Rates and Mechanisms of the Reactions of Octacyanomolybdate(V) Anion with L-cysteine, Penicillamine and Thioglycolic Acid in Aqueous Acidic Solutions

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Abstract

The rates and mechanisms of the reactions of octacyanomolybdate(V) anion with L-cysteine, penicillamine and thioglycolic acid have been studied in aqueous acidic solution and constant ionic strength $I = 1.00$ mol dm^{-3} ($NaClO_4$) for cysteine and $I = 0.10$ mol dm^{-3} ($NaClO_4$) for penicillamine and thioglycolic acid respectively. The reactions show a second order substrate dependence and the rates are found to decrease with increasing hydrogen ion concentration [H^+]. This is attributed to the deprotonation of the –SH and $-CO_2H$ groups in these thiols prior to electron-transfer. No evidence was found for the formation of an intermediate complex of significant stability. The reactions are interpreted in terms of outer-sphere mechanism.

Introduction

Reactions of metal complexes with thiols are of interest as possible models for similar reactions in biological systems. Various complexes of tungsten and molybdenum(VI) [1–3] other than the cyano complexes have been used to oxidize the thiols to their corresponding disulphides in different media. Similarly, the reactions of other metal complexes of Fe(III) [4, 5], Co(III) [6], Tl(III) [7] and Cr(VI) [8, 9] with the same set of thiols have also been reported. In almost all the cases, transient intermediates have been identified as being formed prior to electron transfer.

In spite of the fact that the reactions of octacyanomolybdate(V) anion with inorganic substrates have been well documented [10–20], no other reactions of the oxidant with sulphur containing organic substrates have been reported except for the one involving thiourea [21]. This paper is therefore an account of the kinetic investigation of the reactions of octacyanomolybdate(V) anion with some sulphur-containing organic substrates such as L-cysteine, penicillamine and thioglycolic acid (mercaptoacetic acid).

Experimental

Materials

Potassium octacyanomolybdate(IV) 2-hydrate was prepared by the method of Furman and Miller [22] and characterised for purity by its UV–Vis spectra [12, 23]. Potassium octacyanomolybdate(V) was prepared using the method of Thielke [24] in which potassium octacyanomolybdate(IV) 2-hydrate was oxidized to potassium octacyanomolybdate(V) with acidified potassium permanganate solution. The solution was stored in a brown bottle and kept from strong light and was used before 10 days after which decomposition could occur [24].

L-cysteine (B.D.H. Reagent), thioglycolic acid (Analar grade) and penicillamine (Koch light) were used without further purification. Perchloric acid (A.R. grade) was used to investigate the effect of hydrogen ions on the rates of reaction while sodium perchlorate (fluka puriss) was employed in maintaining a constant ionic strength.

Kinetics

The reactions of the three thiols were found to be very slow under the experimental conditions used; consequently, the kinetics of the reactions were monitored by following the decrease in the concentration of octacyanomolybdate(V) anion at 388 nm on a Pye Unicam SP 1750 spectrophotometer. Pseudo-first-order conditions were ensured by using the following reactant concentrations: $[Mo(CN)_8^{3-}] = (2.50–5.00) \times 10^{-5}$ mol dm^{-3}; [thiol] = $(0.20–17.50) \times 10^{-3}$ mol dm^{-3}; $[H^+] = 0.02–1.00$ mol dm^{-3} ($HClO_4$) and $I = 1.00$ or 0.10 mol dm^{-3} ($NaClO_4$). Temperature variation within a particular set of runs was not greater than 0.2 °C.

Results and Discussion

Under the experimental conditions used, the reactions were found to be first-order with respect to

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TABLE I. The effect of $[Mo(CN)_8^{4-}]$ on the reaction of L-cysteine with $[Mo(CN)_8^{3-}]$ at 25.0 °C. $[Mo(CN)_8^{3-}] = 5.00 \times 10^{-5}$ mol dm^{-3}; [L-cysteine] = 10.00×10^{-3} mol dm^{-3}; I = 0.10 mol dm^{-3}

