Metal-ion Oxidations in Solution. Part XIII.† The Reaction of Chromium(VI) with L-Cysteine in Perchlorate Media

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The stopped-flow technique has been used to study the reactions between $[HCrO_4]^-$ and L-cysteine, H_2L, with the latter in excess, at $[HClO_4] = 0{\cdot}020$—$0{\cdot}100$M and $I = 1{\cdot}00$M ($NaClO_4$) in the range 15—35 °C. The transient orange species observed is a 1 : 1 chromate ester [equation (i)] with $\lambda_{max.} = 420$ nm, $\varepsilon_{max.} = 1\,410 \pm 60$ l mol^{-1} cm^{-1},

$$H_2L + [(HO)CrO_3]^- \overset{K_1}{\rightleftharpoons} [(HL)CrO_3]^- + H_2O \qquad \text{(i)}$$

and $K_1 = 1\,030 \pm 110$ l mol^{-1} at 25 °C. Evidence regarding sulphur bonding is discussed. The kinetics of the formation reaction conform to the rate law (ii) and, at 25 °C, $k_f' = 130 \pm 20$ l^2 mol^2 s^{-1} and $k_f = 2 \pm 1$ l mol^{-1} s^{-1}.

$$d[\text{Complex}]/dt = (k_f'[H^+] + k_f)[HCrO_4^-][H_2L] \qquad \text{(ii)}$$

For the acid-catalysed path, $\Delta H^\ddagger = 7 \pm 3$ kcal mol^{-1} and $\Delta S^\ddagger = -24 \pm 11$ cal K^{-1} mol^{-1}. For the overall formation reaction, $\Delta G = -4{\cdot}1 \pm 0{\cdot}1$ kcal mol^{-1}, $\Delta H = -5{\cdot}0 \pm 0{\cdot}5$ kcal mol^{-1}, and $\Delta S = -3 \pm 2$ cal K^{-1} mol^{-1}. The rate constant k_f' has a value several orders of magnitude smaller than those found for this parameter in comparable reactions. This is interpreted as evidence that the anation mechanism has some associative character. One mole of Cr^{VI} oxidises three moles of L-cysteine. The redox-reaction kinetics obey the rate law (iii)

$$\frac{-d[Cr^{VI}]}{dt} = \frac{K_1(k_1[H^+] + k_2[H_2L])[H_2L][HCrO_4^-]}{1 + K_1[H_2L]} \qquad \text{(iii)}$$

where, at 25 °C, $k_1 = (1{\cdot}2 \pm 0{\cdot}3) \times 10^{-2}$ l^2 mol^2 s^{-1}, $k_2 = (9{\cdot}4 \pm 0{\cdot}4) \times 10^{-2}$ l^2 mol^2 s^{-1}, $\Delta H_1^\ddagger = 12 \pm 2$ kcal mol^{-1}, $\Delta S_1^\ddagger = -27 \pm 7$ cal K^{-1} mol^{-1}, $\Delta H_2^\ddagger = 10{\cdot}8 \pm 0{\cdot}8$ kcal mol^{-1}, and $\Delta S_2^\ddagger = -27 \pm 3$ cal K^{-1} mol^{-1}. The nature of the chromium(III) products of this reaction is described. The significance of second-order reductant terms for reactions of this oxidant is discussed.

L-CYSTEINE, $HS{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$, is known to form stable complexes with metal ions [1] and has three possible co-ordination sites at the N, O, and S centres. The configuration adopted in these species is largely dependent on the reacting metal ion.[1] Transient intermediates have been identified in the oxidations of this substrate by iron(III) [2] and cobalt(III).[3] The phenomenon of ligand replacement as a prerequisite to redox processes has been discussed [4] as has the correlation between the rates of oxidations by oxo-anions and those of their ligand-exchange reactions.[4] In reactions of chromium(VI), where the ability to form complexes with electron-pair donors is well established, co-ordination of the reductant to the metal centre in a step preceding oxidation has been observed in several instances.[5] The formation of such intermediates provides a low-energy path for electron transfer. There

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† Part XII is ref. 27.

[1] C. A. McAuliffe and S. G. Murray, *Inorg. Chim. Acta Rev.*, 1972, **6**, 103.

[2] F. M. Page, *Trans. Faraday Soc.*, 1955, **51**, 919.

[3] A. McAuley, unpublished work.

[4] E. Chaffee and J. O. Edwards, *Progr. Inorg. Chem.*, 1970, **13**, 205.

[5] J. K. Beattie and G. P. Haight, jun., *Progr. Inorg. Chem.*, 1972, **17**, 93.

is also current interest in redox reactions of Cr^{VI} with sulphur-containing substrates[6,7] where formation constants for the transient esters observed are much larger than those for the corresponding oxygen-bonded species. In addition, it is possible to correlate bathochromic shifts in the electronic spectra of these complexes with the electronegativity of the co-ordinating ligand.[8]

It was considered of interest to apply these criteria to data concerning the orange transient species observed in this study of the reaction of Cr^{VI} with L-cysteine in order to ascertain the nature of the linkage involved.

EXPERIMENTAL

L-Cysteine, H_2L (Koch–Light, pure), was used without further purification. Potassium dichromate (B.D.H., AnalaR) was used for kinetic runs. Sodium dichromate (B.D.H., Reagent) was used in some of the studies of the stoicheiometry and final products where concentrations of Cr^{VI} were such as to have caused precipitation of potassium perchlorate had the potassium salt been used. Mixtures of sodium perchlorate (Fluka, puriss p.a.) and perchloric acid (AnalaR) were used to maintain a constant ionic strength of 1·00M at varying hydrogen-ion concentrations.* Concentrations of stock solutions of perchloric acid were determined by titration against weighed quantities of sodium tetraborate.

