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Kinetics of the Formation and Hydrolysis Reactions of some Thiomolybdate(VI) Anions in Aqueous Solution

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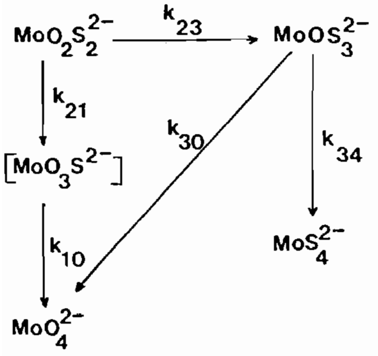
Abstract

The kinetics of the formation of the thiomolybdate ions $MoOS_3^{2-}$ and MoS_4^{2-} were determined spectroscopically from the addition of excess sulphide to $MoO_2S_2^{2-}$ in pH buffered media (6–8) at 30 °C. The reverse (hydrolysis) reactions of $MoO_2S_2^{2-}$ and $MoOS_3^{2-}$ were measured under the same conditions. The reaction rates measured are shown below:



Values of the rate-constants (s^{-1}) obtained at pH 7.0 were k_{10} 2.4×10^{-3}, k_{21} 1.5×10^{-5}, k_{30} 2.1×10^{-5}, k_{23} 6.0×10^{-4}, and k_{34} 1.9×10^{-5}; where the results are comparable they are in good agreement with those obtained by earlier workers, although different conditions were used. However, in this work it was found that certain reactions had to be mathematically treated as two consecutively occurring reactions. There is also a difference in interpretation of the mechanism of the hydrolysis reactions of the tri- and tetrathio ions. In general the lability towards further S replacement of O atoms, and the reverse reaction, decreased with increased S substitution. All reaction rates increased with increasing H^+ ion concentration, mostly this was a linear relationship over the limited pH range examined. The effect of the H^+ ion is interpreted in terms of protonation of the oxythiomolybdate ions at an O atom leading to increased lability.

Introduction

The thiomolybdate(VI) anions, $MoO_xS_{4-x}^{2-}$ ($x = 0$–3) are of both chemical and biochemical importance [1–3]. In particular, there is now abundant evidence that these anions are the likely intermediates in the Cu–Mo antagonism that seriously afflicts ruminants [1, 4, 5]. In our earlier studies we showed that the ions could form from molybdate ion, under simulated rumen conditions, by the sequential replacement of O^{2-} by S^{2-} ion, to give ultimately the MoS_4^{2-} ion [4, 5]. The rate of O^{2-} replacement decreased with increasing S substitution, the reverse reaction rates, giving ultimately the molybdate ion, showed a similar trend *i.e.* MoS_4^{2-} being the least reactive.

In this report we present more detailed kinetic results on some of the sulphide formation and reverse (hydrolysis) reactions under near-biological (rumen) conditions. Kinetic data on some of the same reactions have been given by Harmer and Sykes [6], but under different conditions. We also differ in the method of treatment of the experimental results.

Experimental

The compounds $(NH_4)_2MoO_2S_2$, K_2MoOS_3, $(NH_4)_2MoOS_3$, K_2MoS_4 and $(NH_4)_2MoS_4$ were prepared according to established methods [4, 5] and were stored under vacuum. They were characterised by their distinctive, and well-documented, UV–Vis and IR spectra [4]; these are the best criteria for establishing any contamination by neighbouring oxythio ions. $(NH_4)_2MoO_2S_2$ which is the most difficult to prepare was also characterised by

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elemental analysis (University of Manchester). Found: N, 11.5; H, 3.3; S, 26.3; Mo, 42.8; Calc.: N, 12.28; H, 3.50; S, 28.07; Mo, 42.10%.

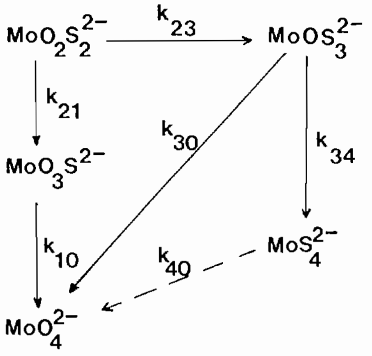
Other reagents used were of 'AnalaR' or similar grade. Water was distilled and de-ionised and stored under a nitrogen atmosphere. Stock sulphide solutions were prepared from 'AnalaR' $Na_2S \cdot 9H_2O$ and standardised by iodometric titration; the concentrations calculated from the weight taken were in excellent agreement with those obtained from the titrations.