10^5 $[Mo(CN)_8^{4-}]$ (mol dm^{-3})	$10^2 k_{obs}$ (s^{-1})	
	[H$^+$] (mol dm^{-3})	0.04	0.10
0.00		40.00	18.60
1.00		36.20	16.80
5.00		26.70	14.80
10.00		18.00	11.10

$Mo(CN)_8^{3-}$. Plots of $\log_{10}(A_t - A_\infty)$ against time (A_∞ is the absorbance at the end of the reaction and A_t is the absorbance at time t) gave straight lines to about 70% of the reaction for mercaptoacetic acid and cysteine while those of penicillamine were linear to about 90% of the reaction. Pseudo-first-order rate constants k_{obs} were obtained from the gradients of these plots at various [H$^+$] and [thiol]. The strict linearity of the plots for penicillamine does suggest that there is no strong inhibition of the reaction by the product formed while in the case of cysteine and thioglycolic acid, the deviation from linearity at higher extent of the reaction shows that some retardation by the product $Mo(CN)_8^{4-}$ might be occurring in the system. Kinetic measurements were accordingly carried out in which various concentrations of $Mo(CN)_8^{4-}$ were added, and some of the results obtained for these runs are shown in Table I.

On ploting $k_{obs}/[H_2L]$ against $[H_2L]$ when H_2L = penicillamine, straight lines were obtained suggesting that the rates of the redox reactions are second-order in this thiol (Fig. 1). Plots of slopes of these lines as a function of $[H^+]^{-2}$ gave a straight line passing through the origin at constant temperature (Fig. 2). On the other hand, when H_2L is thioglycolic acid, plots of $k_{obs}/[H_2L]$ *versus* $[H_2L]$ (Fig. 3) indicate that two reaction pathways are concurrently operative in the system, one being first-order in the substrate while the other has a second-order substrate dependence. Gradients of these plots vary in a linear manner with $[H^+]^{-2}$ at constant temperature (Fig. 4). Similarly, when H_2L is cysteine, plots of $k_{obs}/[H_2L]$ *versus* $[H_2L]$ (Fig. 5) indicate that two reaction pathways are also currently operative in this system, one of which is independent of the acid (hence the same slope for the various acidities used) while the other has $[H^+]^{-2}$ dependence. A plot of the intercepts *versus* $[H^+]^{-2}$ (Fig. 6) gave a straight line passing through the origin at constant temperature.

Taking the observed experimental data for these thiols into consideration, it can be postulated that

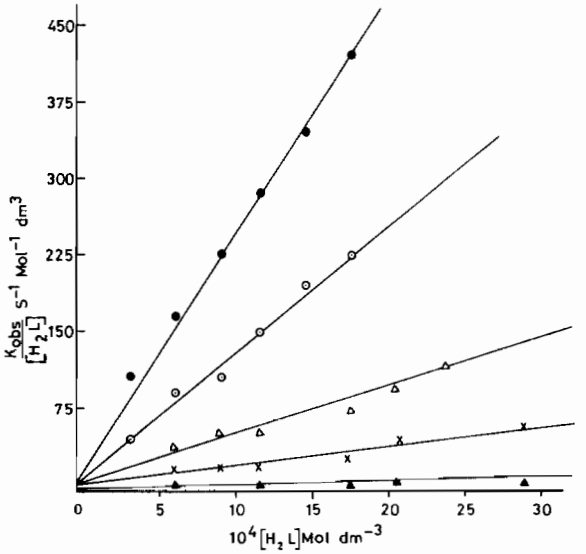

Fig. 1. Dependence of $k_{obs}/[H_2L]$ on $[H_2L]$ where H_2L = penicillamine for the reaction of $Mo(CN)_8^{3-}$ with penicillamine at 25 °C. [H$^+$] = 0.02 mol dm^{-3} (●); 0.03 mol dm^{-3} (⊙); 0.04 mol dm^{-3} (△); 0.06 mol dm^{-3} (×); 0.08 mol dm^{-3} (▲).

