Metal-ion Oxidations in Solution. Part XII.† Oxidation of Thiourea and *NN'*-Ethylenethiourea by Chromium(VI) in Perchlorate Media

By **M. Adegboyega Olatunji** and **Alexander McAuley**,* Department of Chemistry, University of Glasgow, Glasgow G12 8QQ

The oxidation of thiourea and its *NN'*-ethylene derivative (L) proceeds *via* the formation of 1 : 1 complexes, $[O_3CrL]$, which are considered to be sulphur bonded. These intermediates, formed within the time of mixing in the stopped-flow apparatus, have been characterised spectroscopically and thermodynamic parameters for reactions (i) have been measured. At 25 °C for thiourea, $K = 380 \pm 25$ l^{-2} mol^{-2}, $\Delta H = -9{\cdot}8 \pm 0{\cdot}6$ kcal mol^{-1},

$$H^+ + [(HO)CrO_3]^- + L \overset{K}{\rightleftharpoons} [O_3CrL] + H_2O \qquad (i)$$

and $\Delta S = -21 \pm 3$ cal K^{-1} mol^{-1}, whilst for *NN'*-ethylenethiourea $K = 211 \pm 20$ l^{-2} mol^{-2}, $\Delta H = -8{\cdot}8 \pm 0{\cdot}9$ kcal mol^{-1}, and $\Delta S = -19 \pm 4$ cal K^{-1} mol^{-1}. The kinetics of the electron-transfer reactions to yield Cr^{III} have been investigated. The reaction products in both cases are $[Cr(H_2O)_6]^{3+}$ and $[\text{Chromium(III)–L}]^{3+}$ complexes. In both systems, the principal path involves a reaction of overall stoicheiometry (ii) with the formation of a Cr^{IV}

$$2H^+ + [O_3CrL] + L \xrightarrow{k} Cr^{IV} + L{-}L \qquad (ii)$$

intermediate which undergoes further reduction. For L = thiourea at 25 °C, $k = 33$ l^3 mol^{-3} s^{-1}, $\Delta H^\ddagger = \leqslant 1$ kcal mol^{-1}, and $\Delta S^\ddagger = -45 \pm 6$ cal K^{-1} mol^{-1}, whilst for *NN'*-ethylenethiourea $k = 47{\cdot}5$ l^3 mol^{-3} s^{-1}, $\Delta H \leqslant 1{\cdot}5$ kcal mol^{-1}, and $\Delta S^\ddagger = -45 \pm 5$ cal K^{-1} mol^{-1}. Details of other hydrogen ion-catalysed reactions are presented and the data are compared with those for other systems of this type.

REACTIONS of chromium(VI) with sulphur-containing ligands have been the subject of several recent studies.[1-4] In some instances the formation of Cr–S bonded intermediates has been postulated, the species being characterised by a red shift of the charge-transfer band in the near-u.v. region. Also, in the oxidation reactions of thiocyanate [4] and thiosulphate,[1] paths involving second-order terms in the ligand have been observed [1] consistent with an increase of the co-ordination number of the Cr^{VI} complex ion.

In this paper we present data on the reactions of this oxidant with thiourea and the *NN'*-ethylene-substituted analogue. Complex formation has been observed for both substrates and it is of interest to compare these data with those of other ligands [4] where the possibility may arise of either *N*- or *S*-co-ordination to the metal centre, since if the former is the case then the greatly increased steric hindrance in the reaction of the ethylene-substituted ligand should be reflected in the thermodynamic parameters for complex formation.

EXPERIMENTAL

Potassium dichromate (AnalaR), sodium perchlorate (Fluka, puriss p.a.), and perchloric acid (AnalaR) were used without purification and enabled variation of hydrogen-ion concentration at a constant ionic strength (1·0M).‡ Thiourea (B.D.H.) and *NN'*-ethylenethiourea (Aldrich) were recrystallised twice from ethanol–water (50/50 v/v) and gave analyses consistent with at least 99·9% purity. All solutions were made using water prepared from an all-glass still.

Kinetic measurements were made using a stopped-flow spectrophotometer,[5] solutions being allowed to thermostat for at least 30 min prior to any readings being taken. Voltage readings at various times from photographs of oscilloscope traces were referred to a known voltage and converted to absolute optical densities using a Nova 1200 computer. First-order kinetic plots were linear to greater than 85% completion of reaction. Duplicate measurements gave results in agreement to ±2%. Comparison of initial optical densities with those for solutions of chromium(VI) of identical concentration showed that a complex was formed within the time of mixing of the reagents. The spectra of the intermediates were derived from the variation of optical densities at $t = 0$ and are shown in Figure 1.