Kinetics.—The stopped-flow apparatus used to study the formation reaction has been described previously,[9] the optical path length being either 2·20 or 5·00 mm. Oscilloscope displays of transmission curves were photographed using a Polaroid camera, and using a known reference voltage the optical density of any point on a trace could be calculated using a Nova 1200 computer.

The slower redox reaction was monitored using a hand-driven (two-jet glass mixer) stopped-flow system which utilised a Unicam SP 800 spectrophotometer as both the monochromatic light source and detection system. Experiments were carried out using a 1·00 cm flow-through cell, the dead time being shown to be 0·30 ± 0·05 s. Since all kinetic runs on this apparatus had half-lives greater than 1 min, the fraction of reaction occurring before observation was negligible. The reservoir and drive syringes and the mixing chamber were all housed in a Plexiglass water-bath situated directly above the cell compartment of the spectrophotometer.

Stoicheiometry.—Attempts were made to determine the stoicheiometry of the overall redox reaction by spectrophotometric titration using $[H_2L] = 4 \times 10^{-2}$M and varying $[Cr^{VI}]$ in the range $0{\cdot}4 \times 10^{-2}$—$2{\cdot}6 \times 10^{-2}$M at $[H^+] = 0{\cdot}10$ and $I = 1{\cdot}00$M. This method indicated a variable stoicheiometry as has been observed for the corresponding reaction with thiosulphate.[10] For this reason, and because it was desirable to measure the stoicheiometry under conditions related directly to the kinetic data, acidimetric titration of the mercapto-group[11] was used. This involved mixing a solution (50 cm^3) of *ca.* 0·2M-L-cysteine, of known concentration, with *ca.* 6×10^{-2}M-Cr^{VI} (20 cm^3) and the requisite volumes of stock sodium perchlorate and perchloric acid to give $[H^+] = 0{\cdot}10$ and $I = 1{\cdot}00$M when the mixture was diluted to 100 cm^3. When reaction was complete, a sample (25 cm^3) of this mixture was used to charge a Dowex 50W X8 100/200 mesh cation-exchange resin. The column was rinsed first with water and then with a solution having $[H^+] = 0{\cdot}10$ and $I = 1{\cdot}00$M. Successive column fractions were titrated until no L-cysteine could be detected.

Products.—Separation of the Cr^{III} final products present in the reaction mixture was achieved using nitric acid solutions of varying concentrations. Use of this eluant showed no differences in the products from those obtained using $HClO_4$. Solutions containing 8×10^{-4}M-Cr^{VI}, $3{\cdot}7 \times 10^{-2}$M-L-cysteine, and $9{\cdot}5 \times 10^{-2}$M-$HClO_4$, having been allowed to react to completion, were used to charge columns of the same resin as was used in the stoicheiometry experiments. In order to minimise any aquation of the chromium(III) products, the ion-exchange column was maintained at 0 °C during the separation procedure in which use was made of suction at a water pump. The chromium content of the product complexes was determined using bromine oxidation in basic media with spectroscopic measurement of the resulting $[CrO_4]^{2-}$ (ε 4 810 l mol^{-1} cm^{-1} at λ 372 nm).[12]

RESULTS AND DISCUSSION

Nature of Reacting Species.—A detailed knowledge of the form of the reactants is necessary for interpretation of the data. It is possible to calculate, using known values of K_d at unit ionic strength for the dimerisation of $[HCrO_4]^-$,[13,14] that when the initial Cr^{VI}

$$2[HCrO_4]^- \overset{K_d}{\rightleftharpoons} [Cr_2O_7]^{2-} + H_2O \qquad (1)$$

concentration, $[Cr^{VI}]_0$, is 4×10^{-4}M, as is the case in most of this work, *ca.* 91% Cr^{VI} exists as $[HCrO_4]^-$ at 35 °C; this percentage increases with decreasing temperature. The maximum value of $[Cr^{VI}]_0$ was 8×10^{-4}M. At 30 °C, the highest temperature where this concentration was employed, $[HCrO_4]^-$ is 87% of total Cr^{VI}. At the highest acid concentration used in this study, 0·10M, $[H_2CrO_4]/[HCrO_4^-] \approx 0{\cdot}02$.[15] Protonation of $[HCrO_4]^-$ was therefore neglected, as was its dissociation since the acid-dissociation constant is *ca.* 10^{-6} mol l^{-1}.[16] Thus, as in previous studies where similar concentrations of Cr^{VI} and H^+ were used,[6,7,17,18] the results are interpreted in terms of $[HCrO_4]^-$ being the sole reactant species, with no account being taken of parallel reactions of $[Cr_2O_7]^{2-}$. The lability of the oxygen atoms of $[HCrO_4]^-$ compared with the relative

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* 1M = 1 mol dm^{-3}, 1 cal = 4·184 J.

[6] I. Baldea and G. Niac, *Inorg. Chem.*, 1970, **9**, 110.

[7] K. A. Muirhead and G. P. Haight, jun., *Inorg. Chem.*, 1973, **12**, 1116.

[8] I. Baldea and G. Niac, *Inorg. Chem.*, 1968, **7**, 1232.

[9] K. J. Ellis and A. McAuley, *J.C.S. Dalton*, 1973, 1533.

[10] M. I. Edwards, K. E. Howlett, and B. L. Wedzicha, *J. Chem. Soc.* (*A*), 1970, 2866.

[11] R. Benesch and R. E. Benesch, *Biochim. Biophys. Acta*, 1957, **44**, 183.

[12] G. W. Haupt, *J. Res. Nat. Bur Stand.*, 1952, **48**, 414.

[13] J. Y. Tong and E. L. King, *J. Amer. Chem. Soc.*, 1953, **75**, 6180.

[14] L. G. Hepler, *J. Amer. Chem. Soc.*, 1958, **80**, 6181.