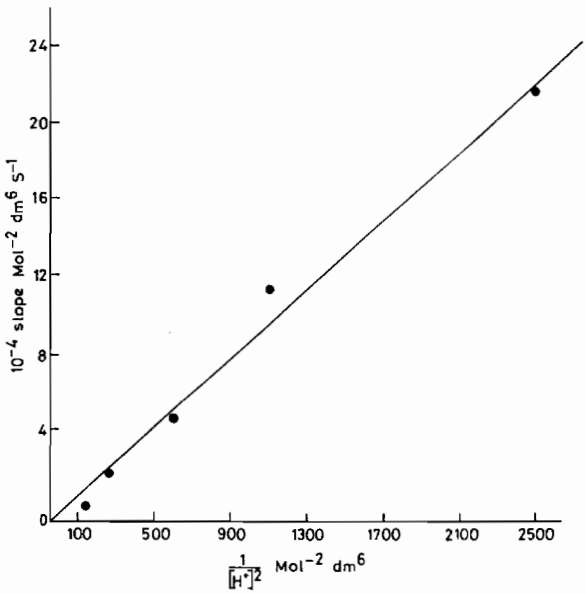

Fig. 2. Plot of slope in Fig. 1 *vs.* $1/[H^+]^2$ for the reaction of $Mo(CN)_8^{3-}$ with penicillamine at 25 °C.

the first step in each case involves the deprotonation of the thiols:

$$H_3L^+ \rightleftharpoons HL^- + 2H^+ \quad (1)$$

$$H_2L \rightleftharpoons L^{2-} + 2H^+ \quad (2)$$

(where H_3L^+ represents protonated cysteine and penicillamine and H_2L represents thioglycolic acid). The protons released are from the sulfhydryl and carboxylic acid groups [25].

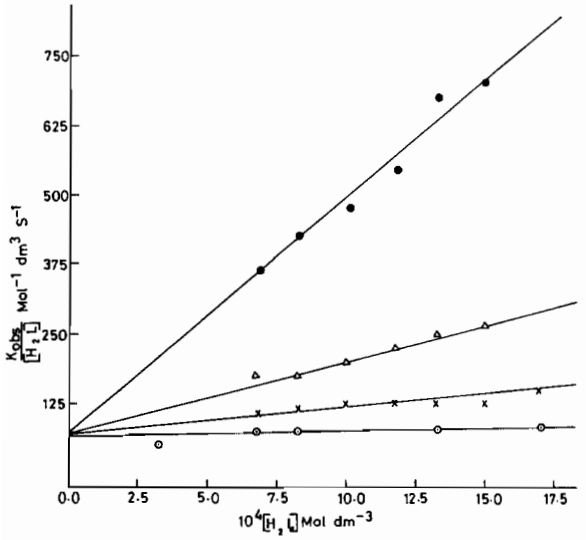

Fig. 3. Dependence of $k_{obs}/[H_2L]$ on $[H_2L]$ where H_2L = thioglycolic acid for the reaction of $Mo(CN)_8^{3-}$ with thioglycolic acid at 25 °C. $[H^+]$ = 0.02 mol dm^{-3} (●); 0.04 mol dm^{-3} (△); 0.06 mol dm^{-3} (X); 0.08 mol dm^{-3} (⊙).

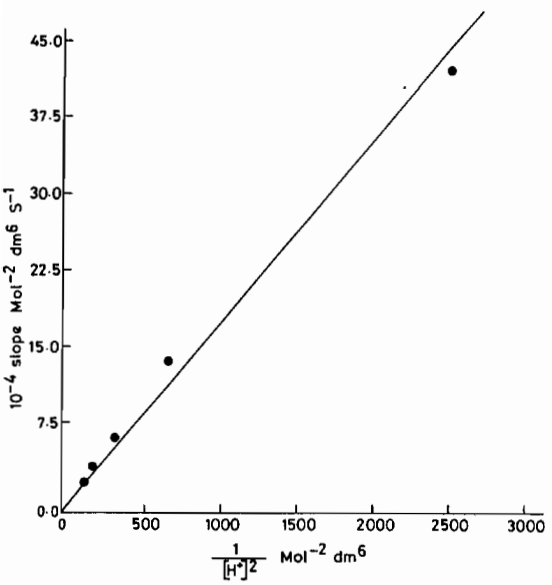

Fig. 4. Plot of slope in Fig. 3 *vs.* $1/[H^+]^2$ for the reaction of $Mo(CN)_8^{3-}$ with thioglycolic acid.

