k_f is dependent on $[H^+]$, Figure 4. Thus (7) holds, where $k_{01} = (4.0 \pm 0.3) \times 10^9$ M^{-2}

$$k_f = k_{01}[H^+] \qquad (7)$$

s^{-1}. The ratio $k_{01}/k_{10} = 6.2 \times 10^{11}$ M^{-2} is in good agreement with the equilibrium constant $K_{01} = 5.8 \times 10^{11}$ M^{-2} as determined above.

Kinetics of the Aquation of $MoOS_3^{2-}$. This reaction was studied over two ranges of pH. At the higher pH's in the range 8.27–9.70 (0.25 M NH_3/NH_4^+ buffer) an equilibration process (eq 8) is observed. Absorbance changes were followed

$$MoOS_3^{2-} + H_2O \underset{k_{23}}{\overset{k_{32}}{\rightleftharpoons}} MoO_2S_2^{2-} + HS^- + H^+ \qquad (8)$$

at 393 nm at which wavelength absorption coefficients are ε 8400 M^{-1} cm^{-1} for $MoOS_3^{2-}$ and ε 3200 M^{-1} cm^{-1} for $MoO_2S_2^{2-}$. For a run at pH 8.45, Figure 5, the absorbance–time plot clearly indicates the approach to an equilibrium position. When H_2S is removed by bubbling a steady stream of N_2 through the solution, the reaction proceeds further as indicated. From the initial slopes of concentration–time plots (pH 8.3–9.4) k_{32} = ca. 3 × 10^{-5} s^{-1}, which is independent of $[H^+]$. An approximate range of values for the equilibrium constant $K_{32} = (3–5) \times 10^{13}$ M^{-2} was also obtained from information as in Figure 5, with the assumption of no loss of H_2S during the initial (ca. 200 min) period and that equilibria involving further loss of HS^- are not relevant.

Aquation studies over a pH range 3.6–5.6 were carried out by using acetate buffer (0.02 M), when the increased H^+ removed HS^- (as H_2S) from the right-hand side of (8) and aquation proceeded to completion. At such $[H^+]$ values the absorbance (ε) of $MoOS_3^{2-}$ at 393 nm remains unchanged with no evidence for protonation. The same (±5%) rate constant (k) was obtained on decreasing the concentration of acetate 10-fold. Within this pH range k values, Table II, gave a $[H^+]$ dependence (eq 9, Figure 6). The small intercept k_{32} = (3.8

$$k = k'_{32}[H^+] + k_{32} \qquad (9)$$

± 1.0) × 10^{-5} s^{-1} corresponds to and is in satisfactory agreement with the value obtained at higher pH. The $[H^+]$-dependent path gives $k'_{32} = 2.9 \pm 0.1$ M^{-1} s^{-1}.

Table II. Rate Constants k (25 °C) for the Aquation of (Ca. 6 × 10^{-5} M) to $MoO_2S_2^{2-}$ at pH 3.69–4.92 (0.02 M Acetate Buffer, Except As Stated), $I = 0.50$ M (NaCl), and λ 395 nm

pH	10^3k, s^{-1}	pH	10^3k, s^{-1}
3.69	6.25	4.80	0.69
3.90	4.5	4.80	0.66[a]
4.45	1.5	4.92	0.60
4.50	1.7		

[a] Acetate buffer concentration 0.02 M.

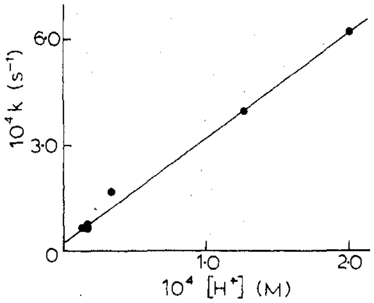

Figure 6. The dependence of rate constant k for the aquation of $MoOS_3^{2-}$ on $[H^+]$ in acetate buffer ($I = 0.50$ M (NaCl) at 25 °C).