Preliminary experiments established that neither the presence of air, the level of phosphate used, nor the nature of the cation (NH_4^+ or K^+), had any significant influences on the reaction rates. All solutions contained 0.1 M* potassium dihydrogen phosphate with NaOH or HCl added to obtain the desired buffering within the pH range 6–8. In the preparation of the stock sulphide solutions it was found necessary to re-adjust the pH after the dissolution of the sodium sulphide in the buffered medium; this was done by the addition of *ca.* 0.5–1.0 cm^3 of a 1 M HCl solution. Kinetic runs were initiated by the rapid addition of a freshly prepared buffered thiomolybdate solution (1 cm^3) to a further 20 cm^3 of buffered solution (containing sulphide for the formation reactions). All solutions were pre-thermostatted at the required reaction temperature 30.0 ± 0.5 °C. The formation reactions were studied under pseudo-first order conditions with total sulphide at a minimum of a fifty-fold excess over the Mo concentration.

Initially the reactions were monitored by scanning the UV–Vis range 500–260 nm as a function of time until reaction was complete. Because of the distinctive UV–Vis spectra [4, 6] of the three thiomolybdate anions the scanning of the total spectrum clearly shows the course of a reaction. For the subsequent collection of rate data, absorbances at selected wavelengths were digitally recorded. All reactions were recorded at least in duplicate to obtain consistent results. For most runs a Perkin-Elmer 555 spectrophotometer with thermostatted cell-block was used. For the two-phase aquation of $MoO_2S_2^{2-}$ the data were collected and treated as previously described [7]. Results from the two-phase trithio- and tetrathiomolybdate formation from dithiomolybdate were treated by the use of a computer program designed for treating consecutively occurring reactions based on the mathematical treatment of Alcock *et al.* [8].

Results

The reactions studied (at 30 °C, 0.1 M phosphate solutions, pH 6–8) are shown in Scheme 1. Direct studies of the reactions of MoO_3S^{2-} were not pursued because preparation of salts of this compound are difficult and its reaction rates are very fast. However, in the above scheme the aquation of the dithiomolybdate(VI) ion definitely proceeds via MoO_3S^{2-} as a detectable intermediate (*vide infra*). Aquation of MoS_4^{2-} was also not followed because of the extreme slowness of this reaction under the conditions used.



Scheme 1.

Aquation of $MoOS_3^{2-}$

The spectrum of this ion undergoes an overall decrease in absorbance (Fig. 1), consistent with the formation of molybdate ion as the product (molybdate shows no absorbance above *ca.* 260 nm). The same uniform collapse has been noted previously for this ion and for MoS_4^{2-} in acid solutions [9]. The rate of aquation of $MoOS_3^{2-}$ shows first-order dependence on the thio ion (Fig. 2) and, from the limited amount of data, a linear dependence on H^+

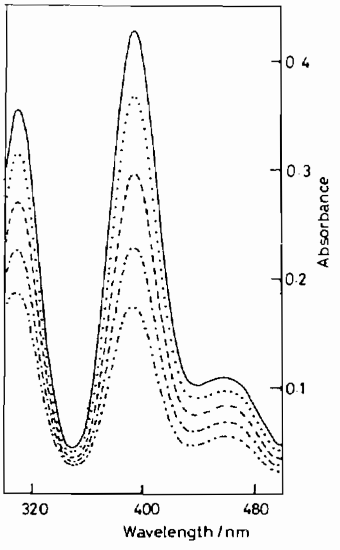


Fig. 1. The UV–Vis spectrum of an aqueous solution of K_2MoOS_3 (*ca.* 5×10^{-5} M, pH 7.0, 30 °C) as a function of time: ———, 3 min; ······, 133 min; ------, 253 min; -·-·-, 373 min; ··–··, 493 min.

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*M = mol dm^{-3}.

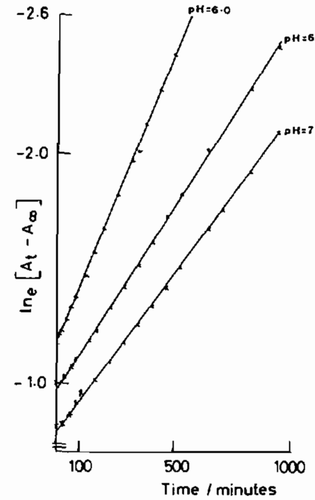


Fig. 2. First-order plots of the hydrolysis of K_2MoOS_3 at different pH values.