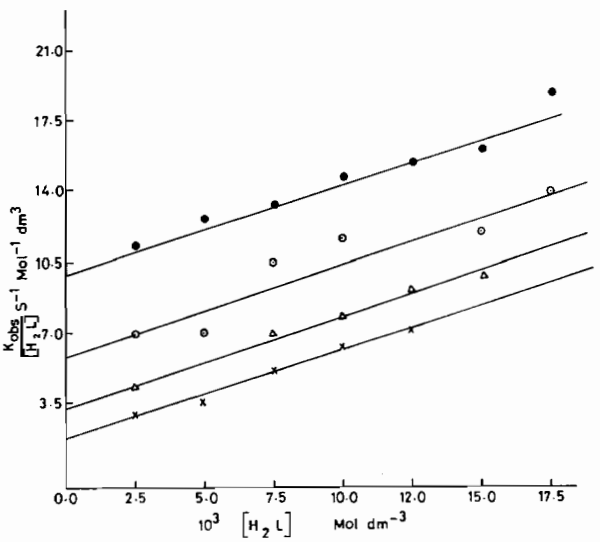

Fig. 5. Dependence of $k_{obs}/[H_2L]$ on $[H_2L]$ where $[H_2L]$ = L-cysteine for the reaction of $Mo(CN)_8^{3-}$ with L-cysteine at 25 °C. $[H^+]$ = 0.25 mol dm^{-3} (●); 0.35 mol dm^{-3} (⊙); 0.50 mol dm^{-3} (△); 0.75 mol dm^{-3} (X).

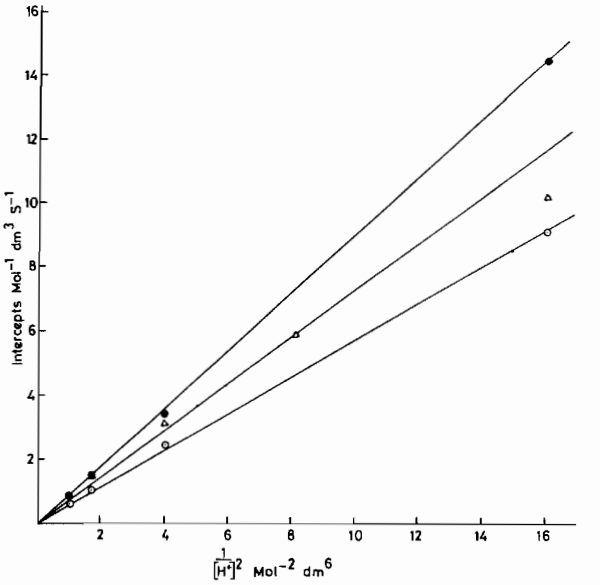

Fig. 6. Plots of intercepts in Fig. 5 *vs.* $1/[H^+]^2$ for the reaction of $Mo(CN)_8^{3-}$ with L-cysteine at T = 20 °C (⊙); 25 °c (△) and 30 °C (●) respectively.

Based on the experimental data obtained, the following mechanisms can be postulated for the reaction of penicillamine with octacyanomolybdate(V) ion.

Mechanism I

$$H_3L^+ \overset{K}{\rightleftharpoons} HL^- + 2H^+ \qquad (3)$$

$$Mo(CN)_8^{3-} + HL^- \overset{K_1}{\rightleftharpoons} [Mo(CN)_8, HL]^{4-} \qquad (4)$$

$$[Mo(CN)_8, HL]^{4-} + H_3L^+ \xrightarrow{k_1} Mo(CN)_8^{4-} + H_2LLH^{\bullet} + H^+ \qquad (5)$$

$$Mo(CN)_8^{3-} + H_2LLH^{\bullet} \xrightarrow{\text{fast}} Mo(CN)_8^{4-} + HLLH + H^+ \qquad (6)$$

