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The Kinetics of the Reaction of Chromium(III) with L-Cysteine

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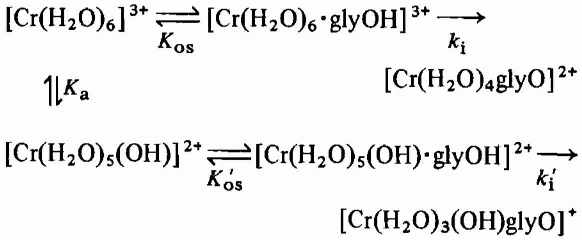
Introduction

We have recently studied [1] the reaction of glycine with chromium(III) in moderately acidic solutions. We concluded that a scheme of the kind shown below accounted for our observations. Under first order conditions with an excess of the amino acid, the reaction followed the rate law $k_{obs} = k + k'[H^+]^{-1}$ and was zero order in the glycine concentration. The mechanism is essentially of the Eigen–Wilkins [2] type with two distinct reactive outer sphere complexes, derived from hexaquachromium(III) and its conjugate base respectively. Activation parameters were consistent with a dissociative reaction for the hydroxy-complex and an associative (I_a) process for reaction from the aqua complex. We have now conducted a similar study of the reaction of L-cysteine with chromium(III).



$$\begin{tikzcd}
{[Cr(H_2O)_6]^{3+}} \arrow[r, shift left, "K_{os}"'] \arrow[d, shift left, "K_a"] & {[Cr(H_2O)_6\cdot glyOH]^{3+}} \arrow[l, shift left] \arrow[r, "k_i"'] & {} \\
& & {[Cr(H_2O)_4glyO]^{2+}} \\
{[Cr(H_2O)_5(OH)]^{2+}} \arrow[u, shift left] \arrow[r, shift left, "K_{os}'"'] & {[Cr(H_2O)_5(OH)\cdot glyOH]^{2+}} \arrow[l, shift left] \arrow[r, "k_i'"'] & {} \\
& & {[Cr(H_2O)_3(OH)glyO]^{+}}
\end{tikzcd}$$

[Glycine, protons and water are omitted; K_{os} are the outer sphere association constants; k_i are interchange rate constants].

Scheme 1.

Experimental

The methods and reagents used in this paper were essentially as described in our earlier paper [1]. However in the present study the reaction was followed using a Thorn-NPL polarimeter type 243. The mercury green 546 nm line was used; the rotation of the complex was much greater than that of the free amino acid, hence complexation could be followed. Good first order plots were obtained. As in the earlier study the solution was thermostatted and circulated through a flow-cell using a perstaltic pump; pH was maintained using a Radiometer Automatic Titrator 45646. Typical conditions are given in Table I.

TABLE I. Typical First-Order Rate Constants.[a]

pH	$10^5 k_{obs}/s^{-1}$	
4.2	56.4	$k_{obs} = 0.809 \times 10^{-5} + 3.73 \times 10^{-8}[H^+]^{-1}$
4.1	52.0	
4.0	37.6	
3.9	32.7	
3.75	19.9	
3.40	9.50	

[a] $[Cr(III)] = 1 \times 10^{-2}$ mol dm^{-3}, [cys] = 0.1 mol dm^{-3}, I = 0.5 mol dm^{-3}, 44.25 °C.

Results

The rate of complex formation was studied under a variety of conditions. First-order plots of ln ($\phi_{obs} - \phi_\infty$) *vs.* time were good straight lines over two to three half-lives. All reactions followed a single first-order process which strongly suggests that ring closure is rapid. The most striking results were that the reaction was zero order in the L-cysteine concentration up to $\sim 2 \times 10^{-1}$ mol dm^{-3}, and obeyed the above rate law. The acid-independent rate constants obtained from plots of k_{obs} *vs.* $[H^+]^{-1}$ are summarized in Table I and illustrated in Fig. 1.

Discussion

Although the present study of L-cysteine complexation is limited, the similarity to our earlier study of glycine complexation is marked. Table I shows that the acid independent rate constants are very similar to those measured for glycine; $k = 3.55 \times 10^{-5}$ s^{-1} and $k' = 3.63 \times 10^{-8}$ s^{-1} (I = 0.4 mol dm^{-3}, 44.5 °C). We therefore suggest that complex formation by L-cysteine proceeds by a similar mechanism to that previously proposed [1] for glycine complexation (see Scheme 1). In common with Maslowska and Chruscinski [3] we would suggest that in moderately acidic solutions the chromium(III) cysteine complex initially formed is an N,O chelate. This is in contrast with the known N,O,S coordination in the biscysteine complex isolated by de Meester *et al.* [4].

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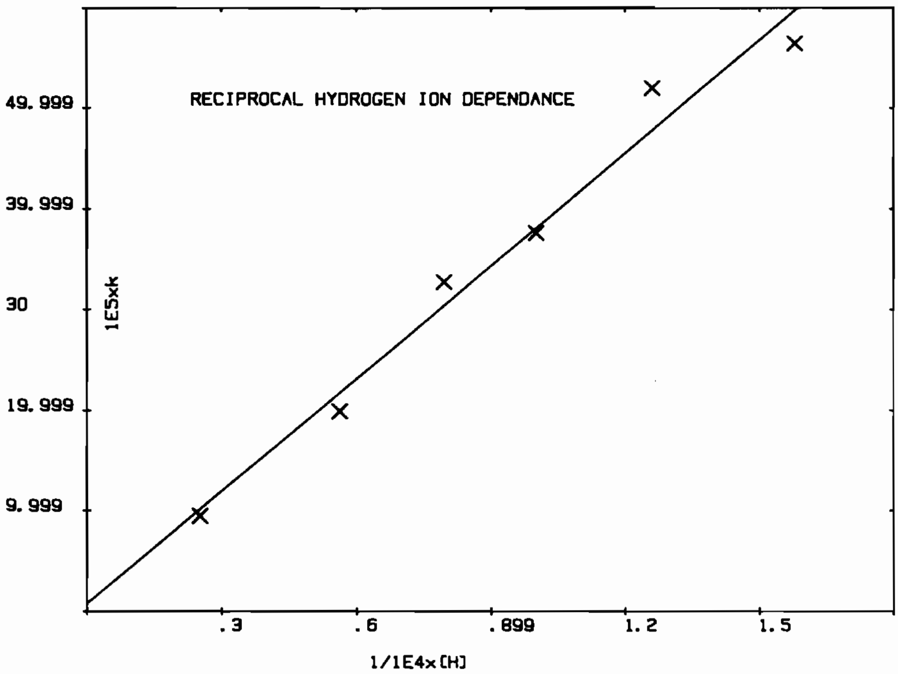

Fig. 1. Dependence of the pseudo first order rate constant on reciprocal hydrogen in concentration; conditions as in Table I; x axis: $10^5 \times k_{obs}\ s^{-1}$; y axis: $[H^+]^{-1}/10^4\ mol^{-1}\ dm^3$.

References

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