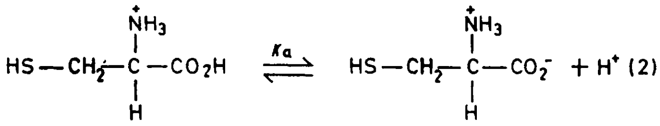
[15] J. Y. Tong, *Inorg. Chem.*, 1964, **3**, 1804.

[16] 'Stability Constants of Metal–Ion Complexes,' *Chem. Soc. Special Publ.*, No. 17, 1964; No. 25, 1971.

[17] K. A. Muirhead, G. P. Haight, jun., and J. K. Beattie, *J. Amer. Chem. Soc.*, 1972, **94**, 3006.

[18] C.-T. Lin and J. K. Beattie, *J. Amer. Chem. Soc.*, 1972, **94**, 3011.

inertness of $[CrO_4]^{2-}$ adds weight to this assumption.[19] The ion $[HCr_2O_7]^{2-}$ is generally considered to be insignificant in concentration.[15]



$$HS-CH_2-\underset{H}{\overset{\overset{+}{N}H_3}{C}}-CO_2H \overset{K_a}{\rightleftharpoons} HS-CH_2-\underset{H}{\overset{\overset{+}{N}H_3}{C}}-CO_2^- + H^+ \quad (2)$$

For the dissociation of monoprotonated L-cysteine [equation (2)], K_a has a value of *ca.* 10^{-2} mol l^{-1}.[20] pK_a Values corresponding to loss of a proton by SH or NH_3 of RCO_2^- groups are generally >8. Hence, although under the conditions used in this study the zwitterion is the dominant species, there is usually a significant proportion of monoprotonated L-cysteine present.

Formation of the Intermediate Species: Characterisation.—(a) *Spectrum.* No absorbance change could be detected when solutions of Cr^{VI} were mixed under typical reaction conditions with ' blank ' solutions containing no L-cysteine. Superimposition of an oscilloscope trace from such an experiment on one obtained from a normal run showed the initial absorbance, D_0, of the latter trace to correspond to that of Cr^{VI}. If $D_{max.}$ is defined as the absorbance corresponding to maximum concentration of intermediate species and $(D_{max.} - D_0)$ defined as ΔD, then ΔD is given by equation (3)

$$\Delta D = \log_{10}(I_{H_2O}/I_{max.}) - \log_{10}(I_{H_2O}/I_0) = \log_{10}(I_0/I_{max.}) \quad (3)$$

where I_i is the intensity of light corresponding to D_i. ΔD Can thus be easily calculated from stopped-flow traces. By measuring ΔD at suitable wavelengths under normal reaction conditions it was possible to compile the spectrum of the orange species; $\lambda_{max.}$ was found to be 420 nm (Figure 1). Kinetic and equilibrium measurements were therefore carried out at this wavelength.

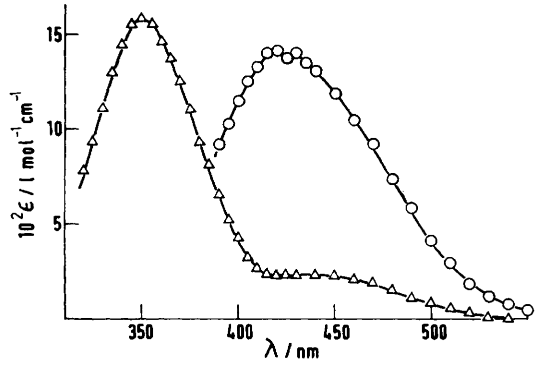


FIGURE 1 Spectra of $[HCrO_4]^-$ (△) and intermediate complex (○)

(b) *Absorption coefficients and equilibrium constants.* In the acid concentration range 0·01—0·10M, formation of the intermediate species was sufficiently fast with respect to the subsequent decay for the assumption to be reasonably made that the absorbance maximum observed in traces obtained at 420 nm corresponded to a state of equilibrium between reactants and intermediates. It was found that, when $[H_2L]_0$ was increased with $[Cr^{VI}]_0$ and $[H^+]_0$ held constant, $D_{max.}$ did not increase beyond a limiting value which was directly proportional to $[Cr^{VI}]_0$. This is consistent with all the Cr^{VI} being present as intermediate at equilibrium. Under such conditions, as in the kinetic studies of the decay, a value for an apparent absorption coefficient, ε_{app}, could be obtained using equation (4) where D_{eqm} is the absorbance at equilibrium, l the

$$\varepsilon_{app} = D_{eqm}/xl \quad (4)$$

optical path length, and x the concentration of complex present which is equal to the concentration of Cr^{VI} initially present. Calculation of the molar absorption coefficient using this method yielded a value of 1 375 ± 25 l mol^{-1} cm^{-1}.

Under conditions where uncomplexed Cr^{VI} was present at equilibrium, *i.e.* in the kinetic studies of the intermediate formation, the measured value of D_{eqm} was found to be independent of $[H^+]_0$. Since $[HCrO_4]^-$ is generally considered to form only 1 : 1 complexes under the conditions employed in these studies, the equilibrium constant was assumed to be as formulated in equation (5) were x is the concentration of metal

$$K = x/(a - x)(b - x) \quad (5)$$

complex, $a = [Cr^{VI}]_0$, and $b = [H_2L]_0$. Values of K and $\Delta\varepsilon$ (Table 1) were obtained by evaluating equation (5) using the relation (6). $\Delta\varepsilon$ Was varied at intervals

$$x = \Delta D/l\Delta\varepsilon \quad (6)$$

of 20 l mol^{-1} cm^{-1} in order to minimise variations in the value of K thus obtained. (Such values were higher than those yielded from a Benesi–Hildebrand plot. It had previously been noted[21] that, when the concentration of complex is not negligible compared with that of the reagent in excess, an equilibrium constant derived from such a plot is always less than the true constant.) The good agreement between the two values of $\Delta\varepsilon$ (ε 228 l mol^{-1} cm^{-1} for $[HCrO_4]^-$ at 420 nm[8]) indicates that the assumption of solely 1 : 1 formation is justified.