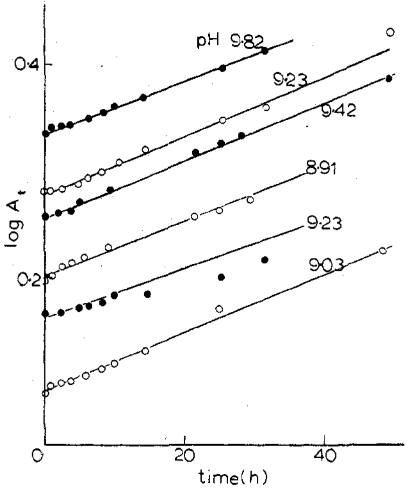

Figure 7. First-order plots for the aquation of MoS_4^{2-} (10 M) in 0.25 M NH_3/NH_4^+ buffer (pH 8.9–9.8, $I = 0.50$ M (NaCl) at 25 °C). Slow reactions followed for at most to one half-life (ca. 50 h).

Kinetics of the Aquation of MoS_4^{2-}. Absorbance changes were monitored at the MoS_4^{2-} peak position at 470 nm (ε 12400 M^{-1} cm^{-1}). Exploratory experiments demonstrated that the aquation (eq 10) is an order of magnitude slower than k_{32}.

$$MoS_4^{2-} + H_2O \xrightarrow{k_{43}} MoOS_3^{2-} + HS^- + H^+ \qquad (10)$$

Only $MoOS_3^{2-}$ (ε 2300 M^{-1} cm^{-1}) of the other sulfido complexes absorbs at 470 nm. Conditions investigated were T = 25 °C, pH 8.9–9.8 (0.25 M NH_3/NH_4^+ buffer), and $I = 0.50$ M (NaCl). On the assumption that the final absorbance is zero, first-order plots gave satisfactory linearity over the time monitored (periods up to the $t_{1/2}$ of ca. 50 h) (see Figure 7). Rate constants k_{43}, Table III, were evaluated and gave (1.64 ± 0.15) × 10^{-6} s^{-1}. No attempt was made to purge the solution

Table III. Rate Constants k_{43} (25 °C) for the Aquation of MoS_4^{2-} (Ca. 4 × 10^{-5} M) to $MoOS_3^{2-}$ at pH 8.2–9.8 (0.25 M NH_3/NH_4^+ Buffer) and I = 0.50 M (NaCl)

pH	10^6k_{43}, s^{-1}	pH	10^6k_{43}, s^{-1}
8.23	1.60	9.23	1.72
8.91	1.62	9.42	1.76
9.02	1.77	9.82	1.58

Table IV. Summary of Rate and Equilibrium Constants Defined According to Number of Sulfur Atoms in Reactant and Product (25 °C), I = 0.50 M (NaCl), for the Interconversion of $MoO_xS_{4-x}^{2-}$ Species in the pH Range 8.2–10.2 (NH_3/NH_4^+ Buffer)

formatn,[a] M^{-2} s^{-1}	aquatn, s^{-1}	equil, M^{-2}
4 × 10^9 (k_{01})	6.5 × 10^{-3} (k_{10})	5.8 × 10^{11} (K_{01})
ca. 1.2 × 10^9 (k_{23})[b]	(3–6) × 10^{-5} (k_{32})[c,d]	ca. 4 × 10^{13} (K_{23})
<1.6 × 10^6 (k_{34})	1.6 × 10^{-6} (k_{43})	<10^{12} (K_{34})[e]

[a] Rate constant defined by rate law involving $MoO_xS_{4-x}^{2-}$. [b] Obtained from $K_{23}k_{32}$ and dependent therefore on the accuracy of the estimate for K_{23}. [c] Rate defined by values obtained at pH 8.3–9.4 and 3.6–5.6. [d] Additional [H^+]-dependent term 3.0 M^{-1} s^{-1} obtained from data at pH 3.6–5.6. [e] Data at I = 2.0 M (NaCl) gives K_{34} ca. 2 × 10^9 M^{-2}.