Mechanism II

$$H_3L^+ \overset{K_2}{\rightleftharpoons} HL^- + 2H^+ \quad (7)$$

$$Mo(CN)_8^{3-} + H_3L^+ \overset{K_3}{\rightleftharpoons} [Mo(CN)_8,H_3L]^{2-} \quad (8)$$

$$[Mo(CN)_8,H_3L]^{2-} + HL^- \overset{k_2}{\longrightarrow} Mo(CN)_8^{4-} + HLLH^{\cdot} + 2H^+ \quad (9)$$

$$Mo(CN)_8^{3-} + HLLH^{\cdot} \overset{\text{fast}}{\longrightarrow} Mo(CN)_8^{4-} + HLLH \quad (10)$$

These reaction schemes are consistent with the kinetic data obtained, and the rate of loss of $Mo(CN)_8^{3-}$ is as expressed in eqns. (11) and (12)

$$-d[Mo(CN)_8^{3-}]_T/dt = \{k_1K_1K[H_3L^+]^2[H^+]^{-2}[Mo(CN)_8^{3-}]_T\} / \{1 + KK_1[H_3L^+][H^+]^{-2}\} \quad (11)$$

$$-d[Mo(CN)_8^{3-}]_T/dt = \{k_2K_2K_3[H_3L^+]^2[H^+]^{-2}[Mo(CN)_8^{3-}]_T\} / \{1 + K_2K_3[H_3L^+][H^+]^{-2}\} \quad (12)$$

where $[Mo(CN)_8^{3-}]_T$ is the total concentration of $Mo(CN)_8^{3-}$ ions. If $1 \gg KK_1[H_3L][H^+]^{-2}$ in eqn. (11) and also greater than $K_2K_3[H_3L^+][H^+]^{-2}$ in eqn. (12) then the observed rate constants k_{obs} from the two mechanisms I and II can be derived.

$$k_{obs} = k_1K_1K[H_3L^+][H^+]^{-2} \quad (13)$$

$$k_{obs} = k_2K_2K_3[H_3L^+]^2[H^+]^{-2} \quad (14)$$

Equations (13) and (14) explain the kinetic results displayed in Figs. 1 and 2.

Values of the composite rate constants k_2' where $k_2' = k_1K_1K$ or $k_2K_2K_3$ derived at 25 °C are shown in Table II.

The absence of any detectable intermediate of significant stability does suggest that reactions (4) from Mechanism I and (8) from Mechanism II involve the formation of an outer-sphere or ion-pair complexes. In Mechanism I, the ion-pair complex formed involves two negatively charged ions and repulsion is bound to occur resulting in a low value for K_1 while the succeeding step which is the rate determining step involves two oppositely charged ions and the value of the rate constant k_1 may be large. On the other hand, in Mechanism II, eqn. (8) involves two oppositely charged ions and the value of K_3 is expected to be higher than the corresponding value in eqn. (4) because of the attraction between the oppositely charged ions. However the succeeding step involves two negatively charged ions, and the repulsion between them is expected to make the value of k_2 smaller. From the rate law, it is evident that the rate constant k_2' is a composite of k_1K_1K or $k_2K_2K_3$ and that both mechanisms are kinetically indistinguishable.

TABLE II. Rate Constants for the Reactions of $Mo(CN)_8^{3-}$ with L-cysteine, Penicillamine and Thioglycolic Acid

T (°C)	Rate constants	
	k_3' (mol dm^{-3} s^{-1})	$10^{-2} \times k_4'$ (mol^{-2} dm^6 s^{-1})
L-cysteine		
20	0.56 ± 0.01	2.11 ± 0.20
25	0.61 ± 0.03	4.34 ± 0.35
30	0.78 ± 0.10	6.48 ± 0.50
	k_2' (s^{-1})	
Penicillamine		
25	99.61 ± 5.1	
	k_5' (mol^{-1} dm s^{-1})	k_6' (s^{-1})
Thioglycolic acid		
25	62.66 ± 7.2	164.01 ± 11.0

In the reaction of $Mo(CN)_8^{3-}$ with cysteine, the two-term experimental rate law encountered appears to require two parallel reaction pathways leading to the disulphide product. Mechanisms consistent with these kinetic observations are embodied in eqns. (15)–(21).