The red shift in the charge-transfer band in the electronic spectrum of the chromium species is almost twice as large as that found[8] for $[CrO_3 \cdot S_2O_3]^{2-}$ where the shift of $\lambda_{max.}$ to 390 nm has been interpreted as

TABLE 1

K_1 and ε for $[(HL)CrO_3]^-$ at λ = 420 nm and I = 1·00M

θ_c/°C	K_1/mol l^{-1}	$\Delta\varepsilon$ */l mol^{-1} cm^{-1}
15	1 280 ± 160	1 230 ± 10
25	1 030 ± 110	1 180 ± 40
30	830 ± 200	1 160 ± 20
35	760 ± 60	1 160 ± 20

ΔG = −4·1 ± 0·1 kcal mol^{-1}, ΔH = −5·0 ± 0·5 kcal mol^{-1}, and ΔS = −3 ± 2 cal mol^{-1} K^{-1}.

* ε = 228 l mol^{-1} cm^{-1} for $[HCrO_4]^-$ at 420 nm.[8]

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[19] H. Taube and G. Gordon, *Inorg. Chem.*, 1962, **1**, 69.

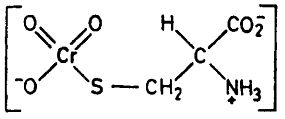
[20] G. E. Clement and T. P. Hartz, *J. Chem. Educ.*, 1971, **48**, 395.

[21] D. A. Deranleau, *J. Amer. Chem. Soc.*, 1969, **91**, 4044.

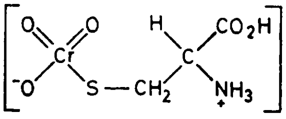
evidence for a chromium–sulphur linkage.[8] The values of $\varepsilon_{max.}$ for these species are very similar ($\varepsilon_{max.}$ for $[CrO_3\cdot S_2O_3]^{2-}$ is 1 400 l^{-1} mol^{-1} cm^{-1}). The magnitude of the equilibrium constant provides further indirect evidence for such a bond on the basis of arguments reported elsewhere[17] where comparison is made of equilibrium constants for various chromate esters. Thus it would appear likely that both reactions (7) and (8) are contributing to intermediate formation.

$$[HCrO_4]^- + H_2L \overset{K_1}{\rightleftharpoons} [(HL)CrO_3]^- + H_2O \quad (7)$$

$$[HCrO_4]^- + H_3L^+ \overset{K_2 = k_f/k_b}{\rightleftharpoons} [(H_2L)CrO_3] + H_2O \quad (8)$$



(I)



(II)

The values of $\Delta\varepsilon$ and K were found to be independent of acid concentration, indicating that, within the errors of experiment, $\Delta\varepsilon_{(I)} = \Delta\varepsilon_{(II)}$ and $K_1 = K_2$, making differentiation between the overall complex-formation reactions involving the two predominant species of L-cysteine impossible. Thus it seems that the acid-dissociation constant of the carboxy-group of L-cysteine is not radically changed by co-ordination of this ligand to $[HCrO_4]^-$.

Formation kinetics.—All the kinetic data were obtained using an excess of L-cysteine. Plots of ln ($D_\infty - D_t$) as a function of time were linear to at least 80% completion of reaction, usually more. Evaluation of the gradients of these lines gave pseudo-first-order rate constants, k_{obs}. These were independent of the wavelength used to monitor the reaction. Degassing reactant solutions had no effect on reaction rates. Plots of $k_{obs.}$ against $[H_2L]_0$ at constant $[H^+]_0$ yielded good straight lines with positive intercepts. Since $[H_2L]_0$ was usually comparable in magnitude with $[H^+]_0$, the concentrations of free hydrogen ion, c_{H^+}, were obtained by calculating the concentration of H_3L^+ at known total concentrations of L-cysteine and hydrogen ion using $K_a = 0{\cdot}01$ mol l^{-1}. Considerable variation in the value of K_a used ($\pm$50%) had a negligible effect on the calculated values of c_{H^+}.

From the known dependence of $k_{obs.}$ on $[H_2L]_0$ it was possible to plot $k_{obs.}$ against c_{H^+} at constant $[H_2L]_0$. Representative data at 25 °C are presented in Table 2.* Such plots were linear with positive intercepts. Similar behaviour was exhibited by a plot (Figure 2) of initial rate against c_{H^+}. The gradients of these graphs were a linear function of $[H_2L]_0$, yielding positive intercepts. If the predominant species H_2L and H_3L^+ react with differing rates, curvature would be observed in the plots of initial rates against hydrogen-ion concentration in the region corresponding in magnitude to the value of K_a of L-cysteine.† In the present study it was found that a plot of initial rate as a function of c_{H^+}, varying from 0·026 to 0·096M, was linear with a positive intercept. We attribute this to the absence of a difference in the rates of complex formation of the two predominant L-cysteine species, thus rendering it unnecessary, as in the overall equilibrium study, to distinguish between them.