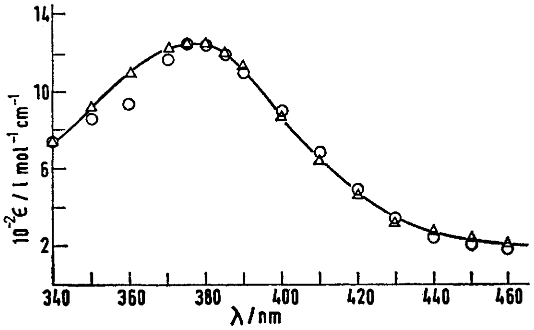


FIGURE 1 Spectra of intermediate complexes: (○), thiourea; (△), *NN'*-ethylenethiourea

Reaction stoicheiometries were determined using spectrophotometric titrations. Spectra of solutions containing various concentrations of Cr^{VI} and a constant ligand concentration were measured after reaction had occurred, the residual chromium(VI) being monitored at wavelengths where there was little or no absorbance from the chromium(III)-complex products. Similar results were obtained when the reaction products were removed using a cation-exchange column and the unreacted (negatively charged) chromium(VI) was determined. In the reaction with thiourea 3·2 ± 0·1 mol of substrate were consumed per mol of oxidant, and for ethylenethiourea 3·0 ± 0·1 mol

---

† Part XI, Z. Amjad and A. McAuley, *J.C.S. Dalton*, 1974, 2521.

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

[1] I. Baldea and G. Niac, *Inorg. Chem.*, 1968, **7**, 1232; 1970, **9**, 110.

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

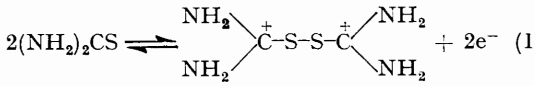
[3] K. A. Muirhead, G. P. Haight, jun., and J. K. Beattie, *J. Amer. Chem. Soc.*, 1972, **94**, 3006.

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

[5] A. McAuley and R. Shanker, *J.C.S. Dalton*, 1973, 2321.

reacted, consistent with the formation of 1·5 mol disulphide per mol of Cr^{VI}.

The reaction products were confirmed as follows. In the case of thiourea, a stoicheiometric excess (*ca.* 30 mmol) of sodium dichromate dissolved in water (15 cm^3) was added slowly to a cooled acidic (*ca.* 0·5M) solution (35 cm^3) containing thiourea (50 mmol). The solution rapidly turned green and four volumes of ethanol were then added followed by conc. HCl (50 cm^3). On cooling, crystals of *CC'*-dithiobis(formamidinium) were obtained identical to those prepared by hydrogen peroxide oxidation,[6] the S–S bond being confirmed by Raman spectroscopy. The overall half-reaction of thiourea may thus be represented as (1). Further confirmation of this disulphide as a



$$2(NH_2)_2CS \rightleftharpoons (NH_2)_2\overset{+}{C}\text{-S-S-}\overset{+}{C}(NH_2)_2 + 2e^- \quad (1)$$

product was given by the ready decomposition to sulphur in acid media. In the reactions of ethylenethiourea, although the characteristic green colouration of Cr^{III} complexes was given under conditions identical to those above, no protonated disulphide was precipitated. After such a reaction carried out at $[H^+] = 0{\cdot}25M$, however, addition of base increasing the pH to *ca.* 8 (just prior to any precipitation being evident), followed by diethyl ether extraction and concentration of the ether solution on a rotary evaporator, yielded a white solid. Elemental analysis was consistent with bis(dihydroimidazol-2-ylio)-disulphide and the peak at 502 cm^{-1} in the Raman spectrum confirmed the disulphide link.[7] For comparison the corresponding spectrum of L-cystine was run where a peak at 498 cm^{-1} was observed.

The metal-ion reaction products in the presence of excess of both reductants were hexa-aquachromium(III) and chromium(III)–thiourea complexes together with a small amount of a highly charged ion. In the case of thiourea, two cationic species were identified and isolated using a Dowex 50W X8 (100—200 mesh) ion-exchange column. Comparative elution rates with ions of known charge confirmed these both to be +3 overall charge. Separation was effected using sodium perchlorate–perchloric acid solution as eluant and the spectrum of the non-sulphur-containing fraction was identical with that of $[Cr(OH_2)_6]^{3+}$. In order to determine the total number of moles of reductant reacting with the chromium(VI), experiments were carried out in which thiourea was in excess and immediately after reaction an aliquot portion of solution was transferred to a Dowex 50W X8 ion-exchange column. In previous studies on thiourea and its derivatives, it has been considered[5,8] that one of the nitrogen atoms is protonated in accord with the data of Walter *et al.*[9] These data in fact relate to dioxan–water mixtures and may not be extrapolated to acidic aqueous media.[10,11] Under such conditions, the pK_a values of the conjugate acids of thiourea and its derivatives fall in the range −1·2 to −1·9[12] so that no protonation would be expected even in the most acidic media studied here. The uncharged unreacted thiourea in the sample transferred to the ion-exchange column was therefore eluted without retention and was monitored using a silver-ion titration in basic media,[13] in which a known volume of silver(I) is added to the thiourea solution. After removal of the silver sulphide formed, the excess of silver ion was titrated with ammonium

$$(NH_2)_2CS + 2Ag^+ + 2NH_3 \longrightarrow H_2N{\cdot}CN + Ag_2S + 2NH_4^+ \quad (2)$$