Mechanism III

$$H_3L^+ \overset{K_4}{\rightleftharpoons} HL^- + 2H^+ \quad (15)$$

$$Mo(CN)_8^{3-} + HL^- \overset{K_5}{\rightleftharpoons} [Mo(CN)_8,HL]^{4-} \quad (16)$$

$$Mo(CN)_8^{3-} + H_3L^+ \overset{K_6}{\rightleftharpoons} [Mo(CN)_8,H_3L]^{2-} \quad (17)$$

$$[Mo(CN)_8,HL]^{4-} \overset{k_3}{\longrightarrow} Mo(CN)_8^{4-} + HL^{\cdot} \quad (18)$$

$$[Mo(CN)_8,H_3L]^{2-} + H_3L^+ \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} Mo(CN)_8^{4-} + H_3LLH^{\ddagger} + 2H^+ \quad (19)$$

$$Mo(CN)_8^{3-} + H_3LLH^{\ddagger} \overset{k_5}{\longrightarrow} Mo(CN)_8^{4-} + HLLH + 2H^+ \quad (20)$$

$$2HL^{\bullet} \xrightarrow{\text{fast}} HLLH \quad (21)$$

The reverse reaction in eqn. (19) is incorporated to explain the deviation from linearity at higher extent of reaction observed in the log plots.

Using the steady state assumption, the concentration of $H_3LLH^{\ddagger}$ is calculated and the rate of formation of $Mo(CN)_8^{4-}$ is as in eqn. (22)

$$\begin{aligned} d[Mo(CN)_8^{4-}]/dt = & \\ & \{2k_4k_5K_6[Mo(CN)_8^{3-}]^2[H_3L^+]^2 \\ & + k_3k_{-4}K_4K_5[Mo(CN)_8^{3-}][H_3L^+][Mo(CN)_8^{4-}] \\ & + k_3k_5K_4K_5[Mo(CN)_8^{3-}]^2[H_3L^+][H^+]^{-2}\} \\ & /\{k_{-4}[Mo(CN)_8^{4-}][H^+]^2 + k_5[Mo(CN)_8^{3-}]\} \end{aligned} \quad (22)$$

At the initial stages of the reaction when the concentration of $Mo(CN)_8^{4-}$ formed is small, $k_5[Mo(CN)_8^{3-}] \gg k_{-4}[Mo(CN)_8^{-4}][H^+]^2$. Equation (22) therefore simplifies to eqn. (23)

$$\begin{aligned} d[Mo(CN)_8^{4-}]/dt = & \\ & (2k_4K_6[H_3L^+]^2 + k_3K_4K_5[H_3L^+][H^+]^{-2}) \\ & \times [Mo(CN)_8^{3-}] \end{aligned} \quad (23)$$

Hence

$$k_{obs}/[H_3L^+] = 2k_4K_6[H_3L^+] + k_3K_4K_5[H^+]^{-2} \quad (24)$$

This is in agreement with the experimental rate law.

Equation (22) explains the observed curvature at higher extent of reaction which is a confirmation that the product $Mo(CN)_8^{4-}$ affects the rate of this redox reaction and that the rate may not be first order in the oxidant.

Equation (24) explains the kinetic variations displayed in Figs. 5 and 6. Values of k_3' where $k_3' = k_3K_4K_5$ and k_4' where $k_4' = 2k_4K_6$ derived at different temperatures are shown in Table II.

In the reaction of $Mo(CN)_8^{3-}$ with mercaptoacetic acid, the mechanism consistent with the kinetic data is shown in eqns. (25)–(31).

Mechanism IV

$$H_2L \overset{K_7}{\rightleftharpoons} L^{2-} + 2H^+ \quad (25)$$

$$Mo(CN)_8^{3-} + H_2L \overset{K_8}{\rightleftharpoons} [Mo(CN)_8,H_2L]^{3-} \quad (26)$$

$$Mo(CN)_8^{3-} + L^{2-} \overset{K_9}{\rightleftharpoons} [Mo(CN)_8,L]^{5-} \quad (27)$$

$$[Mo(CN)_8,H_2L]^{3-} \xrightarrow{k_6} Mo(CN)_8^{4-} + HL^{\bullet} + H^+ \quad (28)$$

$$[Mo(CN)_8,L]^{-5} + H_2L \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} Mo(CN)_8^{4-} + HLLH^{-\bullet} \quad (29)$$

$$Mo(CN)_8^{3-} + HLLH^{-\bullet} \xrightarrow{k_8} Mo(CN)_8^{4-} + HLLH \quad (30)$$

$$2HL^{\bullet} \xrightarrow{\text{fast}} HLLH \quad (31)$$

The reverse reaction in eqn. (29) is incorporated to explain the observed retardation of the reaction by the product $Mo(CN)_8^{4-}$.