TABLE 2

Rate constants for formation of the Cr^{VI}–L-cysteine complex at $[Cr^{VI}] = 4 \times 10^{-4}$M; $I = 1{\cdot}00$M, $\lambda = 420$ nm, and 25 °C

$10^3[H_2L]$/M	$10^2c_{H^+}$/M	$10^3k_{obs.}$/s^{-1}
1·0	3·92	1·52
	4·92	1·92 (1·89)
	5·91	2·19
	6·91	2·57
	7·91	2·94
	8·91	3·34
2·0	3·84	2·15
	4·83	2·71 (2·66)
	5·83	3·09
	6·83	3·58
	7·82	4·00
	8·82	4·54
3·0	3·76	2·76
	4·75	3·50 (3·36)
	5·74	3·98
	6·74	4·57
	7·73	5·08
	8·73	5·74
4·0	3·69	3·38
	4·67	4·29 (4·08)
	5·66	4·87
	6·65	5·56
	7·65	6·15
	8·64	6·94
5·0	3·61	4·00
	4·59	5·07 (4·79)
	5·58	5·76
	6·57	6·56
	7·56	7·22
	8·55	8·14
6·0	3·53	4·62
	4·51	5·86 (5·50)
	5·49	6·66
	6·48	7·56
	7·47	8·29
	8·46	9·34

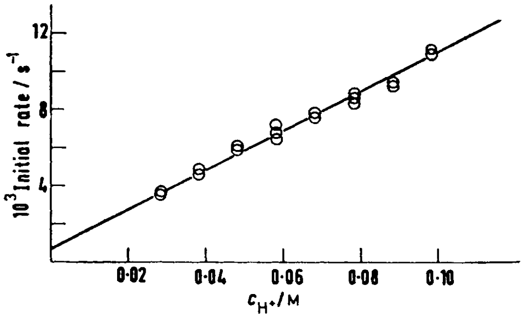


FIGURE 2 Plot of initial rate against c_{H^+} at $[Cr^{VI}]_0 = 5{\cdot}0 \times 10^{-4}$M, $[H_2L]_0 = 2{\cdot}304 \times 10^{-3}$M, 25·0 °C, $\lambda = 420$ nm, and $I = 1{\cdot}00$M

Representing the total L-cysteine as the predominant form H_3L^+, the reaction scheme can be simplified to

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* Fuller versions of Tables 2 and 4 may be found in Supplementary Publication No. SUP 21272 (10 pp.). For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1974, Index issue.

† Baldea and Niac (personal communication) in a separate study of this reaction confirm linearity of plots of $k_{obs.}$ against c_{H^+} in the range c_{H^+} = 0·005—0·100M.

equations (8) and (9). On this basis equation (10)

$$\mathrm{H^+ + [HCrO_4]^- + H_3L^+ \underset{k_b'}{\overset{k_f'}{\rightleftharpoons}} [(H_2L)CrO_3] + H_2O + H^+} \tag{9}$$

can readily be derived, which on rearrangement yields

$$k_{\mathrm{obs.}} = (k_f + k_f' c_{\mathrm{H^+}})[\mathrm{H_2L}]_0 + (k_b + k_b' c_{\mathrm{H^+}}) \tag{10}$$

(11). Plots of α against $[\mathrm{H_2L}]_0$ were linear (Figure 3)

$$k_{\mathrm{obs.}} = (k_f'[\mathrm{H_2L}]_0 + k_b')c_{\mathrm{H^+}} + (k_f[\mathrm{H_2L}]_0 + k_b) = \alpha c_{\mathrm{H^+}} + \beta \tag{11}$$

with gradient k_f' and intercept k_b'. Similarly the hydrogen-ion-independent rate constants were derived from linear variations of β with ligand concentration.

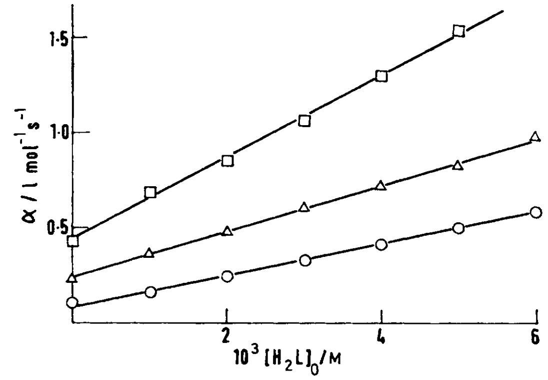


FIGURE 3 Plots of α against $[\mathrm{H_2L}]_0$ [equation (11)] at 15·0 (○), 25·0 (△), and 35·0 °C (□)

Values of these constants at various temperatures are presented in Table 3.

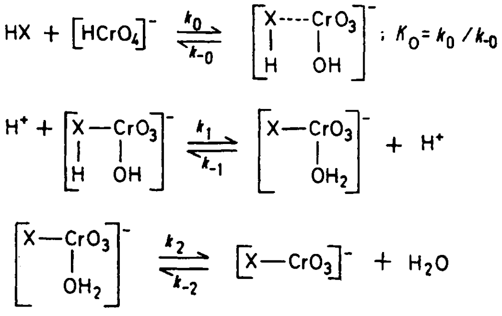
TABLE 3

Dependence of k_f' and k_f on temperature

θ_c/°C	k_f' */l² mol⁻² s⁻¹	k_f/l mol⁻¹ s⁻¹
15·0	84 ± 15	0·5 ± 0·5
25·0	130 ± 20	2 ± 1
30·0	204 ± 20	
35·0	216 ± 20	2 ± 1

* $\Delta H^{\ddagger} = 7 \pm 3$ kcal mol⁻¹ and $\Delta S^{\ddagger} = -24 \pm 11$ cal K⁻¹ mol⁻¹.

