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KINETICS AND MECHANISM OF THE OXIDATION OF L-METHIONINE BY AQUEOUS SOLUTION OF CHROMIUM(VI)

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Abstract—The kinetics of the reduction of Cr(VI) by L-methionine (represented by $RSCH_3$) have been studied in aqueous perchloric acid. The data are consistent with the rate law:

$$\frac{-d[\mathrm{Cr(VI)}]}{dt} = (k_1 + k_2[\mathrm{H^+}]^2[\mathrm{RSCH_3}])[\mathrm{Cr(VI)}]$$

with $k_1 = (3.1 \pm 0.5) \times 10^{-4}\ \mathrm{s^{-1}}$; $k_2 = 12.3 \pm 1.1\ \mathrm{mol^{-3}\ dm^9\ s^{-1}}$ at $I = 1.0\ \mathrm{mol\ dm^{-3}}$ ($NaClO_4$), $[H^+] = 0.04$–$0.10\ \mathrm{mol\ dm^{-3}}$ and T = 25.1°C. The corresponding activation parameters are $\Delta H^{*}_{1} = 26.2 \pm 0.4\ \mathrm{kJ\ mol^{-1}}$; $\Delta S^{*}_{1} = -224 \pm 1\ \mathrm{JK^{-1}\ mol^{-1}}$; $\Delta H^{*}_{2} = 33.9 \pm 0.01\ \mathrm{KJ\ mol^{-1}}$; $\Delta S^{*}_{2} = -111 \pm 1\ \mathrm{JK^{-1}\ mol^{-1}}$. The above rate is very much slower than those of other related reactions. This is interpreted in terms of a rate-determining Cr—S bonded intermediate which undergoes hydrolysis after electron transfer to yield Cr(III) and methionine sulphoxide. The significance of pathways involving second-order substrate dependence is also discussed.

Chromate ester formation is a common feature of chromium(VI) reduction by electron pair donors.[1–7] Presumably because of their medical significance,[8] more attention has been given to sulphur-bonded esters which are characterized by their formation constants and electronic spectra.[6,9] These intermediates are thought to provide low energy pathways for subsequent electron-transfer. Thus any factor that inhibits their formation is known to affect the reduction markedly.[10,11]

The reaction of Cr(VI) with L-methionine was investigated for several reasons. Firstly, L-methionine like L-cysteine[4] and other related thiols[1,2] has three coordinating centres *viz*: O, N and S. Of these, sulphur has been established as the most susceptible to attack by Cr(VI). However, this site is partially blocked by a methyl group within the substrate and it is therefore of interest to study the effect of this on the reactivity of the substrate. Secondly, although the reaction had been investigated by different workers[12,13] in the past, conflicting views had been expressed as to the nature of one of the final products. While one group[12] postulated a disulphide as one of the products of the reaction, the other group[13] was able to establish a sulphoxide as the corresponding final product. It is thought that the present investigation would be able to resolve the conflict and throw more light on the mechanism of the reaction.

EXPERIMENTAL

L-methionine (Koch-Light, Pure) was used without further purification. Potassium dichromate (Analar grade) was used for the kinetic runs while the sodium salt (B.D.H. Reagent) was used for the product analysis where concentrations were such as to cause precipitation of potassium perchlorate had the potassium salt been used. Mixtures of sodium perchlorate (Fluka, puriss) and perchloric acid (Analar Reagent) were used to maintain a constant ionic strength of $1.0\ \mathrm{mol\ dm^{-3}}$ at varying hydrogen ion concentrations $[H^+]$. Stock solutions of perchloric acid were analysed by titration against weighed quantities of sodium tetraborate.

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Kinetics

Under the conditions used for the kinetics $HCrO_4^-$ has been established[4] as the reacting species of the oxidant. Kinetic measurements were therefore made at 350 and 420 nm by monitoring the absorbance changes due to it on a Pye Unicam SP 8000 spectrophotometer with fully thermostated cell compartments. The concentration of the oxidant was kept constant at 4.0×10^{-4} mol dm^{-3} while L-methionine concentrations were varied between $(5.0–25.0) \times 10^{-3}$ mol dm^{-3} and the ionic strength of the medium was kept constant at 1.0 mol dm^{-3} using sodium perchlorate. Pseudo first-order plots were linear to more than three half lives and duplicate measurements agreed to ±2%.

