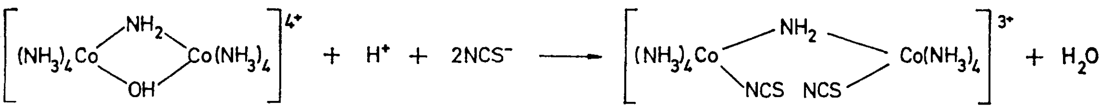
Reactions of μ-Hydroxo-dicobalt(III) Complexes. Part XIII.† Further Kinetic Studies on the Reaction of Thiocyanate with the μ-Amido-μ-hydroxo-bis[tetra-amminecobalt(III)] Complex

By **Keith L. Scott, Roger S. Taylor, Roland K. Wharton,** and **A. Geoffrey Sykes,*** Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT

Further studies have been made on the reaction of the μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] complex with a large excess of thiocyanate, (i), in aqueous perchloric acid solutions I = 2.0 M ($NaClO_4$). Hydroxo-bridge cleavage is observed, where the concentration dependence of pseudo-first-order rate constants, k_{obs}, at low $[H^+]$ and $[NCS^-]$ is of the form (ii), with k_2 small and negligible at high $[H^+]$ and $[NCS^-]$. A non-linear dependence on hydrogen-ion concentration has to be taken into account with $[H^+] \geqslant 0.5$M. At 25 °C, k_1 = (4.7 ± 0.1) × 10^{-4} l^2 mol^{-2} s^{-1}, and activation parameters are $\Delta H^{\ddagger}_1$ = 17.5 ± 0.4 kcal mol^{-1} and $\Delta S^{\ddagger}_1$ = −14.7 ± 1.4 cal K^{-1} mol^{-1}.

$$k_{obs} = k_1[H^+][NCS^-] + k_2[NCS^-] \qquad (ii)$$


(i)

THE product of the reaction of the μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] complex (hereafter μ-amido-μ-hydroxo) with thiocyanate ion has previously been isolated and characterised as the μ-amido-bis[tetra-amminethiocyanatocobalt(III)] complex.[1] Some kinetic data at 25 °C were also presented, but more recent experience with systems of this kind [2] has suggested that the interpretation given may not be correct. Furthermore, during a study of the reaction of another binuclear species, the μ-hydroxo-bis[penta-amminecobalt(III)] complex, with thiocyanate,[3] it was observed that solutions of thiocyanate in aqueous perchloric acid assume a reddish brown coloration. This coloration, which was not

---

† Part XII is J. D. Edwards, K. Wieghardt, and A. G. Sykes, *J.C.S. Dalton*, 1974, 2198.

[1] S.-W. Foong, M. B. Stevenson, and A. G. Sykes, *J. Chem. Soc. (A)*, 1970, 1064.

[2] A. G. Sykes, *Chem. in Britain*, 1974, **10**, 170 and references therein.

[3] R. K. Wharton and A. G. Sykes, *J.C.S. Dalton*, 1973, 439.

detected in earlier studies of the reaction of the μ-amido-μ-hydroxo-complex with thiocyanate, now appears to be highly relevant. The present work was undertaken in order to reappraise the existing data and interpretation, and to obtain activation parameters for the hydroxo-bridge cleavage process.

RESULTS

The reaction of Thiocyanate with Perchloric Acid.—On addition of perchloric acid solution to lithium or sodium thiocyanate solutions a reddish brown coloration is produced instantaneously (<1 s). The absorbance at *ca*. 460 nm due to the species formed, which is a linear function of $[H^+]$ when $[H^+] \geqslant 0.5$M, partially disappears over a period of 30 min at room temperature. We have now established that the first stage in the original study [1] corresponds to this side reaction, and is not, therefore, a reaction involving the complex. The coloration was not detected in the earlier study because perchloric acid and thiocyanate were mixed only in the presence of the red dicobalt complex, which masks the colour due to the side reaction. Repeated recrystallisation of the thiocyanate salts, and the use of air-free techniques employing Teflon needles, have failed to eliminate formation of the initial colour (the origin of which is at present uncertain). It was decided, therefore, simply to minimise the effect by working in 1-cm cells, thus enabling higher concentrations of complex to be used, and by preparation of run solutions using a different procedure (see Experimental section).