The Hydrogen-ion Dependent Path.—There has been some recent controversy concerning the nature of the general mechanism of acid-catalysed substitution of OH in the hydrogenchromate anion.[18,22] All rate constants so far determined for such reactions have values in the range 1×10^{-5}—7×10^{5} l² mol⁻² s⁻¹. To explain the independence of the magnitude of this parameter on the nature of the ligand involved, Lin and Beattie[18] postulated that this phenomenon was a result of the rate-determining step being diffusion-controlled protonation of co-ordinated hydroxide. The mechanism suggested involves three stages. The first stage, (12), is diffusion-controlled formation of a weak complex and the second, (13), involves diffusion-controlled protonation of OH co-ordinated to the chromium centre, with subsequent loss of a proton from the substrate resulting in formation of a fully five-co-ordinate intermediate. Knowing that the overall rate of this pathway is proton dependent, the authors reasoned that the rate-determining step was either (13) or (14). Since the acid-catalysed rate constants for the anation reaction, k_f', are independent of the acid strength of the substrate, it was necessary to assume that loss of the proton from the substrate took place after the transition state, thus leading to the conclusion that the rate-determining step is (13). On the basis of this reaction scheme, $k_f' = K_0 k_1$. To explain the fact that K_0 is independent of the chemical nature of HX it was proposed[17] that K_0 was determined mainly by electrostatic factors. It has been shown by Haim,[22] however, that for k_{-0} to have a physically possible value k_0 must be less than *ca.* 5×10^4 l mol⁻¹ s⁻¹. He also expressed doubt that K_0 would in reality be as invariant as would be required by this scheme and concluded that a more likely mechanism is one involving protonation of $[\mathrm{HCrO_4}]^-$ as the first step with loss of water being rate determining. Moreover, the formation of the first intermediate, assuming that release of the proton and the water molecule occur faster, would in fact be the rate-determining step. This, however, would not give rise to the observed dependence of the rate on hydrogen-ion concentration.



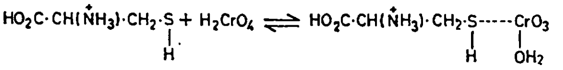
$$\mathrm{HX} + [\mathrm{HCrO_4}]^- \underset{k_{-0}}{\overset{k_0}{\rightleftharpoons}} \left[\begin{array}{cc} \mathrm{X} & \cdots\cdots \mathrm{CrO_3} \\ | & | \\ \mathrm{H} & \mathrm{OH} \end{array}\right]^- ; K_0 = k_0/k_{-0} \tag{12}$$

$$\mathrm{H^+} + \left[\begin{array}{cc} \mathrm{X} & \!\!-\!\!\mathrm{CrO_3} \\ | & | \\ \mathrm{H} & \mathrm{OH} \end{array}\right]^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left[\begin{array}{cc} \mathrm{X} & \!\!-\!\!\mathrm{CrO_3} \\ & | \\ & \mathrm{OH_2} \end{array}\right]^- + \mathrm{H^+} \tag{13}$$

$$\left[\begin{array}{cc} \mathrm{X} & \!\!-\!\!\mathrm{CrO_3} \\ & | \\ & \mathrm{OH_2} \end{array}\right]^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [\mathrm{X{-}CrO_3}]^- + \mathrm{H_2O} \tag{14}$$

Since k_f' for substitution of L-cysteine on $[\mathrm{HCrO_4}]^-$ is *ca.* 10^3 times smaller than for all other similar reactions previously studied,[23] it seems reasonable to conclude that in this present reaction either formation of the Cr–S bond or dissociation of the S–H bond is rate determining. Protonation occurs before the rate-determining step, and co-ordination of sulphur either is the rate-determining step or occurs before it. Assuming the general mechanism preferred by Haim[22] to hold, water loss, which is not rate-determining in this reaction, takes place with a specific rate probably greater than 10^5 s⁻¹ as the equilibrium constant for formation of $[(\mathrm{H_2O})\mathrm{CrO_3}]^-$ is almost certainly less than 1.

$$[\mathrm{HCrO_4}]^- + \mathrm{H^+} \rightleftharpoons \mathrm{H_2CrO_4} \tag{15}$$



$$\mathrm{HO_2C{\cdot}CH(\overset{+}{N}H_3){\cdot}CH_2{\cdot}}\underset{\substack{|\\ \mathrm{H}}}{\mathrm{S}} + \mathrm{H_2CrO_4} \rightleftharpoons \mathrm{HO_2C{\cdot}CH(\overset{+}{N}H_3){\cdot}CH_2{\cdot}}\underset{\substack{|\\ \mathrm{H}}}{\mathrm{S}}\cdots\cdots\underset{\substack{|\\ \mathrm{OH_2}}}{\mathrm{CrO_3}} \tag{16}$$

If the rate of protonation of $\mathrm{HO_2C{\cdot}CH(\overset{+}{N}H_3){\cdot}CH_2{\cdot}S^-}$

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[22] A. Haim, *Inorg. Chem.*, 1972, **11**, 3147.

[23] G. P. Haight, jun., *Inorg. Chem.*, 1973, **12**, 1461.

is diffusion controlled[24] and the strength of the S–H bond is unaffected by a weak S · · · Cr linkage, the rate of deprotonation of $HO_2C{\cdot}CH(\overset{+}{N}H_3){\cdot}CH_2{\cdot}SH$ can be estimated from the known dissociation constants, K_a', for the two species of L-cysteine. Values of k_d

$$HO_2C{\cdot}CH(\overset{+}{N}H_3){\cdot}CH_2{\cdot}SH \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} HO_2C{\cdot}CH(\overset{+}{N}H_3){\cdot}CH_2{\cdot}S^- \qquad (17)$$

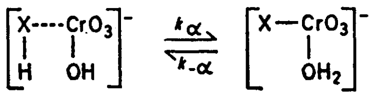
$$K_a' = k_d/k_{-d} \qquad (18)$$

$$k_d \approx 10^{10}K_a' \qquad (19)$$

obtained in this way are less than 10^2 s^{-1}. Thus one might expect water loss to be faster than deprotonation, which would then be the final step.

We conclude, therefore, that either deprotonation or formation of the Cr–S bond is the rate-determining process. This conclusion is reinforced by the magnitude of k_f' for the corresponding reaction of penicillamine with $[HCrO_4]^-$ (40 l^2 mol^{-2} s^{-1}).[25] Assuming that bond making is the rate-determining process, the lower value of k_f' for penicillamine can be explained in view of steric hindrance caused by the methyl groups present. Further data on the deprotonation aspect seem desirable.