Products

The main product methionine sulphoxide was characterized as follows:

A reaction mixture containing 2.0×10^{-3} mol sodium dichromate, 2.5×10^{-2} mol methionine and 5.0×10^{-3} mol perchloric acid in a 50 cm^3 solution was allowed to stand for about 2 h. Thereafter 10 cm^3 of 0.4 mol dm^3 sodium bicarbonate was added and stirred vigorously followed by dropwise addition of benzoyl chloride solution until precipitation was completed. The precipitate obtained *N*-benzoyl methionine sulphoxide which is a derivative of methionine sulphoxide was confirmed by its melting point 183°C.[13] The yield obtained was about 70%.

A second method[14] for the characterization of the product was employed by adding an acetone–ethanol mixture (1 : 1 vol. ratio) to a similar reaction mixture as above which had previously been brought to pH 4. The precipitate of methionine sulphoxide was identified by its melting point which was found to be 238°C.[14] The yield obtained was about 86%.

RESULTS AND DISCUSSION

The linearity of the pseudo first-order plots implies that the reaction is first-order in Cr(VI). Representative values of the pseudo first-order constant, k_{obs} obtained at different methionine concentrations, hydrogen ion concentrations $[H^+]$, wavelength and ambient temperatures are shown in Table 1.

Plots of k_{obs} as a function of methionine concentration for different $[H^+]$ at constant temperature were linear with a common positive intercept (Fig. 1). The slopes of these lines vary linearly with the square of the hydrogen ion concentration $[H^+]^2$ (Fig. 2).

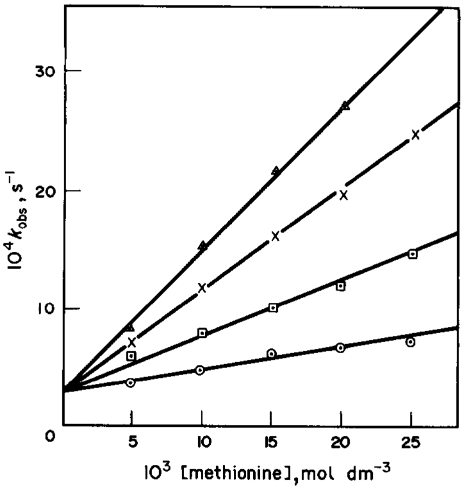


Fig. 1. The dependence of observed rate constant (k_{obs}) on the concentration of methionine at 25.1°C. $[Cr(VI)] = 4.0 \times 10^{-4}$ mol dm^{-3}; I = 1.0 mol dm^{-3} ($NaClO_4$); $[H^+] = 0.04$ mol dm^{-3} (⊙); $[H^+] = 0.06$ mol dm^{-3} (⊡); $[H^+] = 0.08$ mol dm^{-3} (×); $[H^+] = 0.10$ mol dm^{-3} (△).

From these results, the reaction is considered to proceed via two parallel pathways and the overall mechanism for the reaction can be represented by eqs (1)–(5). Under the conditions of the experiment, protonated methionine $CH_3SCH_2CH_2CH(\overset{+}{N}H_3)CO_2H$ represented as $RSCH_3$ is the predominant species in line with the argument presented elsewhere.[1,2,4,12] The mechanism is therefore given as:

$$HCrO_4^- + RSCH_3 \xrightleftharpoons{K} R^1(CH_3)SCRo_3^- + H_2O \quad (1)$$

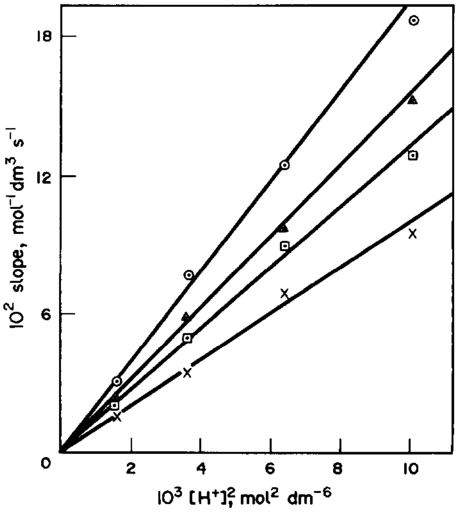


Fig. 2. Plots of slope [eq. (9)] as a function of $[H^+]^2$. = 20.1°C (⊙); 25.1°C (⊡); 30.1°C (△); 35.0°C (×).