of H_2S formed. It is likely (see previous section) that some $MoOS_3^{2-}$ is retained, and an appropriate absorbance A (other than zero) should therefore be used. On the assumption that the reaction proceeds only as far as $MoOS_3^{2-}$, then a recalculation of k_{43} gives values 36% greater. This is a small effect compared to the magnitude of rate constant variations for the $MoO_xS_{4-x}^{2-}$ series as a whole, and although it should not be entirely disregarded, it is overlooked for present purposes.

Reaction of H_2S with $MoOS_3^{2-}$. For conditions 25 °C, pH 9.2 (0.25 M NH_3/NH_4^+), I = 0.50 M (NaCl), with [$MoOS_3^{2-}$] = 5 × 10^{-5} M and [H_2S] = 10^{-2} M, no change in absorbance was observed at 470 nm over 1 h. It is concluded that the formation rate constant is <1 × 10^{-3} M^{-1} s^{-1} for reaction of $MoOS_3^{2-}$ and HS^-. On the assumption of a first-order [H^+] dependence, this gives a value of k_{34} < 1.6 × 10^6 M^{-2} s^{-1}. Only at higher H_2S with combined NH_3/NH_4^+ concentrations up to 0.74 M (see below), I = 2.0 M (NaCl), was significant reaction observed. At pH 8.3 with [H_2S] = 0.20 M first-order plots were linear to ca. 35% and with [H_2S] > 0.69 M were linear to >90% completion. Under these extreme conditions rate constants 10^4k_{34} (s^{-1}) at the different H_2S concentration (M) were 6.6 (0.69), 7.7 (0.75), 9.0 (0.83), and 11.0 (0.88), and over this admittedly narrow range an $[H_2S]^2$ dependence gave the best fit. We are not confident that this is a meaningful result, since to obtain sufficient buffer capacity of solutions some variation in [NH_4^+] (and [NH_3]) composition of reactant solutions (M), 0.53 (0.030), 0.58 (0.034), 0.64 (0.037), and 0.70 (0.040), respectively, was introduced. The experiments do however support the estimate k_{34} < 1.6 × 10^6 M^{-2} s^{-1} and suggest an approximate value of K_{34} of 2 × 10^9 M^{-2}. From rate constants K_{34} (=k_{34}/k_{43}) is <10^{12} M^{-3}. Details of the preparation of $(NH_4)_2[MoS_4]$ and the conditions adopted (see Experimental Section) are of interest in this context, where high Mo(VI), high NH_3, and insolubility of the product in the medium used are noted.

Discussion

Table IV summarizes rate and equilibrium constant data obtained in this study. An interpretation of the rate constant k_{01} in terms of the pathway MoO_4H^- + HS^- is preferred rather than the alternative MoO_4^{2-} + H_2S. The basis of this preference is that reactions of MoO_4^{2-} appear to be slow unless prior protonation with consequent weakening of the Mo–O bond occurs. Protonation has the effect of activating the Mo(VI) coordination sphere both to substitution and to addition.[14-17] Although in many reactions studied proton ambiguities exist and the interpretation is not clearcut, in at least one case, that of the [H^+]-dependent path in the reaction of $Co(NH_3)_5H_2O^{3+}$ with MoO_4^{2-}, it is clear that MoO_4H^- is involved.[18] With additional data obtained from $H_2^{18}O$ exchange studies on MoO_4^{2-}, which also provide evidence for a fast [H^+]-dependent exchange process incident at pH <11,[19] the summary in Table V is obtained. Interpretation in terms of a reaction of MoO_4H^- with HS^- (rate constant of 1.3 × 10^6 M^{-1} s^{-1}) seems much more realistic than MoO_4^{2-} with H_2S (rate constant 4 × 10^2 M^{-1} s^{-1}). The influence of H^+ on the reactivity of MoO_4^{2-} is all the more remarkable because protonation (3 × 10^3 M^{-1}) is by no means extensive, and protonation of HS^-, while still small, is more extensive.

