

## KINETICS AND MECHANISM OF THE REDUCTION OF DODECATUNGSTOCOBALTATE (III) BY AQUEOUS SOLUTIONS OF L-METHIONINE

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**ABSTRACT.** The kinetics of the reduction of dodecatungstocobaltate (III) anion by L-methionine have been studied in aqueous hydrochloric acid. The data can be fitted into the rate equation  $-d[\text{Oxidant}]/dt = k_2[\text{Reductant}][\text{Oxidant}]$ , with  $k_2 = 0.16 \pm 0.02 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ ,  $\Delta H = 35.41 \pm 0.50 \text{ kJ mol}^{-1}$  and  $\Delta S = 5.89 \pm 0.41 \text{ J K}^{-1} \text{ mol}^{-1}$  at  $I = 1.0 \text{ mol dm}^{-3}$  (NaCl),  $[\text{H}^+] = 0.05 - 0.50 \text{ mol dm}^{-3}$  and  $T = 25.0^\circ\text{C}$ .

Comparision with reactions of other thiols with the oxidant have been made and the reaction is discussed in terms of the outer sphere mechanism.

### INTRODUCTION

Thiols are widely used as reductants in reactions of metal ion complexes [1-7]. Except in a few cases [5-7], the reactions generally occur *via* intermediates with inner-sphere character. For example inspite of the fact that the sulphur co-ordinating site is blocked by a methyl group in L-methionine, we recently reported [1] that its interaction with Cr (VI) probably involves a rate-determining Cr-S bonded intermediate. Such sulphur-bonded intermediates are not only thought to provide low energy pathways for subsequent electron transfer steps, their medical significance has long been recognised [8-9].

We now report the result of the reaction of L-methionine with the substitution-inert dodecatungstocobaltate (III) anion. Our interest in this reaction is prompted by three factors. Firstly, it had previously been shown that dodecatungstocobaltate (III) anion reacts with a wide range of thiols, including L-cysteine [6], mercaptoacetic acid [6], mercaptoethylamine [6], glutathione [7], thiourea and substituted thioureas [10] without evidence for the formation of sulphur-bonded intermediates prior to electron transfer. It is therefore considered worthwhile to see whether the title reaction will conform to this pattern. Secondly, in the unlikely event that an intermediate complex is important in this study, it is desirable to compare the reaction mechanism with those involving L-methionine and Cr (VI) or related metal ions [1]. Thirdly, the inverse hydrogen ion dependence term encountered in reactions of dodecatungstocobaltate (III) with L-cysteine, mercaptoacetic acid, mercaptoethylamine and glutathione [6,7] were rationalised in terms of the dissociation of the sulphhydryl group, -SH, prior to electron transfer. This group is absent in L-methionine and the interpretation of any hydrogen ion dependence term in the present investigation is of interest. Although Olatuunji and Ishola [11] had made a preliminary survey of the title reaction, their data base was too weak to permit any meaningful mechanistic conjectures. For convenience, dodecatungstocobaltate (III) anion,  $\text{CoW}_{12}\text{O}_{40}^{5-}$ , and dodecatungstocobaltate (II)  $\text{CoW}_{12}\text{O}_{40}^{6-}$  are subsequently abbreviated as  $\text{Co}^{\text{III}}\text{M}$  and  $\text{Co}^{\text{II}}\text{M}$  ( $\text{M} = \text{W}_{12}\text{O}_{40}^{8-}$ ), respectively.

## EXPERIMENTAL

**Materials.** The method of preparation and standardization of potassium dodecatungstocobaltate (III) was described earlier [12]. L-methionine (B.D.H reagent) was used without further purification. Hydrochloric acid (Analar grade) was used to investigate the effect of hydrogen ions on the rates of reaction, while sodium chloride (BDH reagent) was employed to maintain a constant ionic strength.