Table 1. Observed rate constant (k_{obs}) for the reaction of Cr(VI) and L-methionine [RSCH$_3$] at different hydrogen ion concentrations [H$^+$] and temperatures. [Cr(VI)] = 4×10^{-4} mol dm^{-3}, I = 1.0 mol dm^{-3} (NaClO$_4$) and λ = 420 nm

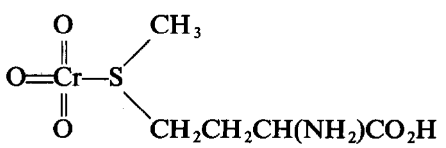
10^3 [RSCH$_3$] (mol dm^{-3})	[H$^+$] (mol dm^{-3})	$10^4\ k_{obs}$, s^{-1}		
	0.04	0.06	0.08	0.10
$T = 20.1$°C				
5.0	2.5	3.6	5.6	6.6
10.0	3.9	5.8	9.6	11.8
15.0	4.8	7.8	12.3	17.0
20.0	5.4	8.5	16.0	18.8
25.0	5.8	10.6	18.8	25.1
$T = 25.1$°C				
5.0	3.0 (3.0)	4.7	6.7	8.4 (8.4)
10.0	4.8 (4.9)	8.0	12.0 (12.0)	15.6
15.0	6.4 (6.2)	10.3 (10.0)	16.5 (16.2)	22.2
20.0	6.9	11.8 (11.6)	19.9 (19.2)	27.5 (27.4)
25.0	7.2	14.8 (14.7)	25.1	30.4
$T = 30.1$°C				
5.0	3.9	5.8	8.3	11.0
10.0	5.6	10.0	14.0	18.9
15.0	7.2	12.2	18.9	25.7
20.0	7.7	15.4	21.5	31.9
25.0	8.1	17.6	25.7	35.5
$T = 35.1$°C				
5.0	4.8	7.8	9.8	13.1
10.0	7.6	11.1	16.7	21.4
15.0	8.3	16.0	26.9	32.1
20.0	10.5	20.6	29.6	39.2
25.0	11.3	21.8	34.0	49.1

( ) Values at λ = 350 nm.

$$R^1(CH_3)SCrO_3^- \xrightarrow[H_2O]{k_1} Cr(IV) + R^1(CH_3)S{=}O \quad (2)$$

$$R^1(CH_3)SCrO_3^- + RSCH_3 \xrightarrow[2H_3O^+]{k_2} Cr(IV) + R^1(CH_3)S{=}O + RSCH_3 + 2H^+ \quad (3)$$

where $R^1(CH_3)SCrO_3^-$ is



other contributing steps are as in (4)–(5).

$$2Cr(IV) \xrightarrow{fast} Cr(III) + Cr(V) \quad (4)$$

$$Cr(V) + RSCH_3 \xrightarrow[H_2O]{fast} Cr(III) + R^1(CH_3)S{=}O. \quad (5)$$

On the basis of this scheme the rate of loss of [HCrO$_4^-$] can be readily derived [eq. (6)]

$$\frac{-d[HCrO_4^-]_T}{dt} = \frac{K[RSCH_3](k_1 + k_2[RSCH_3][H^+]^2)[HCrO_4]_T}{1 + K[RSCH_3]}. \quad (6)$$

But

$$\frac{-d[HCrO_4^-]_T}{dt} = k_{obs}[HCrO_4^-]_T \quad (7)$$

therefore

$$k_{obs} = \frac{K[RSCH_3](k_1 + k_2[RSCH_3][H^+]^2)}{1 + K[RSCH_3]}. \quad (8)$$

If $K[RSCH_3] \gg 1$, eq. (8) becomes

$$k_{obs} = k_1 + k_2[H^+]^2[RSCH_3]. \quad (9)$$

Table 2. Rate constants k_1 and k_2 for the reaction of Cr(VI) with L-methionine at different temperatures

T/°C	$^{a}k_1/\mathrm{s}^{-1}$	$^{a}k_2/\mathrm{Mol}^{-3}\,\mathrm{dm}^{9}\,\mathrm{s}^{-1}$
20.1	2.5 ± 0.3	9.4 ± 0.8
25.1	3.1 ± 0.5	12.3 ± 1.1
30.1	3.8 ± 0.5	15.3 ± 1.2
35.0	4.5 ± 0.5	19.3 ± 1.4

$\Delta H^{*}_{1} = 26.2 \pm 0.4\ \mathrm{kJ\ mol^{-1}}$;

$\Delta S^{*}_{1} = -224 \pm 1\ \mathrm{JK^{-1}\ mol^{-1}}$

$\Delta H^{*}_{2} = 33.9 \pm 0.01\ \mathrm{kJ\ mol^{-1}}$;

$\Delta S^{*}_{2} = -111 \pm 1\ \mathrm{JK^{-1}\ mol^{-1}}$

[a] Error expressed as standard deviation.

The observation that plots of k_{obs} vs $[\mathrm{RSCH_3}]$ gave good straight lines at constant $[\mathrm{H^+}]$ and temperature is consistent with the above mechanism. The various rate constants k_1, derived from the intercepts of such plots and k_2, obtained from the graph of slope vs $[\mathrm{H^+}]$ at different temperatures are shown in Table 2 together with their corresponding activation parameters.