thiocyanate using iron(III) alum as indicator. Repeated determinations indicated that 3·8 ± 0·1 mol of thiourea reacted per mol of Cr^{VI} and since 3 mol were oxidised to the disulphide, the remainder is considered to be bound in the inert Cr^{III} complex. Some disulphide may be weakly bound in the complex ion since S analyses of ion-exchange eluates based on SO_4^{2-} indicated high S : Cr ratios. The chromium content of the separated fractions was determined by bromine oxidation in basic media and subsequent monitoring of the $[CrO_4]^{2-}$ peak at 372 nm[14] (ε 4 810 l mol^{-1} cm^{-1}). In this way, the relative proportions of two +3 product ions were characterised as $[Cr(H_2O)_6]^{3+}$ (35%) and $[(H_2O)_5Cr\{(NH_2)_2CS\}]^{3+}$ (59—62%). The small band of more highly charged (>4+) material retained on the column thus amounted to <5% of the initial chromium ion, and may also have some thiourea co-ordinated. The formulation of a 1 : 1 Cr^{III} : thiourea complex is thus consistent with the earlier observation of 0·8 ± 0·1 mol reductant co-ordinated, although the possibility of small amounts of a 1 : 2 complex being present cannot be completely eliminated. The spectrum of the sulphur-containing fraction (Figure 2) was obtained (after separation on the column) by elution with *ca.* 5M-sodium perchlorate containing *ca.* 0·5M-$HClO_4$. In this way solutions *ca.* 0·01M in complex ion were prepared.

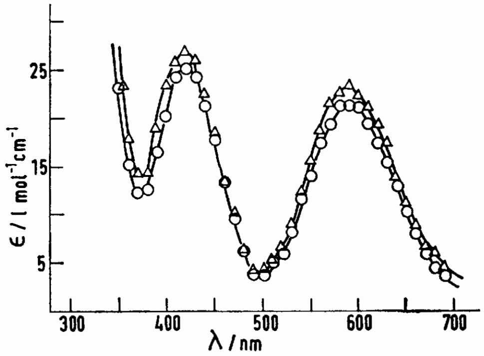


FIGURE 2 Spectra of *N*-bonded 1 : 1 Cr^{III}–thiourea products: (○), thiourea; (△), *NN'*-ethylenethiourea

A similar procedure adopted for the ethylenethiourea reaction revealed the existence of three products one of which was much more readily eluted from the column. Reaction of the excess of thiourea in a manner similar to that described above resulted in quantitative precipitation of the 1 : 1 silver(I)–ethylenethiourea complex. The excess of silver ion was then titrated against NH_4NCS. Repeated determinations revealed a retention of 0·6 ± 0·1 mol of reductant per mol of Cr^{III} produced. Only two of the fractions showed significant amounts of sulphur to be present, the third being identified as $[Cr(H_2O)_6]^{3+}$ (*ca.* 30%).

---

[6] P. W. Preisler and L. Berger, *J. Amer. Chem. Soc.*, 1947, **69**, 232.

[7] E. J. Bastian and R. B. Martin, *J. Phys. Chem.*, 1973, **77**, 1129.

[8] G. Davies, *Inorg. Chem.*, 1972, **11**, 2488.

[9] J. L. Walter, J. A. Ryan, and T. J. Lane, *J. Amer. Chem. Soc.*, 1956, **78**, 5560.

[10] M. J. Janssen, *Recueil*, 1962, **81**, 650.

[11] R. Zahradnik, *Coll. Czech. Chem. Comm.*, 1959, **24**, 3678.

[12] M. R. Hoffmann, personal communication.

[13] S. D. Nogare, *Org. Analysis*, 1953, **1**.

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

Again small amounts of highly charged species were not eluted. Comparison of the chromium(III) content and co-ordinated-reductant figures indicate that two isomeric forms of the 1 : 1 complex are formed and the first fraction (*ca.* 15%) is considered to be the *S*-bonded isomer $[(H_2O)_5Cr^{III}(S\overset{}{C}{:}NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH)]$ in which there is substantial charge separation with protonation of one of the ring nitrogen atoms in acidic media. The third fraction (44—48%) (Figure 2) is then thought to be the *N*-bonded isomer similar to the major reaction component of the unsubstituted thiourea system. The possible formation of the *S*-bonded isomeric species which undergoes ready hydrolysis may result from steric hindrance of the substituted reductant.

Attempts were made to further identify the green complexes formed. After elution from the ion-exchange column, the solution was concentrated on a rotary evaporator. In this way the $NaClO_4$ was separated and the chromium(III) complex redissolved in diethyl ether containing the minimum amount of methanol. Repeated reduction to a solid followed by extraction gave a green solution which when finally dried at reduced pressure over P_2O_5 yielded a purple solid. When the redox reaction with thiourea was carried out in chloride media, some $[CrCl]^{2+}$ (*ca.* 10%) was formed and, using the method described above, the purple compound $[Cr(H_2O)_5\{(NH_2)_2CS\}]Cl_3{\cdot}HCl$ was produced (Found: C, 4·6; H, 4·0; Cl, 40·9; Cr, 14·2; N, 7·8. Calc.: C, 3·3; H, 4·2; Cl, 39·3; Cr, 14·4; N, 7·8%). These purple solids are extremely hygroscopic and readily revert to the green solutions. The isolation of these species thus confirms the ion-exchange results that the cationic species produced are Cr^{3+} and $[Cr\{(NH_2)_2CS\}]^{3+}$ respectively.