Reaction of Thiocyanate with the μ-Amido-μ-hydroxo-complex.—The reaction was monitored by following the increase in absorbance at 520 nm. Plots of log ($OD_\infty - OD_t$) against time were linear to at least three half-lives, and there was no initial non-linear portion as was observed previously. The dependence of pseudo-first-order rate constants, k_{obs}, on reactants, $[H^+] \leqslant 0.4$M and $[NCS^-] \leqslant 0.4$M, was investigated at 25 °C (Table 1). The data obtained conform to (1), see Figure 1.

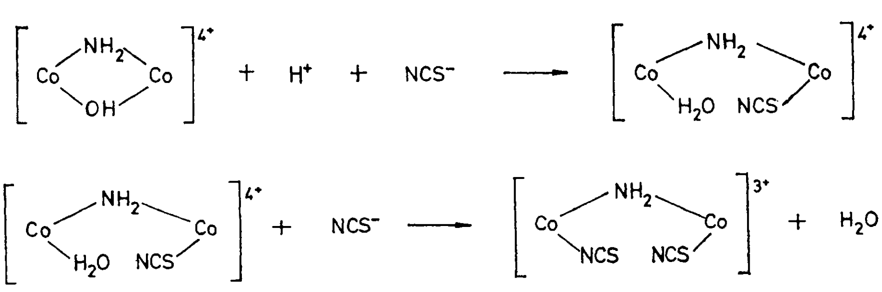
$$k_{obs} = k_1[H^+][NCS^-] + k_2[NCS^-] \qquad (1)$$

TABLE 1

Pseudo-first-order rate constants, k_{obs}, for the reaction of the μ-amido-μ-hydroxo-complex, concentration $(1.4—4.8) \times 10^{-3}$M with NCS^- ($[NCS^-]$ and $[H^+] \leqslant 0.4$M) at 25 °C, $I = 2.0$M ($NaClO_4$)

$[H^+]$ / M	$[NCS^-]$ / M	10^5k_{obs} / s^{-1}
0.10	0.10	0.32
	0.20	0.71
	0.30	1.06
	0.40	1.44
0.20	0.10	0.67
	0.20	1.33
	0.30	1.85
	0.40	2.60
0.30	0.10	0.87
	0.20	1.96
	0.30	2.64
	0.40	3.46
0.40	0.10	1.15
	0.20	2.32
	0.30	3.31
	0.40	4.61

Contributions from the intercept k_2 are small, and k_1 is dominant for the range of concentrations investigated. It is concluded that the principal reaction path is as in equation (2). Evidence that the subsequent step (3) is rapid was obtained by carrying out experiments in 8M-$HClO_4$ with only one equivalent of thiocyanate per binuclear complex, when the bisthiocyanato-complex ($\lambda_{max.}$ 515 nm, ε 733 l mol^{-1} cm^{-1}) was the only identifiable product.



(2)

(3)

For runs with $[H^+]$ and $[NCS^-] \leqslant 0.4$M, the rate of ammonia loss from the μ-amido-μ-hydroxo-complex [4] becomes comparable to the rate of anation. This is particularly important for temperatures above 25 °C. A higher range of H^+ and NCS^- concentrations was therefore investigated in order to determine activation parameters for k_1.

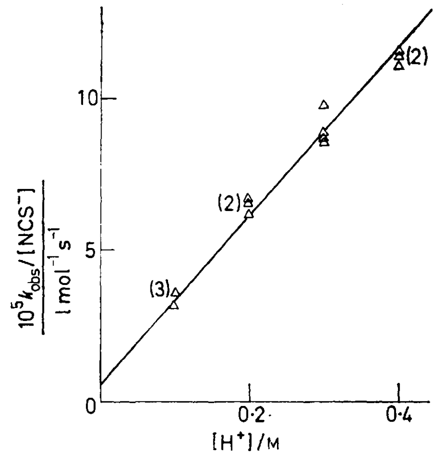


FIGURE 1 The dependence of $k_{obs}/[NCS^-]$ on $[H^+]$ for the reaction of NCS^- with the μ-amido-μ-hydroxo-complex at 25.0 °C, under conditions $[H^+]$ and $[NCS^-] \leqslant 0.4$M, $I = 2.0$M ($NaClO_4$)