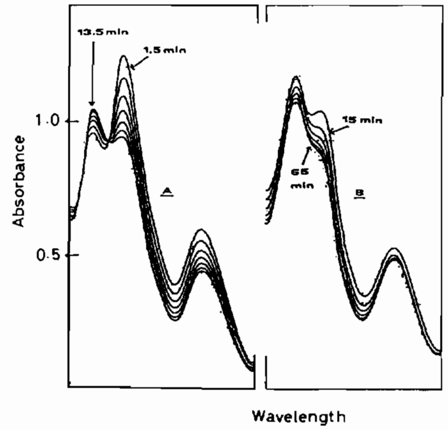


Fig. 3. UV–Vis spectrum of an aqueous solution of $K_2MoO_2S_2$ (2.4×10^{-4} M, pH 7.0, 30 °C) as a function of time. (a) 2 min scans over the period 1.5–15 min (note isobiestic point at 300 nm); (b) 10 min scans over the period 15–65 min. Both sets cover the range 260–440 nm (left to right).

ion concentration over the pH range 6–7. From these results we obtain the relationship

$$k_{30}\ \mathrm{s}^{-1} = 21.7\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}\ [\mathrm{H}^+] + 1.93 \times 10^{-5}\ \mathrm{s}^{-1} \qquad (1)$$

Aquation of $MoO_2S_2^{2-}$

The spectroscopic changes (Fig. 3) are consistent with two consecutive first-order processes. This two phase process is most apparent from the absorbance changes around 285 nm, these show an initial increase over the first 15 min followed by a slower decrease in absorbance, eventually reaching zero absorbance. An isobiestic point is evident at 300 nm for the first part of the reaction. These changes were observed over the pH range 6–7, a linear dependence on H^+ ion concentration was observed over the same pH range (Fig. 4). The results at pH 7 were treated mathematically as two- consecutive reactions giving rate constants of $1.5 \pm 0.1 \times 10^{-5}$ s^{-1} and $2.4 \pm 0.05 \times 10^{-3}$ s^{-1}. The ion MoO_3S^{2-} is known to have an intense absorption centred at 288 nm with an extinction coefficient estimated to be 8000 [9] or 7400 M^{-1} cm^{-1} [6]. At the same wavelength the extinction coefficient for $MoO_2S_2^{2-}$ is considerably smaller, 3900 M^{-1} cm^{-1}. The changes in absorbance are therefore consistent with a two-step process in which hydrolysis to the monothio ion is the first step (see Scheme 1) followed by molybdate ion formation. However, assignment of the two rate constant values is not unambiguous, as Alcock *et al.* [8] point out, an absorbance that rapidly increases and then slowly declines, as in the present case, does not necessarily imply a fast first and a slow second reaction. The mathematical solution depends on the absorbance of the intermediate, thus the two observed rates could correspond to either the more rapid formation of a weakly absorbing intermediate or to the slower formation of a strongly absorbing intermediate. From the above, MoO_3S^{2-} is the likely intermediate, in which case the two rate values can be assigned as $k_{21} = 1.5 \times 10^{-5}$ s^{-1} and $k_{10} = 2.4 \times 10^{-3}$ s^{-1}. The more rapid aquation of the monothio ion is also in keeping with previous reports [4, 6].

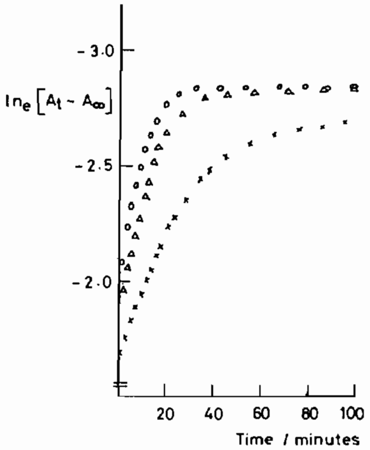


Fig. 4. First-order plots of the hydrolysis of $K_2MoO_2S_2$ at different pH values; o, pH 6.0; △, pH 6.5; X, pH 7.0.

Formation of $MoOS_3^{2-}$ and MoS_4^{2-} from $MoO_2S_2^{2-}$

Addition of excess sulphide to $MoO_2S_2^{2-}$ solutions results first in the formation of $MoOS_3^{2-}$ and then MoS_4^{2-}, consequently the results needed to be treated in terms of two consecutively occurring reactions. Typical reaction profiles and their fits are shown in Fig. 5 and the rate constants obtained are given in Table I. No ambiguity exists in assigning the two rate values since k_{34} was also measured independently, under the same conditions, from the reaction of $MoOS_3^{-2}$ with excess sulphide. The