Table V. Summary of Existing Data for Substitution on MoO_4^{2-}

pathway	rate const
MoO_4^{2-} + OH^- [a]	2.2 M^{-1} s^{-1}
MoO_4^{2-} + H_2O[a]	0.33 s^{-1}
MoO_4H^- + $Co(NH_3)_5H_2O^{3+}$ [b]	3.2 × 10^5 M^{-1} s^{-1}

[a] Reference 19; I = 1.0 M ($NaClO_4$), pH >11. [b] Reference 18; I = 0.5 M ($NaClO_4$), pH 7.1–8.0.

Some evidence has been reported for singly[20] or doubly[21] protonated MoO_4^{2-} interacting with solvent water to give octahedral species. If such a change in coordination geometry occurs at the pHs under investigation, then substitution of the octahedral form rather than addition to the tetrahedral form may well occur. Gilbert and Kustin[22] have considered the full implication of these different pathways in their study on the complexing of catechol derivatives with Mo(VI). Although similar discussion applies here, for brevity we only refer to the tetrahedral forms. There is no evidence for protonation and change of geometry of MoS_4^{2-}, and the behavior of other $MoO_xS_{4-x}^{2-}$ species in this same context is not established.

Since protonation constants of oxo ligands in the MoO_xS_{4-x} species have not been determined, it is necessary to compare third-order k_{01}, k_{23}, and k_{34} values in Table IV. The trends observed are the combined effect of different protonation constants for MoO_4^{2-}, $MoO_2S_2^{2-}$, and $MoOS_3^{2-}$ and rate constants for the reactions of MoO_4H^-, $MoO_2S_2H^-$, and $MoOS_3H^-$, respectively. An [H^+] dependence is implied for all the formation reactions, since for aquation k_{10}, k_{32}, and k_{43} were all found to be [H^+] independent at pHs 8.2–10.2.[23]

The rate constants for aquation also indicate a slowing down in substitution as more sulfides are introduced into the Mo(VI) coordination sphere. These effects are contrary to previously reported effects observed for other transition-metal octahedral complexes, where the presence of sulfur-donor ligands generally results in a labilization of other ligands.[7,9,24] The slower rate constant k_{34} for $MoOS_3^{2-}$ prevails in spite of the Mo–O distance of 1.79 Å,[5] which is no longer than in related Mo(VI) compounds MoO_4^{2-} (1.76 Å),[6] MoO_3(dien) (1.74 Å),[25] and $Mo_2O_5(C_2O_4)_2(H_2O)_2^{2-}$ (terminal Mo–O 1.69 Å).[26] Crowding of the Mo(VI) site by the S^{2-} ligands seems to be

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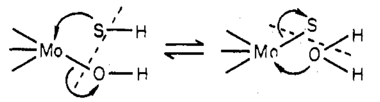
Table VI. Comparison of Acid Dissociation pK_a values for H_2O and H_2S in Different Situations[a]

	H_2O	H_2S	ref
uncoordinated	15.7	7	11
$Ru(NH_3)_5H_2X^{2+}$	13.1	4	7
$Cr(H_2O)_5H_2X^{3+}$	4	<<1	9

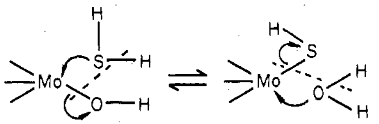
[a] X = O or S.

the most realistic explanation of the trends observed. This coupled with a need for reactions to proceed by an associative type mechanism help to explain the pattern of formation and aquation rate constants observed. The need to invoke an associative mechanism is apparent by consideration of the H^+-independent aquation processes. Departure of S^{2-} from an $MoO_xS_{4-x}{}^{2-}$ coordination sphere in a dissociative process seems unlikely. Instead an associative process, involving the incoming H_2O, with the opportunity provided for proton transfer to the departing S^{2-} seems appropriate. Thus the formation and aquation reactions are believed to occur as in eq 11. Hydrogen bonding as well as proton transfer may be relevant in the activated complex.[27,28]