Rate constants with $[NCS^-] \geqslant 0.5$M are combined with those from the previous study (previously assigned to a second stage and now re-assigned to the first stage) (see Table 2). At $[H^+] = 0.3$M a reasonable (though not precise) first-order dependence on $[NCS^-]$ is observed (see Figure 2). The dependence on $[H^+]$ is less than first order as illustrated

---

[4] R. S. Taylor and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 1426.

in Figure 3. Using a non-linear least-squares programme (weighting k_{obs}^{-2}),[5] the rate constants in Table 2 give a good fit to an equation of the modified form (4). At 25 °C, I = 2.0M (NaClO$_4$), values of $k_1 = (4.7 \pm 0.1) \times 10^{-4}$ l^2 mol^{-2} s^{-1}, $k_2 = (2.8 \pm 0.6) \times 10^{-6}$ l mol^{-1} s^{-1}, and $K = 0.38 \pm 0.04$ l mol^{-1} were obtained. The [H$^+$]-independent pathway, k_2, makes only a small contribution to k_{obs} at [H$^+$] > 0.1M. For the purpose of evaluating activation parameters expression (4) was, therefore, modified with $k_2 = 0$. Hence, from a least-squares treatment of data (weighting k_{obs}^{-2}), $\Delta H^{\ddagger}_1 = 17.5 \pm 0.4$ kcal mol^{-1} and $\Delta S^{\ddagger}_1 = -14.7 \pm 1.4$ cal K^{-1} mol^{-1}.

$$k_{obs} = \frac{k_1[\mathrm{H^+}][\mathrm{NCS^-}] + k_2[\mathrm{NCS^-}]}{1 + K[\mathrm{H^+}]} \qquad (4)$$

TABLE 2

Pseudo-first-order rate constants, k_{obs}, for the reaction of the μ-amido-μ-hydroxo-complex, (0.3—2.0) × 10^{-3}M, with [NCS$^-$] (⩾0.5M) at I = 2.0M (NaClO$_4$). Runs in which the ionic strength was adjusted with LiClO$_4$ are indicated

Temp. / °C	[H$^+$] / M	[NCS$^-$] / M	$10^4 k_{obs}$ [a] / s^{-1}
2.9	1.0	1.0	0.40 [b]
15.0	0.1	1.9	0.395
	0.2	1.8	0.64
	0.3	1.7	0.885
	0.4	1.6	1.04
	0.5	1.5	1.31
20.0	0.1	1.9	0.52
	0.2	1.8	1.03
	0.3	1.7	1.38
	0.4	1.6	1.69
	0.5	1.5	2.02
25.0	0.02	1.98	0.235
	0.1	1.9	1.01
	0.2	1.0	1.04 [c]
	0.2	1.8	1.61
	0.3	0.8	0.93 [b]
	0.3	1.0	1.31 [b]
	0.3	1.3	1.68 [b]
	0.3	1.5	1.95 [b]
	0.3	1.7	2.23
	0.5	0.5	0.90 [b]
	0.5	0.8	1.54(2) [b]
	0.5	1.0	2.03 [b]
	0.5	1.0	1.85 [c]
	0.5	1.3	2.70 [b]
	0.5	1.5	2.89 (2) [b]
	0.7	0.5	1.38 [b]
	0.7	0.8	2.09(5) [b]
	0.7	1.0	2.77 [b]
	0.7	1.3	3.40 [b]
	1.0	0.5	1.68 [b]
	1.0	0.8	2.76(4) [b]
	1.0	1.0	3.50 [b]
	1.0	1.0	3.36
	1.0	1.0	3.40 [c]
	1.2	0.5	1.90 [b]
	1.2	0.8	3.18 [b]
	1.5	0.5	2.14 [b]
30.0	0.1	1.9	1.45
	0.2	1.8	2.61
	0.3	1.7	3.58
	0.4	1.6	4.30
	0.5	1.5	4.34
35.0	0.1	1.9	2.68
	0.2	1.8	4.00
	0.3	1.7	5.14
	0.4	1.6	5.36
	0.5	1.5	6.50