RESULTS AND DISCUSSION

(a) *The Complex Intermediates.*—Studies were made at a wavelength of 380 nm and the presence of complexes was confirmed from initial optical-density measurements. From data where the hydrogen-ion concentration was varied, it was observed that the extent of complex formation depended on the amounts of hydrogen ion present. If L = substrate, the initial rapid reactions may be represented as (3), and at the

$$[(HO)CrO_3]^- + H^+ + L \overset{K}{\rightleftharpoons} [LCrO_3] + H_2O \quad (3)$$

wavelength used where both the uncomplexed and complex forms of chromium(VI) absorb equation (4)

$$\frac{[Cr^{VI}]_T[L][H^+]}{\Delta D} = \frac{[L][H^+]}{\Delta\varepsilon l} + \frac{1}{K\Delta\varepsilon l} \quad (4)$$

may be written,[15,16] where $[Cr^{VI}]_T$ = the total metal-ion concentration, ΔD = the difference in absorbance between the complex and Cr^{VI}, $\Delta\varepsilon$ = the corresponding difference in absorption coefficients, and l = the path length (0·5 cm). The data in Figure 3 represent some of the initial optical-density changes presented in the form of equation (4) from which both the equilibrium constants and the absorption coefficients may be derived. Details of these constants derived at each temperature studied are presented in Table 1 where little temperature variation of the absorption coefficient is observed. A similar complex formation has been observed[4] in the case of the thiocyanate ion and the *K* values of 380 and 211 l^2 mol^{-2} for thiourea and its substituted derivative may be compared with that of 220 l^2 mol^{-2} derived previously (I = 0·3M),[16] whilst the corresponding value for $[CrO_3Cl]^-$ formation is 17 l^{-2} mol^{-2}.[17] There are available few data with which the thermodynamic parameters may be compared. For the formation of the thiosulphato-complex, $[CrO_3(S_2O_3)]^{2-}$, a value of ΔH = −3 kcal mol^{-1} has been derived,[2] but more information is clearly required before conclusions can be drawn as to the significance of such values. It is also of interest to note that in the present investigation the charge-transfer maxima (Figure 1) are at 380 nm similar to that for the thiosulphate complex, $[CrO_3(S_2O_3)]^{2-}$,[1] and identical to that for the thiocyanate species[4] (380 nm) suggesting a common mode of co-ordination to the chromium centre. Also the relatively small changes in *K* in the reactions of the two thioureas would tend to eliminate the possibility of an attachment through the nitrogen atoms since the steric hindrance involved in the case of the substituted molecule would be expected to be much more significant.

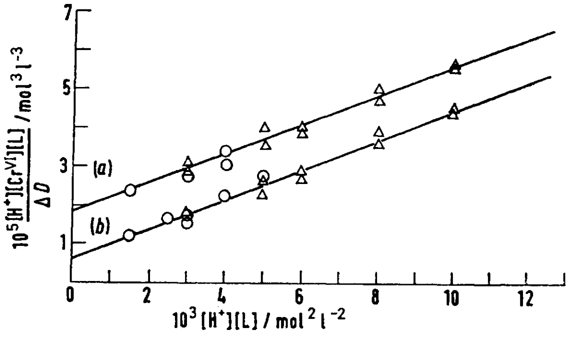


FIGURE 3 Plots of the left-hand side of equation (4) against $[H^+][L]$ for thiourea at 15·2 °C (*a*) and *NN′*-ethylenethiourea at 24·9 °C (*b*): $[H^+]$ = 0·5 (○) and 1·0M (△)

TABLE 1

Thermodynamic parameters for initial complex formation derived using equation (4)

L = Thiourea

θ_c/°C	15·2	20·0	24·9	30·0	35·0
K/l^2 mol^{-2}	648 ± 120	481 ± 100	380 ± 60	280 ± 45	215 ± 40
ε/l mol^{-1} cm^{-1}	1 256	1 230	1 270	1 250	1 254

ΔG = −3·52 ± 0·3 kcal mol^{-1}, ΔH = −9·8 ± 0·6 kcal mol^{-1}, ΔS = −21 ± 3 cal K^{-1} mol^{-1}.

L = *NN′*-ethylenethiourea

θ_c/°C	15·2	20·0	24·9
K/l^2 mol^{-2}	361 ± 18	256 ± 30	211 ± 15
ε/l mol^{-1} cm^{-1}	1 232	1 238	1 263

ΔG = −3·2 ± 0·4 kcal mol^{-1}, ΔH = −8·8 ± 0·9 kcal mol^{-1}, ΔS = −19 ± 4 cal K^{-1} mol^{-1}.

(b) *Kinetics of the Oxidation Reactions.*—The first-order decrease in absorbance at 380 nm was observed to be both ligand and hydrogen-ion dependent, although

---

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

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

[17] G. P. Haight, jun., D. C. Richardson, and N. H. Coburn, *Inorg. Chem.*, 1964, **3**, 1779.

non-integral in order with respect to both. Rate constants at 420 nm in the lower ligand-concentration range were in satisfactory agreement with those at 380 nm. Also, differing hydrogen-ion dependences were noted in the case of the two thioureas.