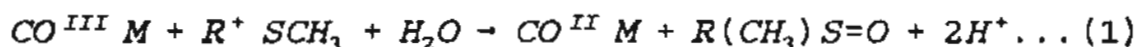
**Kinetics.** The reaction was found to be very slow under the experimental conditions used. Consequently, the rate measurements were conducted using conventional spectrophotometry by following the decrease in the concentration of  $\text{Co}^{\text{III}}\text{M}$  at 390 nm ( $\epsilon = 1180 \pm 20 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ) [13].

**Stoichiometry and product analysis.** The stoichiometry of the reaction was determined spectrophotometrically as described earlier [6]. Product analysis, on the other hand, was carried out as follows:

A reaction mixture containing  $2.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ Co}^{\text{III}}\text{M}$ ,  $2.00 \times 10^{-2} \text{ mol dm}^{-3}$  L-methionine and  $5.0 \times 10^{-3} \text{ mol dm}^{-3}$  hydrochloric acid in a  $25 \text{ cm}^3$  solution was allowed to stand for 3 h.  $10 \text{ cm}^3$  of  $0.4 \text{ mol dm}^{-3} \text{ NaHCO}_3$  was added and stirred vigorously followed by dropwise addition of benzoyl chloride until precipitation was completed. The white precipitate obtained in 67% yield was confirmed by its melting point,  $183^\circ\text{C}$ , [14], to be N-benzoylmethionine sulphoxide. This suggests that the oxidation product is methionine sulphoxide.

## RESULTS AND DISCUSSION

**Stoichiometry.** Spectrophotometric titrations showed that the mole ratio  $[\text{Co}^{\text{III}}\text{M}]/[\text{L-methionine}]$  was  $1.1 \pm 0.06$ . This is consistent with reaction (1), where protonated methionine,  $\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2\text{H}$ , is represented as  $\text{R}^+\text{SCH}_3$ .



$\text{Co}^{\text{II}}\text{M}$  was characterised by its electronic spectrum ( $\lambda_{\text{max}} = 625 \text{ nm}$ ;  $\epsilon = 204 \pm 5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ) [15] while the formation of methionine sulphoxide was confirmed as described in the Experimental section. It appears that as in the reaction of methionine with  $\text{AuCl}_4^-$  [20], there is a direct attack by water at the sulphur atom with eventual transfer of oxygen to the sulphur to give methionine sulphoxide.

Reactions of other thiols with  $\text{Co}^{\text{III}}\text{M}$  [6,7] also displayed 1:1 stoichiometries but the product in each case is the respective disulphide,  $\text{RSSR}$ . Our present result is in line with an earlier postulate [1] that the hydrolysis of the  $\text{H}_3\text{C-S}$  group in methionine, leading to the fission of  $\text{H}_3\text{C-S}$  bond and the formation of a disulphide product is highly unlikely under the acid conditions employed in this study.

**Spectrophotometric Test for Intermediate Complex.** Spectrophotometric test for intermediate complex formation conducted as described elsewhere [6] showed no clear change in the  $\lambda_{\text{max}}$  value of  $\text{Co}^{\text{III}}\text{M}$ . This may suggest the absence of an intermediate complex of significant stability but an intermediate complex with a small formation constant cannot be precluded.

**Tests for Free Radical.** The test for free radicals in the reaction mixtures was carried out in two ways. First, the solutions were degassed with dinitrogen and tested for free radicals as described earlier [15]. Secondly, monitoring of observed rate constants,  $k_{obs}$ , using constant concentrations of  $Co^{III}M$ ,  $H^+$ , and  $L$ -methionine in the presence of various amounts of acrylamide in the range 5-25% (w/v), showed that  $k_{obs}$  was independent of the percentage of acrylamide (Table 1). Both of these results suggest that free radical intermediates, if any, formed during the reaction must be short lived.