(11)

The results for the aquation of $MoOS_3{}^{2-}$ at the lower pHs (3.6–5.6) are of interest in that an [H^+]-dependent contribution k'_{32} is observed, (9). From known acid dissociation pK_a values, Table VI, it is estimated (on the basis of a pK_a of 3.47 for MoO_4H^-)[13] that the pK_a of sulfide should be ca. −5 (i.e., extremely small). In spite of this small value protonation of a sulfide of $MoOS_3{}^{2-}$ seems a likely mechanistic requirement for k'_{32}, since protonation of an oxo ligand would simply initiate exchange with no net reaction. Equation 11 can be modified accordingly to include a formation pathway involving H_2S (eq 12), where the pathway is relevant at the lower pHs only.



(12)

To summarize: interpretation is in terms of associative addition to tetrahedral protonated molybdate or possibly associative substitution on octahedral protonated molybdate. This type of mechanism features prominently in the interpretation of molybdate and tungstate reactions. Gilbert and Kustin, for example, have discussed the results in terms of greater reactivity of the more basic ligands due to the stronger associative bonding of these more nucleophilic ligands.[22] The increase in number of coordinated S^{2-} ligands and crowding of the Mo(VI) decreases both formation and aquation rate constants. It may be that crowding by S^{2-} ligands has the effect of decreasing the amount of octahedral complex present, the formation of which is crucial to the reaction proceeding.

While the kinetic trends in Table IV seem clear-cut, the equilibrium constants are not sufficiently exact to allow further discussion. It is of interest that K_{01} in (3) has a value of 3.3 × 10^6 which gives a free energy change of −8.9 kcal mol^{-1} for this reaction. At first this appears to be a contradiction of hard–soft acid–base theory where Mo(VI) is hard and S^{2-} soft. However literature values of ΔG (kcal mol^{-1})[29] for $MoO_4{}^{2-}$ (−200.4), H_2S (−6.7), and H_2O (−56.7) confirm that MoO_3S^{2-} is less stable than $MoO_4{}^{2-}$ in aqueous solution.[30] The existence of Mo–S bonds in molybdenum enzymes is now well recognized.[31] It is also of interest that with Mo(VI) there is at present no evidence for μ-sulfido bonds, whereas with Mo(V) μ-sulfido bonds are easier to generate than terminal Mo(V)–S^{2-} bonds.[32]

As a result of these studies it is possible to comment on conditions most appropriate for replacement of O^{2-} by S^{2-} on Mo(VI). While high H^+ is beneficial to oxo removal, HS^- is more effective than H_2S (pK_a = 7) as an incoming nucleophile. The most appropriate compromise pH is probably somewhere in the region of 7.3.

Finally attention should be drawn to the observation of Müller et al.[33] that MoO_3S^{2-} and $MoO_2S_2{}^{2-}$ are formed more quickly than WO_3S^{2-} and $WO_2S_2{}^{2-}$. No rate constants were however reported by them in this and other similar investigations relating to the interconversions of $MoO_xS_{4-x}{}^{2-}$ (and $WO_xS_{4-x}{}^{2-}$) species.

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Registry No. $(NH_4)_2[MoS_4]$, 15060-55-6; $(NH_4)_2[MoO_2S_2]$, 16150-60-0; $MoO_4{}^{2-}$, 14259-85-9; MoO_3S^{2-}, 25326-93-6; $MoO_2S_2{}^{2-}$, 16608-22-3; $MoOS_3{}^{2-}$, 19452-56-3; $MoS_4{}^{2-}$, 16630-92-0; H_2S, 7783-06-4.

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