The reaction with thiourea is considered to proceed *via* three paths which may be written in overall form as (5)—(7), and a rate law consistent with a scheme of

$$[O_3CrL] \xrightarrow{k_0} Cr^{V} + L^{\bullet} \tag{5}$$

$$[O_3CrL] + H^+ + L \xrightarrow{k_1} Cr^{IV} + L'\text{–}L' \tag{6}$$

$$[O_3CrL] + 2H^+ + L \xrightarrow{k_2} Cr^{IV} + L'\text{–}L' \tag{7}$$

$$2L^{\bullet} \xrightarrow{\text{fast}} L'\text{–}L' \tag{8}$$

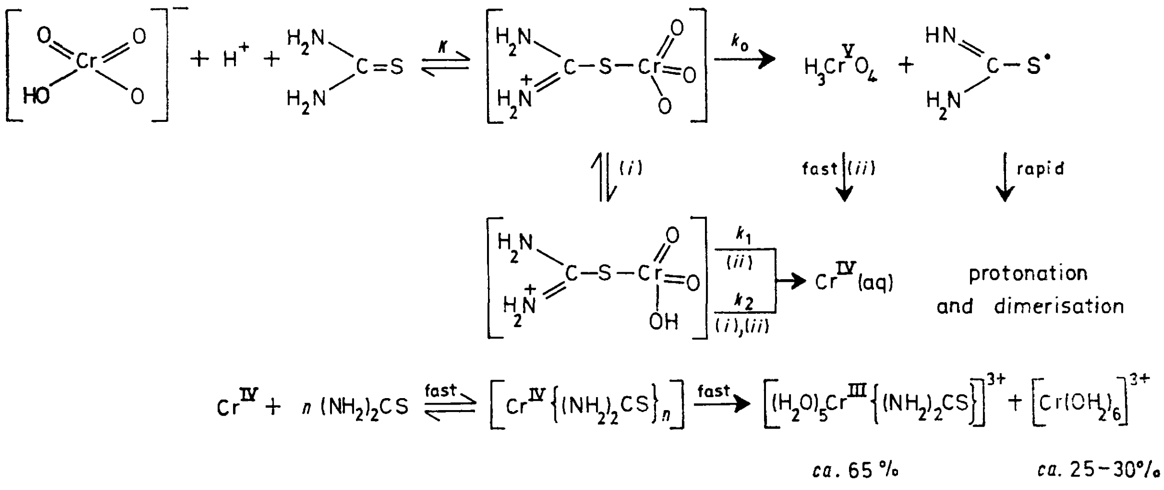
this type may be expressed as (9) conforming to the

$$\text{Rate} = \frac{-d[Cr^{VI}]}{dt} = \frac{\{k_0 + k_1[H^+][L] + k_2[H^+]^2[L]\}K[L][H^+][Cr]_T}{(1 + K[L][H^+])} \tag{9}$$

observed first-order behaviour. Rearrangement of the observed rate constant, $k_{obs.}$, leads to equation (10).

$$\frac{k_{obs.}(1 + K[L][H^+])}{K[L][H^+]} = k_0 + [H^+][L](k_1 + k_2[H^+]) \tag{10}$$

From a knowledge of the equilibrium constants, the left-hand side of equation (10) was evaluated and a straight line obtained on plotting against [L] to yield k_0. From the hydrogen-ion dependence of such plots k_1 and k_2 were derived (Table 2).



SCHEME (*i*), H^+; (*ii*), $(NH_2)_2CS$.

A fuller representation of the reaction paths is provided in the Scheme. From the initial optical-density changes it is known that one proton is required in the formation of the complex. The k_0 path is postulated as a one-electron reduction of Cr^{VI}. In the other studies involving redox processes of this type it has been observed that two protons are required,[18–20] except in the reaction of VO^{2+} where two protons are released on oxidation.[21]

TABLE 2

Rate constants for the reactions of chromium(VI) with thiourea and *NN'*-ethylenethiourea

Thiourea

θ_c/°C	k_0/s^{-1}	k_1/l^2 mol^{-2} s^{-1}	k_2/l^3 mol^{-3} s^{-1}
15·2	0·005 ± 0·005	8·6 ± 1·8	29 ± 6
20·3	0·015 ± 0·01	10·0 ± 1·5	31 ± 3
24·9	0·020 ± 0·01	15·6 ± 1·4	33 ± 2
30·0	0·030 ± 0·01	19·6 ± 1·6	33 ± 2
$\Delta H^{\ddagger}$/kcal mol^{-1}		10·7 ± 2·5	⩽1
$\Delta S^{\ddagger}$/cal K^{-1}		−19 ± 8	−45 ± 6

NN'-Ethylenethiourea

θ_c/°C	k_α/s^{-1}	k_β/l^3 mol^{-3} s^{-1}
15·2	0·12 ± 0·01$_5$	37·0 ± 2·0
20·0	0·20 ± 0·03	46·5 ± 4·0
24·9	0·30 ± 0·04	47·5 ± 4·0
$\Delta H^{\ddagger}$/kcal mol^{-1}	15 ± 1	⩽1·5
$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	−9 ± 3	−45 ± 5

If the one-electron half reaction for thiourea is written as $(NH_2)_2CS \rightleftharpoons NH_2{\cdot}NH{:}C{\cdot}S^{\bullet} + H^+ + e^-$, then the second proton is derived from the substrate itself thus satisfying the formal hydrogen-ion requirements.* Although this path constitutes only a minor route, confirmation of the formation of radicals has been derived from acrylonitrile polymerisation, and a weak electron resonance signal was observed at 77 K (at *X*-band frequency), $g = 2{\cdot}002 \pm 0{\cdot}002$. This is consistent neither with solely a d^1 (Cr^V) complex (expected g 1·98 [22]) nor with an S-containing organic radical (expected g 2·02 [23]) and it may arise from the formation

---

* We thank a referee for this suggestion.