Using the steady state assumption, the concentration of $HLLH^{-\bullet}$ is calculated from which the rate of formation of $Mo(CN)_8^{4-}$ is obtained as expressed in eqn. (32).

$$\begin{aligned} d[Mo(CN)_8^{4-}]/dt = & \\ & \{2k_7k_8K_7K_9[Mo(CN)_8^{3-}]^2[H_2L]^2[H^+]^{-2} \\ & + k_6k_8K_8[Mo(CN)_8^{3-}]^2[H_2L] \\ & + k_6k_{-7}K_8[Mo(CN)_8^{3-}][Mo(CN)_8^{4-}][H_2L]\} \\ & /\{k_{-7}[Mo(CN)_8^{4-}] + k_8[Mo(CN)_8^{3-}]\} \end{aligned} \quad (32)$$

If the concentration of $[Mo(CN)_8^{4-}]$ formed is small, $k_8[Mo(CN)_8^{3-}] \gg k_{-7}[Mo(CN)_8^{4-}]$. Hence eqn. (32) simplifies to eqn. (33).

$$\begin{aligned} \text{Rate} = & (2k_7K_7K_9[H_2L]^2[H^+]^{-2} \\ & + k_6K_8[H_2L][Mo(CN)_8^{3-}] \end{aligned} \quad (33)$$

therefore

$$k_{obs}/[H_2L] = 2k_7K_7K_9[H_2L][H^+]^{-2} + k_6K_8 \quad (34)$$

This is in agreement with the experimental rate law.

The curvature observed in the log plots for this reaction at greater than 70% of the reaction is very similar to the results obtained for the reaction involving cysteine and is explained by eqn. (32). Equation (34) is in agreement with the kinetic data displayed graphically in Fig.s 3 and 4. The composite rate constant k_5' where $k_5' = k_6K_8$ is derived from the common intercept of plots of $k_{obs}/[H_2L]$ against $[H_2L]$ for various acidities while k_6' where $k_6' = 2k_7K_7K_9$ is obtained when the slope of the same graph is plotted against $[H^+]^{-2}$. The values of k_5' and k_6' are also displayed in Table II.

The reactions of these thiols with the oxidant $Mo(CN)_8^{3-}$ show a second order dependence on the substrate in each case. The importance of this process for sulphur containing substrates such as the ones under consideration have been discussed previously [26]; it is thought to provide an easier route for the formation of the disulphide. In terms of the kinetics of the process, although second-order substrate dependence could be obtained through the reaction of a dimer of the substrate with the oxidant

as observed by Carlyle [27], this is not thought feasible in these reactions in view of the kinetic inertness of the dithio anion [28] HLLH. Instead, the second-order process is rationalized in terms of the initial formation of an outer-sphere complex followed by a rate-determining electron transfer reaction between the complex and another molecule/ion of the substrate.

The formation of free radicals in solutions has been discussed generally by Walling [29]. Adams [30] and Karmann *et al.* [31] on the other hand have confirmed the formation of transient dithio radical anion $HLLH^{\cdot-}$ of a variety of thiols while Bridgart and his co-workers [32, 33] have shown that these dithio radicals could be protonated to give $H_2LLH^{\cdot}$ or H_3LLH^{+}. These are in excellent agreement with mechanisms I–IV where radicals such as $H_2LLH^{\cdot}$ (eqn. (6)), $HLLH^{\cdot-}$ (eqn. (9)) and $H_3LLH^{\ddagger}$ (eqn. (19)) are proposed as short-lived products of some of the reactions.

In conclusion, the oxidations of L-cysteine, penicillamine and thioglycolic acid by $Mo(CN)_8^{3-}$ occur through the formation of outer-sphere complexes between the oxidant and the substrates with the corresponding disulphides and $Mo(CN)_8^{4-}$ as products. The mechanisms of the reactions are thought to involve free radical formations.