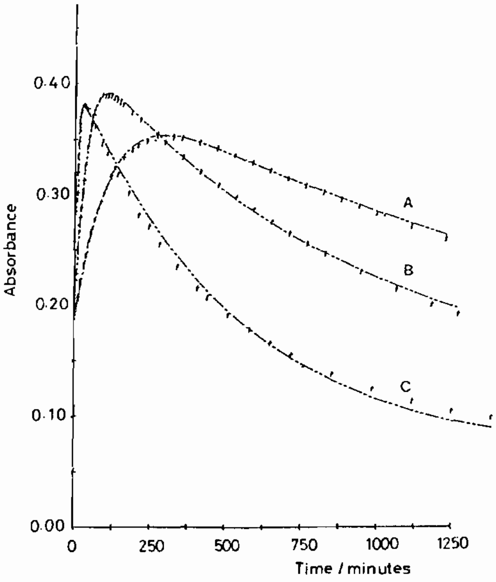


Fig. 5. Some typical curve-fitting results from the application of a consecutive reaction treatment to the experimental results (points) from the reaction between $K_2MoO_2S_2$ (4.76×10^{-5} M) and Na_2S (4.76×10^{-3} M) at 30 °C. (a) pH 7.5; (b) pH 7.0; (c) pH 6.5.

TABLE I. First-order Rate Constants, k_{23} and k_{34}, for the Formation of MoS_4^{2-} from $MoO_2S_2^{2-}$ at 30 °C (from analysis of the consecutive reactions).

Variable	pH	S^{2-} (10^{-3} M)	$Mo_2S_2^{2-}$ (10^{-5} M)	k_{23} (10^{-4} s^{-1})	k_{34} (10^{-4} s^{-1})
pH	8.0	4.76	4.76	*ca.* 0.5	–[a]
	7.5	4.76	4.76	1.5	0.12
	7.0	4.76	4.76	6.0	0.19
	6.5	4.76	4.76	18.8	0.34
	6.0	4.76	4.76	28.0	0.85
Mo(VI)	7.0	4.76	4.76	6.0	1.9
	7.0	4.76	9.52	5.2	1.6
S^{2-}	7.0	4.76	4.76	6.0	0.18
	7.0	2.38	4.76	3.0	0.11

[a] Reactions at this pH were too slow to obtain rate data.

values of k_{34} from the two independent measurements were in exact agreement with each other. Thus, as previously reported, reaction of excess sulphide with $MoO_2S_2^{2-}$ results in the formation of $MoOS_3^{2-}$ followed by the slower formation of MoS_4^{2-}; both processes show a first order dependence on Mo concentration (Fig. 6). Both k_{23} and k_{34} show a strong dependence on H^+ ion concentration; whilst k_{34} shows a linear dependence over the pH range 6–7.5, that of k_{23} appears non-linear.

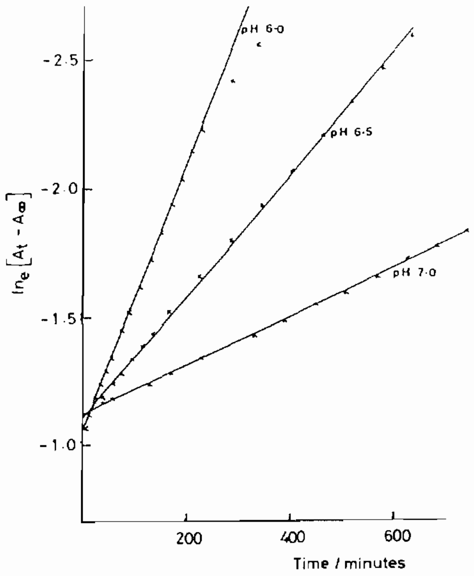


Fig. 6. First-order plots of the reaction between K_2MoOS_3 (4.76×10^{-5} M) and Na_2S (4.76×10^{-3} M) at 30 °C and different pH values.

TABLE II. A summary of the Rate Constants Obtained and a Comparison with Literature Values

Rate constants (S^{-1})	This work[a]	Reference 6[b]
k_{34}	1.9×10^{-5}	
k_{23}	6.0×10^{-4}	
k_{40}	$<1 \times 10^{-6}$ [c]	1.6×10^{-6} [d]
k_{30}	2.1×10^{-5}	3.6×10^{-5} [d]
k_{21}	1.5×10^{-5}	
k_{10}	2.4×10^{-3}	6.5×10^{-3}

[a] At 30 °C, pH 7.0, 0.1 M phosphate buffer. [b] At 25 °C, pH 8.2–10.2, 0.5 M NaCl. [c] Estimated value. [d] The authors refer to constants as k_{43} and k_{32} (see text).