[18] J. H. Espenson, *Accounts Chem. Res.*, 1970, **3**, 341.

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

[20] J. C. Sullivan, *J. Amer. Chem. Soc.*, 1965, **87**, 1495.

[21] D. R. Rosseinsky and M. J. Nicol, *J. Chem. Soc.* (*A*), 1970, 1196.

[22] B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 247.

[23] P. B. Ayscough, 'Electron Spin Resonance in Chemistry,' Methuen, London, 1967, p. 349.

of a $\mathrm{Cr^V}$ complex with an uncharged thiourea molecule acting as a ligand. The magnitude of the signal confirms that the principal paths are probably two-electron steps involving 2 mol of reductant. In the case of the k_2 path, the hydrogen-ion dependence parallels that of the k_0 route in that there may be formation of a complex of the type $[\mathrm{CrO_2(thiourea)_2}]$ analogous to the species $\mathrm{CrO_2Cl_2}$ and $\mathrm{CrO_2F_2}$. The construction of models in which the ligands are sulphur bonded for both reductants indicate that structures of this type are feasible and may be considered as transition states.

In the case of ethylenethiourea, however, only two formal reaction paths were detected, with no evidence for a reaction corresponding to equation (6) above,

$$[\mathrm{O_3CrL}] \xrightarrow{k_\alpha} \mathrm{Cr^V} + \mathrm{L}^{\bullet} \tag{11}$$

$$[\mathrm{O_3CrL}] + 2\mathrm{H^+} + \mathrm{L} \xrightarrow{k_\beta} \mathrm{Cr^{IV}} + \mathrm{L'{-}L'} \tag{12}$$

$$2\mathrm{L}^{\bullet} \xrightarrow{\text{fast}} \mathrm{L'{-}L'} \tag{13}$$

and the rate law may be written as in (14). Treatment

$$\frac{-\mathrm{d}[\mathrm{Cr^{VI}}]}{\mathrm{d}t} = \frac{\{k_\alpha + k_\beta[\mathrm{H^+}]^2[\mathrm{L}]\}K[\mathrm{L}][\mathrm{H^+}][\mathrm{Cr}]_\mathrm{T}}{(1 + K[\mathrm{L}][\mathrm{H^+}])} \tag{14}$$

of the data in a manner similar to that for thiourea yielded the rate constants k_α and k_β (Table 2).

The experimentally derived kinetic data are presented in Table 3 where comparison may be made with the calculated first-order rate constants [equations (9) and (14)] derived from the data in Tables 1 and 2 and where the overall agreement is considered good. The reaction paths k_α and k_β are then analogous to those (k_0 and k_2) depicted in the Scheme and the possibility of a transition state of the type $[\mathrm{CrO_2L_2}]$ in the latter reaction may be considered.

The rate laws observed differ only relatively slightly from those derived previously in oxidations of this type [1,4,24,25] and then only at low ligand concentrations. At the higher concentrations of both thiourea substrates, the predominant paths k_2 and k_β are directly comparable to the route proposed in the thiocyanate study.[4] Also the composite rate constants $k_2 = 34$ and $k_\beta = 47$ $\mathrm{l^3\ mol^{-3}\ s^{-1}}$ may be compared directly with a value of 10 $\mathrm{l^3\ mol^{-3}\ s^{-1}}$ for the corresponding NCS reaction. In all these systems, the presence of a second sulphur-containing ligand in the transition state is considered important. The role of the hydrogen ions may be to doubly protonate an oxygen atom of the original $[\mathrm{HCrO_4}]^-$ ion thus allowing an easier access for coordination of the second thiourea to give a transition state which may be formulated as either square pyramidal, (I), or trigonal bipyramidal, (II), in configuration. Were the $\mathrm{H_2O}$ molecule to dissociate

TABLE 3

Comparison of observed and calculated (in parentheses) rate constants [equation (10)] at various ligand and hydrogen-ion concentrations, $I = 1·0\,\mathrm{M}$, and 380 nm