Table 1. Effect of acrylamide on pseudo-first-order rate constants at 25°C

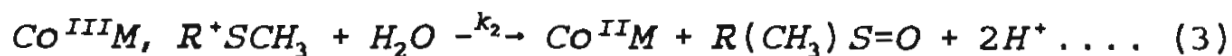
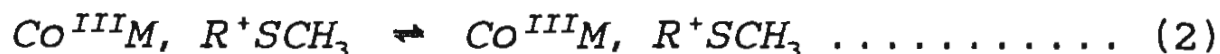
$[Co^{III}M] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[H^+] = 0.05 \text{ mol dm}^{-3}$ ,  
 $[R^+SCH_3] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$ , and  $I = 1.0 \text{ mol dm}^{-3}$

Acrylamide (% w/v)	0	0.25	0.05	0.75	1.00	1.50	2.00	2.50
$10^3 k_{obs} (s^{-1})$	0.96	0.98	1.00	1.01	0.99	1.00	0.96	0.97

**Kinetics and Mechanism.** Under the experimental conditions used, plots of  $\log_{10} (A_t - A_\infty)$  against time ( $A_t$  and  $A_\infty$  are the absorbances at times  $t$  and at the end of reaction, respectively) were linear to about 80% of the reaction. Pseudo-first-order rate constants,  $k_{obs}$ , obtained from the gradients of these plots at various  $[H^+]_0$  and  $[L\text{-methionine}]_0$  are presented in Table 2.

Plots of  $k_{obs}$  as a function of methionine concentration were linear with positive slopes, suggesting that the reaction is first-order with respect to methionine. The slopes of these lines yielded the second order rate constants, presented in Table 3. Values of  $k_{obs}$  were independent of hydrogen ion concentrations in the 0.05 - 0.50  $\text{mol dm}^{-3}$  range (Table 1). It therefore seems that partition of reactants between protonation levels is negligible in the acid range studied. In line with arguments presented earlier [1,4,6], the protonated methionine,  $R^+SCH_3$ , is thought to be the principal reductant species under our experimental conditions.

On the basis of the results discussed above, the following mechanism may be postulated for the reaction.



Thus, the rate of loss of  $Co^{III}M$  may be expressed as

$$\frac{-d[Co^{III}M]_T}{dt} = \frac{k_2 K [R^+SCH_3] [Co^{III}M]_T}{1 + K [R^+SCH_3]} \dots \dots \dots (4)$$

$$K_{obs} = \frac{k_2 K [R^+SCH_3]}{1 + K [R^+SCH_3]} \dots \dots \dots (5)$$

Table 2. Pseudo-first-order rate of reduction of  $R^+SCH_3$  by  $Co^{III}M$ ,  $\lambda = 390$  nm and  $I = 1.0$  mol  $dm^{-3}$  (NaCl).

T (°C)	$10^4 \times [Co^{III}M]$ (mol $dm^{-3}$ )	$10^3 \times [R^+SCH_3]$ (mol $dm^{-3}$ )	$[H^+]$ (mol $dm^{-3}$ )	$10^3 \times K_{obs}$ ( $s^{-1}$ )
20.0	2.00	2.00	0.05	0.28
	2.00	4.00	0.40	0.55
	1.00	6.00	0.20	0.75
	4.00	8.00	0.50	1.00
	2.00	10.00	0.50	1.25
	2.00	12.00	0.05	1.50
	2.00	14.00	0.50	1.76
	2.00	16.00	0.10	2.00
25.0	2.00	2.00	0.50	0.33
	2.00	4.00	0.50	0.67
	2.00	6.00	0.50	0.96
	2.00	8.00	0.50	1.23
	2.00	10.00	0.50	1.50
	2.00	12.00	0.50	1.81
	2.00	14.00	0.50	2.13
	2.00	16.00	0.50	2.50
	2.00	6.00	0.05	1.00
	2.00	6.00	0.10	1.02
	2.00	6.00	0.20	0.97
	2.00	6.00	0.25	0.99
	2.00	6.00	0.30	1.01
	2.00	6.00	0.40	1.02
	2.00	6.00	0.50	0.96
	4.00	6.00	0.50	1.00
3.00	6.00	0.50	1.01	
1.00	6.00	0.50	0.78	
30.0	2.00	2.00	0.50	0.46
	2.00	4.00	0.50	0.85
	2.00	6.00	0.20	1.21
	2.00	8.00	0.10	1.65
	2.00	10.00	0.50	2.14
	2.00	12.00	0.50	2.43
	2.00	14.00	0.05	2.84
	2.00	16.00	0.50	3.33
35.0	2.00	2.00	0.50	0.55
	2.00	4.00	0.50	1.11
	2.00	6.00	0.50	1.59
	2.00	8.00	0.50	2.10
	2.00	10.00	0.10	2.58
	2.00	12.00	0.50	3.15
	2.00	14.00	0.20	3.72
	2.00	16.00	0.20	4.25