The Hydrogen-ion Independent Path.—A general mechanism has been proposed[18] for acid-independent substitutions on $[HCrO_4]^-$ where it is necessary to postulate internal proton transfer to form the departing water molecule [equation (20)], assuming that general acid



$$\left[\begin{array}{ll}X\cdots & CrO_3\\ | & |\\ H & OH\end{array}\right]^- \underset{k_{-\alpha}}{\overset{k_\alpha}{\rightleftharpoons}} \left[\begin{array}{c}X-CrO_3\\ |\\ OH_2\end{array}\right]^- \qquad (20)$$

catalysis is not occurring. The approximate proportionality of k_f to the acid strength of HX has led to the proposal[18] that loss of a proton from the loosely co-ordinated acidic substrate is rate determining. Values of k_α have been estimated, assuming that it is equal to the proton-dissociation rate constant, k_d, of non-bonded HX, using equation (18). By ascribing to K_0 the estimated value of 10^{-5} l mol^{-1},[17,18] k_f can be calculated from equations (19) and (21). Using the maximum

$$k_f = K_0k_d \qquad (21)$$

possible values of K_0, K_a', and k_{-d}, this procedure yields a value of k_f two orders of magnitude less than that obtained experimentally in this study.

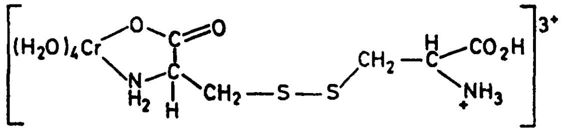
Stoicheiometry and Final Products.—Results obtained by the acidimetric-titration method[11] indicate a value for the L-cysteine : Cr^{VI} ratio of 3·05 ± 0·06, suggesting that the overall reaction is given by equation (22)

$$xH^+ + 2[HCrO_4]^- + 6HS{\cdot}CH_2{\cdot}CH(\overset{+}{N}H_3){\cdot}CO_2H \longrightarrow$$
$$2Cr^{III} + 3HO_2C{\cdot}CH(\overset{+}{N}H_3){\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2{\cdot}CH(\overset{+}{N}H_3){\cdot}CO_2H \qquad (22)$$

with L-cysteine acting as a one-equivalent reductant under conditions of excess of ligand. In spectrophotometric titrations, solutions having Cr^{VI} in excess were found to undergo further reaction, presumably overoxidation of L-cysteine.

Under conditions described in the Experimental section, the chromium(III) products were coloured. Both by using the method of King and Dismukes[26] and by using $[Cr(OH_2)_6]^{3+}$ and $[Cr(OH_2)_5Cl]^{2+}$ as references for comparison of elution rates, it was possible to show that the purple species eluted with 1M-HNO$_3$ was doubly charged and contained *ca.* 60% of the total chromium. Also identified were $[Cr(OH_2)_6]^{3+}$ and a purple species which could not be eluted with 2M-HNO$_3$ but appeared to aquate on prolonged elution to yield $[Cr(OH_2)_6]^{3+}$, which could of course be eluted with this eluant. This latter purple complex is considered to be a dimeric 4+ species formed by parallel reaction of $[Cr_2O_7]^{2-}$, a fact which contrasts with currently held views on the reactivity of this species compared with $[HCrO_4]^-$.

Assuming that the measured stoicheiometry of 3·05 is not a composite value resulting from consumption of L-cysteine not only by oxidation but also by co-ordination to Cr^{III}, followed by separation on the exchange column, the conclusion seems inevitable that it is cystine which is co-ordinated to Cr^{III} in the purple complexes. The structure proposed for the monomeric complex is shown below. Although the overall charge on this species is 3+, the charge separation would seem to be sufficiently great for it to behave as a doubly charged species on the ion-exchange column.



Kinetics of the Electron-transfer Reactions.—In order to simplify the redox kinetics, a sufficient excess of L-cysteine was used so that no free $[HCrO_4]^-$ was present in the redox step. Plots of $\ln(D_t - D_\infty)$ against time were linear to 85—90% completion of reaction. The pseudo-first-order rate constants, k_{obs}, obtained as gradients of these plots, were found to be independent of the wavelength at which measurements were made. Rate constants at various [H$^+$] and [H$_2$L] concentrations at 25 °C are presented in Table 4. Degassing reactant solutions had no effect on reaction rates. No difference was observed in one experiment where 0·0416M-Mn^{II} was present.

Plots of $k_{obs.}$ as a function of $[H_2L]_0$ yielded straight lines with positive intercepts. The gradients of these lines were acid independent, although the cysteine-independent path is hydrogen-ion dependent. If H_2L and H_3L^+ react at different rates it would be expected that gradients of plots of $k_{obs.}$ against ligand would be acid dependent since the proportions of these two species vary much more with $[H_2L]_0$ at the lowest acid

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[24] M. Eigen, *Discuss. Faraday Soc.*, 1965, **39**, 7.

[25] A. McAuley and M. A. Olatunji, unpublished work.

[26] E. L. King and E. B. Dismukes, *J. Amer. Chem. Soc.*, 1952, **74**, 1674.

concentration employed than at the highest. Thus, as in the kinetic and equilibrium studies of the formation of the intermediate complex, it is not possible to distinguish between the reactions of H_2L and H_3L^+ nor of the corresponding complexes $[(HL)CrO_3]^-$, (I), and $[(H_2L)CrO_3]$, (II). Plots of intercept against $[H^+]_0$ suggested that the redox reaction is first order in hydrogen ion. The decrease in absorbance at 420 nm is due solely to the disappearance of the intermediate complexes and the linearity of plots of $\log(D_t - D_\infty)$ against time indicated a reaction order of unity with respect to complex.