Our observed rate law eq. (6) differs only slightly from those derived for other related reactions[1–4] with the predominant path involving two substrate molecules. A comparison of the activation parameters for the predominant path in this and similar Cr(VI) reductions[1,2,4] reveals that such routes involve essentially similar processes. There is a change in coordination number from four in Cr(VI) to six in the kinetically stable Cr(III) products. Therefore, an expansion of coordination shell has to occur somewhere between the two states. It is thought that the coordination of a second substrate facilitates the expansion of Cr(VI) which occurs in reactions (3) where there is a two electron reduction from Cr(VI) to Cr(IV). This requirement for reorganization may account for the slowness and rate-determining character of the step. Another argument that could be advanced in favour of the second substrate is that the substrate being positively charged under the experimental conditions used, would make the central chromium ion more positive and thereby increase the tendency of the metal to oxidize the coordinated substrate. This is very similar to the observation made in the reaction of the same reductant with the $[\mathrm{AuCl_4}]^-$ anion.[14]

Interestingly, the reduction of Cr(VI) by methionine is much slower than the corresponding reductions of the same oxidant by penicillamine[1,2] glutathione[1,2] and cysteine[4] under the same experimental conditions. This is consistent with the postulate[5] that the formation of an intermediate complex is a prerequisite for these redox processes. It also supports reports by McAuley and his coworkers[1,2,4] that the site most susceptible to attack by Cr(VI) in these substrates is sulphur. The presence of an alkyl group at the site appears to inhibit but not totally prevent the coordination of sulphur to the chromium centre. Although the formation of an intermediate complex could not be established from repeated scanning of reaction mixtures, this does not invalidate the postulate that some form of complex formation is involved before electron-transfer.

Comparison of the rate constants k_1 and k_2 in this reaction with those of similar reactions involving the oxidant with penicillamine[2] and cysteine,[4] show that the former rate constants are two orders of magnitude greater than those of cysteine[4] and comparable with those of penicillamine.[2] This is not very surprising judging from the fact that the presence of the methyl group in methionine (which is retained after the electron-transfer process) and two methyl groups attached to the adjacent carbon atom in the case of penicillamine would aid the rapid release of the electrons from sulphur to the oxidant much more than in the case of cysteine[4] (inductive effect). However, in spite of this, the overall rate of oxidation of methionine is slower than those of the latter under the same experimental conditions. This would tend to suggest that substitution into the inner coordination sphere of chromium(VI) is likely to be the rate-determining step in these reactions.

The fate of the intermediate Cr(IV) produced in reactions (2–4) has generated a lot of debate in the past. Westheimer and Watanabe[10,15] considered several possible paths involving the subsequent reactions of Cr(IV), citing experimental evidence that in dilute $\mathrm{HClO_4}$ one subsequent step must involve Cr(VI). However, addition of 0.04 mol $\mathrm{dm^{-3}}$ of Mn(II) had no effect on the rate of the reaction. This would suggest that the oxidant in this investigation is not involved after the rate-determining steps. Rather, a disproportionation of Cr(IV) is assumed to take place followed by a two electron reduction of the Cr(V) produced to give the final products Cr(III) and methionine sulphoxide. A similar observation was made by Haight and his coworkers[16] in the oxidation of hydrazine by Cr(VI).

Srivastava and coworkers[13] in their own investigation of the title reaction have proposed a direct linkage between the sulphur atom in methionine and one of the oxygen atoms in $\mathrm{HCrO_4^-}$ rather than the metal centre in an attempt to rationalize the formation of a sulphoxide as one of the final products. It is difficult to see how this could possibly be the case given the fact that both sulphur and oxygen are highly electronegative elements. On the other hand, Petri and Baldea[12] in their own studies, postulated that the title reaction proceeded via the hydrolysis of H_3C—S group in methionine leading to the formation of the sulphur-bonded $HO_2CCH(NH_2)CH_2CH_2SCrO_3^-$ intermediate before electron transfer. No alcohol was obtained as a product in our own investigation to make us reach such a conclusion. Moreover, the hydrolysis of the H_3C—S group leading to the fission of the C—S bond is highly unlikely in the acid medium used.

In conclusion, the oxidation of methionine is assumed to take place through the formation of a sulphur-bonded intermediate complex which undergoes hydrolysis after the electron transfer to give Cr(III), methionine sulphoxide and possibly substituted $[Cr^{III}(RSCH_3)]$ as the products in line with the suggestion elsewhere.[17,18] The formation of the sulphur-bonded intermediate complex is assumed to be the rate determining step in these reactions.

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