If  $K[R^+SCH_3] \ll 1$  then

$$K_{obs} = k_2 K[R^+SCH_3] \dots\dots\dots (6)$$

Table 3. Second order rate constants  $k_2$

T (°C)	$k_2^a$ (mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup> )
20.0	0.13 ± 0.01
25.0	0.16 ± 0.02
30.0	0.21 ± 0.01
35.0	0.27 ± 0.02

$$\Delta H = 35.41 \pm 0.51 \text{ kJ mol}^{-1}$$

$$\Delta S = 5.89 \pm 0.41 \text{ J K}^{-1} \text{ mol}^{-1}$$

<sup>a</sup>Error expressed as standard deviation

A comparison of this reaction with other reductions of Co<sup>III</sup>M by thiols [6,7], reveal that they involve essentially similar activation processes. The absence of any detectable intermediate of significant stability in these reactions and the substitution inertness of the oxidant [18,19] suggest that the mechanisms involve the formation of outer-sphere or ion-pair complexes. In keeping with this, the complex formed in reaction (2) is expected to be an outer-sphere complex rather than the inner-sphere type proposed earlier in the reactions of HCrO<sub>4</sub><sup>-</sup> [1] and AuCl<sub>4</sub><sup>-</sup> [20] with *L*-methionine. Since the substrate is positively charged under our experimental conditions, the formation of an ion-pair complex would make the cobalt ion positive and increase its tendency to oxidize *L*-methionine. This view is consistent with the facts that initial complexes were formed in the reaction of HCrO<sub>4</sub><sup>-</sup> [1] and AuCl<sub>4</sub><sup>-</sup> [20] with *L*-methionine but not in the corresponding reactions of the positively charged oxidants Fe(bipy)<sub>3</sub><sup>3+</sup> and Fe(phen)<sub>3</sub><sup>3+</sup> [21].

In spite of the apparent similarities in the modes of activation of this and similar Co<sup>III</sup>M-thiol reactions, some differences are noteworthy.

a) The inverse hydrogen ion dependence term usually encountered in the oxidation of thiols by Co<sup>III</sup>M [6,7] are absent in the present study. Since the observation of such [H<sup>+</sup>] terms were attributed to the deprotonation of the sulphhydryl, -SH, group prior to electron transfer, our present result is consistent with the postulate [1] that the attachment of a methyl group to the sulphur atom in methionine would prevent the corresponding cleavage of the H<sub>3</sub>C-S bond under the acid conditions used. Even in the unlikely event that the cleavage takes place, it should not result in any observable variation of rate with [H<sup>+</sup>].

b) Free radical intermediates, which are generally implicated in the reactions of various thiols with Co<sup>III</sup>M [6,7] are not in the title investigation. This is evident from the results of polymerization studies and the invariance of  $k_{obs}$  with addition of different percentages of acrylamide to reaction mixtures. One implication of this is that a one-step oxidation of methionine occurs as shown in our proposed mechanism. Alternatively, the free radicals may be too short-lived to be detected by the method employed.

## CONCLUSION

The oxidation of dodecatungstocobaltate (III) by *L*-methionine occurs *via* the outer sphere mechanism and is in this respect similar to earlier oxidations of a wide range

of organic and inorganic substrates [6,7,10,12,13,15] by this bulky oxidant. Support for the outer sphere mechanism comes mainly from the substitution inertness of the oxidant and the steric hindrance to direct interaction between the deeply imbedded  $\text{Co}^{\text{III}}$  ion and the sterically hindered sulphur atom in the substrate.

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