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References

1 C. E. Callis and R. D. A. Wentworth, *Bioinorg. Chem.*, *7*, 57 (1977).
2 J. F. Martin and J. T. Spence, *J. Phys. Chem.*, *74*, 2863 (1970).
3 J. F. Martin and J. T. Spence, *J. Phys. Chem.*, *74*, 3589 (1970).
4 F. M. Page, *Trans. Faraday Soc.*, *51*, 919 (1955).
5 A. G. Lappin and A. McAuley, *J. Chem. Soc. A*, 1560 (1975).
6 A. McAuley, unpublished work.
7 Z. Amjad, G. Chambers and A. McAuley, *Can. J. Chem.*, *55*, 3575 (1977).
8 J. P. McCann and A. McAuley, *J. Chem. Soc. A*, 783 (1975).
9 A. McAuley and M. A. Olatunji, *Can. J. Chem.*, *55*, 3335 (1977).
10 J. G. Leipoldt, S. S. Basson and L. D. C. Bok, *Inorg. Chim. Acta*, *44*, L99 (1980).
11 M. H. Ford-Smith and J. H. Rawsthorne, *J. Chem. Soc. A*, 160 (1969).
12 F. F. Ferranti, *J. Chem. Soc. A*, 134 (1970).
13 J. G. Leipoldt, C. R. Dennis, A. J. Van Wyk and L. D. C. Bok, *Inorg. Chim. Acta*, *31*, 187 (1978).
14 J. G. Leipoldt, C. R. Dennis, A. J. Van Wyk and L. D. C. Bok, *Inorg. Chim. Acta*, *34*, 237 (1979).
15 J. G. Leipoldt, L. D. C. Bok and C. R. Dennis, *J. Inorg. Nucl. Chem.*, *38*, 1655 (1976).
16 J. G. Leipoldt, L. D. C. Bok, A. J. Van Wyk and C. R. Dennis, *React. Kinet. Catal. Lett.*, *6*, 467 (1977).
17 J. G. Leipoldt, C. R. Dennis and E. G. Grobler, *Inorg. Chim. Acta*, *77*, L45 (1983).
18 C. R. Dennis, S. S. Basson and J. G. Leipoldt, *Polyhedron*, *2*, 1357 (1983).
19 J. G. Leipoldt, S. S. Basson, G. J. Lamprecht and D. R. Rabie, *Inorg. Chim. Acta*, *51*, 67 (1981).
20 H. Hennig, A. Rehorek, D. Rehorek and P. Thomas, *Inorg. Chim. Acta*, *77*, L11 (1983).
21 J. G. Leipoldt, L. D. C. Bok, S. S. Basson, A. J. Van Wyk, C. R. Dennis and P. J. Cilliers, *React. Kinet. Catal. Lett.*, *8*, 93 (1978).
22 N. H. Furman and C. O. Miller, *Inorg. Synth.*, *3*, 160 (1950).
23 J. H. Rawsthorne, *Ph.D. Thesis*, University of Sussex, 1967.
24 H. H. Willard and R. C. Thielke, *J. Am. Chem. Soc.*, *57*, 2609 (1935).
25 J. D. Morris, 'A Biologist's Physical Chemistry', 2nd edn., Edward Arnold, London, 1974, Chap. 6.
26 J. K. Beattie and G. P. Haight, *Prog. Inorg. Chem.*, *17*, 93 (1972).
27 D. W. Carlyle, *J. Am. Chem. Soc.*, *94*, 4525 (1972).
28 A. G. Gilmour and A. McAuley, *J. Chem. Soc. A*, 1006 (1970).
29 C. Walling, 'Free Radicals in Solutions', Wiley, New York, 1957, p. 38.
30 G. E. Adams, *Current Top. Radiat. Res.*, *3*, 35 (1967).
31 W. Karmann, A. Granzow, G. Meissner and A. Henglein, *Int. J. Radiat. Phys. Chem.*, 395 (1968).
32 G. L. Bridgart, M. W. Fuller and I. R. Wilson, *J. Chem. Soc. A*, 1274 (1973).
33 G. L. Bridgart and I. R. Wilson, *J. Chem. Soc. A*, 1281 (1973).