Discussion

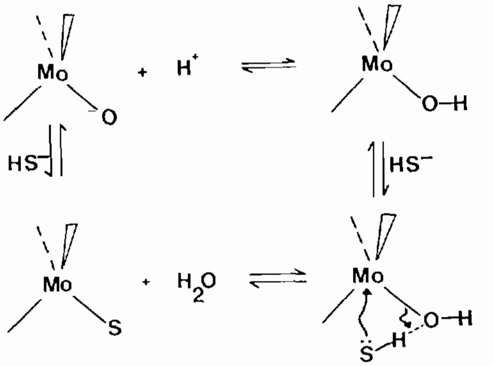
The rate constants obtained are summarised in Table II, together with comparable data from the study of Harmer and Sykes [6]. The results confirm previous observations [4–6] that increasing sulphur substitution at the Mo(VI) centre decreases the lability towards both further S substitution and to hydrolysis (replacement of S by O). Furthermore, all the reaction rates increase with increasing H^+ ion concentration.

Some of the same reaction rates have been previously measured by Harmer and Sykes [6], but under different conditions to the ones used in this work. Thus, they used aqueous 0.5 M NaCl media at 25 °C buffered over the ranges 8.2–10.2 or 3.6–5.6. Data were collected under pseudo-first-order conditions but with Mo(VI) ions in excess; H_2S was used as the reactant. The use of this latter reagent led to problems when high sulphide levels were used and probably explains their tenuous assignment of a $[H_2S]^2$ order in the formation of MoS_4^{2-} from $MoOS_3^{2-}$. Our results clearly show a linear dependence on sulphide concentration. Where the results are comparable there is good agreement, e.g. in the general finding of a linear dependence on H^+ ion concentration and in the rate-equation for the hydrolysis of $MoOS_3^{2-}$ for which Harmer and Sykes obtain $k_{obs} = 2.9\ M^{-1}\ s^{-1}\ [H^+] + 3.8 \times 10^{-5}\ s^{-1}$, which is similar to our eqn. (1). There are, however, differences in treatment and conclusions. The major difference is that the earlier workers [6] did not take into account the occurrence of consecutive reactions which are of particular importance in the hydrolysis reactions. Thus, the hydrolysis of MoS_4^{2-} was reported [6] as resulting in $MoOS_3^{2-}$ as product. Our experience is that for this ion and for $MoOS_3^{2-}$ hydrolysis over the pH range 3–7 shows no detectable intermediate thiomolybdates (e.g. see Fig. 1). The claims for a H^+-independent hydrolysis at pH > 8 for $MoOS_3^{2-}$ and a resulting equilibrium with $MoO_2S_2^{2-}$ are also at variance with the results at pH 7 presented here. The most likely mechanism for the hydrolysis of these ions is that they do proceed with a stepwise loss of S atoms, but with increasing reaction rates, as in eqn. (2)

$$k_{43} < k_{32} < k_{21} < k_{10} \qquad (2)$$

in which case the intermediate thiomolybdate ions may not be observed during the course of the hydrolysis reactions. The trend in rate constant values in (2) is found to be the case as shown by the results in Table II and is apparent from an examination of the data of Harmer and Sykes [6], since our k_{40} and k_{30} values are very similar to their k_{44} and k_{32} constants. Only in the case of $MoO_2S_2^{2-}$ is there clear evidence of the formation of the intermediate (MoO_3S^{2-}) thio ion. Two consecutively occurring reactions are also evident in the formation of MoS_4^{2-} from the dithio ion.

The interpretation of the H^+ ion dependence of both the formation and hydrolysis reactions is complicated by the protonation equilibrium between HS^- and H_2S ($pK_a \sim 7$ at 30 °C [10]) occurring in the pH range examined. Harmer and Sykes [6] consider HS^- to be the more likely reacting nucleophile by analogy with OH^-. The observation of a H^+ dependence in much lower pH solutions [6, 9] points to other protonation step(s) being involved, indeed there are numerous precedents for proton-dependent reactions of Mo(VI) compounds (see ref. 6 and refs. therein). Protonation equilibrium of the molybdate ion has been studied by potentiometric and spectrophotometric methods with a reported acid dissociation constant of *ca.* 10^{-4} at 25 °C [11, 12]. For the thiomolybdate ions protonation can occur at either an O or a S atom. The former seems the more likely in view of the greater basicity of the O atom, furthermore this would have little, if any, effect on the S → Mo charge transfer bands of the UV–Vis spectra. The UV–Vis spectra were in fact found not to show any dependence on the H^+ ion concentration. A possible mechanism which takes the above factors into account is shown in Scheme 2.



Scheme 2.

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