θ_c/°C	$[\mathrm{H^+}]$/M	$10^3[\mathrm{L}]$/M	$k_{\mathrm{obs.}}/\mathrm{s^{-1}}$
L = Thiourea, $[\mathrm{Cr^{VI}}]_\mathrm{T} = 4 \times 10^{-4}$M			
30·0	0·25	10·0	0·038 (0·041)
		15·0	0·0633 (0·069)
		20·0	0·097 (0·099)
		25·0	0·129 (0·1298)
	0·50	5·0	0·0573 (0·050)
		10·0	0·135 (0·133)
		15·0	0·202 (0·2037)
		20·0	0·286 (0·288)
		25·0	0·392 (0·374)
	0·75	10·0	0·268 (0·246)
		15·0	0·424 (0·401)
		20·0	0·56 (0·562)
		25·0	0·76 (0·724)
		30·0	0·89 (0·8874)
	1·0	10·0	0·401 (0·410)
		15·0	0·636 (0·662)
		20·0	0·93 (0·918)
		25·0	1·19 (1·177)
		30·0	1·43 (1·437)
$[\mathrm{Cr^{VI}}]_\mathrm{T} = 2 \times 10^{-4}$—$4 \times 10^{-4}$M			
24·9	0·25	10·0	0·038 (0·039)
		15·0	0·0496 (0·0647)
		20·0	0·094 (0·092)
		25·0	0·115 (0·119)
		30·0	0·156 (0·148)
		40·0	0·214 (0·206)
	0·50	3·0	0·0282 (0·025)
		5·0	0·0512 (0·049)
		6·0	0·0613 (0·625)
		8·0	0·082 (0·090)
		10·0	0·116 (0·119)
		15·0	0·188 (0·195)
		20·0	0·264 (0·273)
		25·0	0·348 (0·352)
		30·0	0·444 (0·431)
		35·0	0·540 (0·511)
	0·75	10·0	0·256 (0·242)
		15·0	0·370 (0·389)
		20·0	0·516 (0·539)
		25·0	0·656 (0·689)
		30·0	0·88 (0·84)
		40·0	1·23 (1·15)
	1·0	3·0	0·109 (0·089)
		5·0	0·177 (0·175)
		6·0	0·222 (0·220)
		8·0	0·295 (0·312)
		10·0	0·390 (0·406)
		15·0	0·612 (0·646)
		20·0	0·860 (0·889)
		25·0	1·16 (1·13)
		30·0	1·36 (1·38)
		35·0	1·59 (1·62)
		40·0	2·04 (1·87)
20·3	0·25	5·0	0·0132 (0·0139)
		10·0	0·0296 (0·032)
		15·0	0·0492 (0·052)
		20·0	0·0696 (0·0728)
		25·0	0·099 (0·094)
	0·50	5·0	0·0456 (0·043)
		10·0	0·100 (0·100)
		15·0	0·171 (0·160)
		20·0	0·228 (0·222)
		25·0	0·318 (0·271)

---

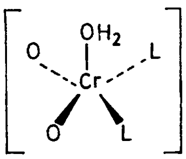
[24] G. P. Haight, jun., E. Perchonock, F. Emmeneger, and G. Gordon, *J. Amer. Chem. Soc.*, 1965, **87**, 3835.

[25] T. J. Kemp, 'Comprehensive Chemical Kinetics,' vol. 7, eds. C. H. Bamford and C. F. H. Tipper, Elsevier, London, 1972, p. 285; A. McAuley, 'Inorganic Reaction Mechanisms,' Specialist Periodical Report, vol. 2, ed. J. Burgess, Chemical Society, London, 1973, p. 47.

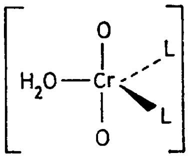
TABLE 3 (*Continued*)

θ_c/°C	[H⁺]/M	10^3[L]/M	$k_{obs.}$/s^{-1}
20·3	0·75	10·0	0·214 (0·205)
		15·0	0·324 (0·325)
		20·0	0·444 (0·446)
		25·0	0·572 (0·568)
		30·0	0·760 (0·773)
	1·0	2·5	0·0744 (0·0635)
		3·75	0·121 (0·107)
		5·0	0·154 (0·154)
		6·25	0·210 (0·207)
		7·5	0·250 (0·250)
		8·75	0·296 (0·298)
		10·0	0·350 (0·348)
		15·0	0·720 (0·747)
15·0	0·25	5·0	0·0112 (0·0111)
		10·0	0·0276 (0·0276)
		15·0	0·046 (0·046)
		20·0	0·0656 (0·0644)
	0·50	3·0	0·0215 (0·0195)
		5·0	0·0387 (0·0388)
		6·0	0·0452 (0·049)
		8·0	0·0636 (0·0703)
		10·0	0·092 (0·092)
		15·0	0·157 (0·150)
	0·75	5·0	0·0812 (0·0842)
		10·0	0·194 (0·193)
		15·0	0·334 (0·305)
	1·0	3·0	0·082 (0·078)
		5·0	0·144 (0·147)
		6·0	0·176 (0·183)
		8·0	0·234 (0·256)
		10·0	0·328 (0·330)
L = Ethylene thiourea, $[\mathrm{Cr^{VI}}]_T = 2 \times 10^{-4}$M			
15·2	0·25	7·5	0·0524 (0·0554)
	0·35	7·5	0·0752 (0·075)
	0·50	3·0	0·078 (0·079)
		6·0	0·094 (0·091)
		7·5	0·115 (0·109)
		8·0	0·12 (0·115)
		10·0	0·143 (0·137)
	0·60	7·5	0·142 (0·136)
	0·80	7·5	0·216 (0·204)
	1·0	3·0	0·122 (0·120)
		5·0	0·193 (0·196)
		6·0	0·231 (0·234)
		7·5	0·278 (0·296)
		8·0	0·296 (0·309)
		10·0	0·380 (0·384)
20·0	1·0	5·0	0·244 (0·243)
		7·5	0·338 (0·361)
		10·0	0·484 (0·478)
		12·5	0·568 (0·595)
		15·0	0·704 (0·712)
		17·5	0·880 (0·829)
		20·0	0·94 (0·945)
		25·0	1·270 (1·18)
24·9	0·25	2·5	0·0356 (0·0358)
		7·5	0·092 (0·091)
	0·35	2·5	0·0476 (0·049)
		7·5	0·128 (0·122)
	0·50	2·5	0·0653 (0·0688)
		3·0	0·082 (0·081)
		5·0	0·122 (0·124)
		6·0	0·146 (0·144)
		7·5	0·194 (0·172)
		8·0	0·192 (0·181)
		10·0	0·220 (0·218)
	0·60	2·5	0·092 (0·082)
		7·5	0·222 (0·209)
24·9	0·80	2·5	0·118 (0·112)
		7·5	0·310 (0·295)
	1·00	2·5	0·151 (0·145)
		3·0	0·173 (0·172)
		5·0	0·276 (0·276)
		6·0	0·310 (0·327)
		7·5	0·440 (0·402)
		8·0	0·416 (0·427)
		10·0	0·524 (0·526)