TABLE 4

Rate constants for the redox reaction at $[Cr^{VI}]_0 = 4 \times 10^{-4}$M, $I = 1{\cdot}00$M, $\lambda = 420$ nm, and 25 °C

$[H^+]_0$/M	$10^2[H_2L]$/M	$10^3k_{obs.}/s^{-1}$
0·020	0·9274	0·947
	1·855	1·75
	2·782	2·64
	3·710	3·61
	4·637	4·79
0·040	0·8479	0·987
	1·696	1·83
	2·544	2·67
	3·392	3·23
	4·240	4·10
0·060	0·8189	1·23
	1·638	2·05
	2·457	2·83
	3·276	3·58
	4·095	4·33
0·080	0·9792	1·72
	1·958	2·84
	2·938	3·69
	3·917	4·68
	4·896	5·47
0·100	0·8954	1·93
	1·791	2·89
	2·686	3·86
	3·582	4·85
	4·477	5·61
	3·078	3·85
	3·078 [a]	3·94
0·100 [b]	0·9500	1·92
	1·900	2·98
	2·850	3·97
	3·800	4·81
	4·750	5·63

[a] Mn^{II} was added. [b] Solutions were degassed.

These results are consistent with the rate scheme given by equations (8), (23), and (24). Hence the rate

$$\text{(II)} + H^+ \xrightarrow{k_1} Cr^{V} \tag{23}$$

$$\text{(II)} + H_3L^+ \xrightarrow{k_2} Cr^{IV} \tag{24}$$

law (25) may be derived where $[Cr^{VI}]_T = [Cr^{VI}]_0$.

$$\frac{-d[Cr^{VI}]_T}{dt} = \frac{K_1(k_1[H^+] + k_2[H_3L^+])[H_3L^+][Cr^{VI}]_T}{1 + K_1[H_3L^+]} = k_{obs.}[Cr^{VI}]_T \tag{25}$$

The quantity γ $\{=k_{obs.}(1 + K_1[H_3L^+])/K_1[H_3L^+]\}$, evaluated using the appropriate values of K_1 in Table 1, was found to be a linear function of $[H_3L^+]$. Plots of γ as a function of $[H_3L^+]$ yielded k_2 directly; k_1 was derived from plots of the intercept against $[H^+]_0$.

The route corresponding to k_1 is considered to involve three consecutive one-electron transfers. Table 6 enables a comparison to be made of $\Delta H_2^\ddagger$ and $\Delta S_2^\ddagger$ with activation parameters of corresponding routes in other chromate oxidations involving second-order ligand dependences. These values indicate that such routes involve similar processes with negligible dissociative character. The significance of such second-order processes has been discussed.[5] For sulphur-containing one-electron reductants such as L-cysteine, routes corresponding to such terms are considered to provide a low-energy path for formation of disulphide in a 'template'-type reaction. The evidence obtained in this study that product disulphide is co-ordinated to Cr^{III} supports this theory because, since Cr^{III} is kinetically inert, cystine must co-ordinate to either Cr^{V} or Cr^{IV}. The latter alternative is considered more likely.

TABLE 5

Dependence of k_1 and k_2 on temperature

θ_c/°C	10^2k_1/l^2 mol^{-2} s^{-1}	10^3k_2/l^2 mol^{-2} s^{-1}
15·0	4·6 ± 0·4	6 ± 1
25·0	9·4 ± 0·4	12 ± 3
35·0	16·9 ± 0·6	26 ± 4

$\Delta H_1^\ddagger = 12 \pm 2$ kcal mol^{-1}, $\Delta S_1^\ddagger = -27 \pm 7$ cal K^{-1} mol^{-1}, $\Delta H_2^\ddagger = 10{\cdot}8 \pm 0{\cdot}8$ kcal mol^{-1}, and $\Delta S_2^\ddagger = -27 \pm 3$ cal K^{-1} mol^{-1}.

TABLE 6

Activation parameters for chromate(VI) oxidation paths involving second-order reductant terms

Reductant	$\Delta H^\ddagger$/ kcal mol^{-1}	$\Delta S^\ddagger$/ cal K^{-1} mol^{-1}	Ref.
L-Cysteine	10·8	−27	*a*
Penicillamine	7·4	−37	25
Thiourea [b]	11	−19	27
Thiosulphate	8·2	−20·8	6
Sulphite	4·5	−13	*c*
Oxalic acid	12·8	−18·6	*d*
Iodide	9·7	−16	28

[a] This work. [b] First-order acid path. [c] G. P. Haight, jun., E. Perchonock, F. Emmenegger, and G. Gordon, *J. Amer. Chem. Soc.*, 1965, **87**, 3825. [d] G. V. Bakore and C. L. Jain, *J. Inorg. Nuclear Chem.*, 1969, **31**, 805.

No effect of Mn^{II} on the reaction rate was observed in studies of the Cr^{VI} oxidations of thiourea,[27] *NN'*-ethylenethiourea,[27] thiocyanate,[7] and iodide.[28] The halving of the rate of other Cr^{VI} oxidations on addition of Mn^{II} has been attributed to removal of Cr^{IV} by reaction with Mn^{II} thus rendering impossible reaction of a second Cr^{VI} species with either Cr^{IV} or the radical produced if the latter were to react with another substrate molecule.[5] Thus, on the basis of the mechanism we propose for reduction of Cr^{VI} by L-cysteine, addition of Mn^{II} would not be expected to affect the rate of reaction. Manganese(II) is reported to inhibit the oxidation of thiosulphate by Cr^{VI}.[7] It is difficult to envisage how

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[27] M. A. Olatunji and A. McAuley, *J.C.S. Dalton*, 1975, 682.

[28] D. C. Gaswick and J. H. Krueger, *J. Amer. Chem. Soc.*, 1969, **91**, 2240.

this would occur under conditions where tetrathionate is produced. However, at high acidities and Cr^{VI} concentrations where sulphate is produced,[6] reaction of Cr^{VI} with either Cr^{IV} or $[S_2O_3]^{-\cdot}$ is considered to take place.

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