rapidly then tetrahedral $[\mathrm{CrO_2L_2}]$ would be formed. If, however, the oxygen atom was only singly protonated, it is still possible for attack by the second molecule of reducing agent which is suggested by the k_1 path for the thiourea reaction. Such a mechanism has also been observed previously in the reactions with thiosulphate [1,2] and with the sulphite ion.[24] The driving force for reactions of this type where a second molecule of substrate is involved may be two fold in that there may be some incipient disulphide formation in the transition states which would result in a more facile two-electron reduction to $\mathrm{Cr^{IV}}$. Experiments carried out in the presence of manganese(II), which is known [26] to act as a trap for $\mathrm{Cr^{IV}}$, showed no difference in the rate, indicating an absence of any reaction between $\mathrm{Cr^{VI}}$ and either $\mathrm{Cr^{IV}}$ or the products of any $\mathrm{Cr^{IV}}$ redox reactions.[26] Under conditions of low ligand concentrations it is considered that reduction to $\mathrm{Cr^{V}}$ [reactions (5) and (11)] is the rate-determining process in accord with the mechanism postulated by King and his co-workers [27] for one-electron reductants. The fact that k_α [reaction (11)] is *ca.* 15 times greater than k_0 [reaction (5)] (Table 2) may be the result of steric effects around the tetrahedral metal centre.



(I)



(II)

The fate of the chromium(IV) is less well identified, but the presence of thiourea ligands in the chromium(III) products is consistent with a labile $\mathrm{Cr^{IV}}$ species rapidly co-ordinating several ligands and undergoing a further one-electron redox reaction with the formation of a

$$\mathrm{Cr^{IV}} + n\mathrm{L} \overset{\text{fast}}{\rightleftharpoons} [\mathrm{Cr^{IV}L}_n] \qquad (15)$$

$$[\mathrm{Cr^{IV}L}_n] \xrightarrow{\text{fast}} [\mathrm{Cr^{III}L}_{n-1}] + \mathrm{L}^{\bullet} \qquad (16)$$

$$2\mathrm{L}^{\bullet} \xrightarrow{\text{fast}} \mathrm{L'}_2 \qquad (17)$$

radical (see above) which rapidly dimerises. There is a change in co-ordination number from tetrahedral $\mathrm{Cr^{VI}}$ ion to the octahedral $\mathrm{Cr^{III}}$ products. The nature of $\mathrm{Cr^{IV}}$ species in solution is not well documented but it has

---

[26] F. H. Westheimer, *Chem. Rev.*, 1949, **45**, 419.

[27] J. Y. Tong and E. L. King, *J. Amer. Chem. Soc.*, 1960, **82**, 3805; C. Altman and E. L. King, *ibid.*, 1961, **83**, 2825; J. H. Espenson and E. L. King, *ibid.*, 1963, **85**, 3328.

been postulated that an increase in co-ordination number takes place on formation of Cr^{IV}. Some support for a labile Cr^{IV} species is also given by our observations that in chloride media, in the thiourea reaction, some $[CrCl]^{2+}$ is formed as well as the Cr^{3+} and $[Cr\{(NH_2)_2CS\}]^{3+}$ complexes. Since Cr^{III} is substitution inert, the chloride ion must have been attached to the chromium centre in a higher oxidation state with the whole complex undergoing reduction.

It is of interest that in these systems where there is a large excess of ligand the products are disulphides with no evidence for further oxidation to sulphones. In this respect these one-electron reductants resemble the corresponding reaction with cysteine[28] but contrast with that with thiocyanate where sulphate is a product.[4]

We thank the Federal Government of Nigeria and Ahmadu Bello University for the award of a grant (to M. A. O.), the S.R.C. for support towards part of the apparatus, Drs. A. L. Porte, A. P. Lane, and Mr. J. P. McCann for valuable discussion and experimental assistance.

[4/1292 *Received, 28th June,* 1974]

---

[28] A. McAuley and J. P. McCann, unpublished work.