[a] Number of runs averaged in parentheses. [b] Ref. 1; [(Co^{III})$_2$] = (2.7—5.9) × 10^{-4}M. [c] Ionic strength adjusted with LiClO$_4$; these runs not included in subsequent computations.

The choice of NaClO$_4$ for maintaining the ionic strength was consistent with previous studies on the μ-amido-μ-hydroxo-complex.[6] Three check runs at [NCS$^-$] = 1.0M were carried out with LiClO$_4$ used to make up the ionic strength, Table 2, when rate constants were the same within experimental error, as those using NaClO$_4$.

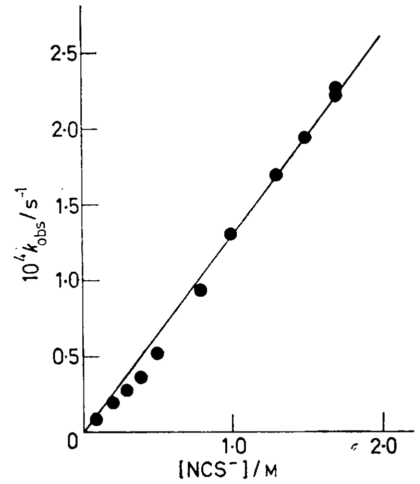


FIGURE 2 The dependence of k_{obs} on [NCS$^-$] at [H$^+$] = 0.3M for the reaction of μ-amido-μ-hydroxo-complex at 25 °C, I = 2.0M (NaClO$_4$)

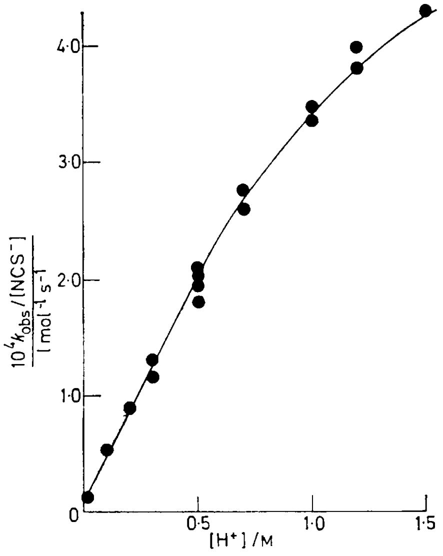


FIGURE 3 The dependence of k_{obs}/[NCS$^-$] on [H$^+$], over an extended range of [H$^+$] up to 1.5M, at 25 °C, I = 2.0 M (NaClO$_4$)

Reaction of Chloride with the μ-Amido-μ-hydroxo-complex.—The bridge cleavage reaction of the μ-amido-μ-hydroxo-complex in the presence of chloride has been studied previously,[7] when no evidence for curvature of the type

---

[5] Los Alamos Report LA 2367 (1959) and Addenda by R. H. Moore and R. K. Zeigler.

[6] R. S. Taylor and A. G. Sykes, *Inorg. Chem.*, 1974, **13**, 2524.

[7] S.-W. Foong, R. D. Mast, M. B. Stevenson, and A. G. Sykes, *J. Chem. Soc. (A)*, 1971, 1266.

discussed above was obtained. Additional runs were, therefore, carried out in order to investigate further a possible non-linear dependence of the kind observed for the hydroxo-bridge cleavage reaction in the presence of thiocyanate. At 25.0 °C, $I = 2.0$M ($NaClO_4$), $[Cl^-] = 1.0$M, the dependence of k_{obs} on $[H^+]$ is shown in Figure 4. Slight curvature is evident under these optimum conditions and a possible value $K = 0.18 \pm 0.04$ l mol^{-1} is indicated. A small amount of the bischloro-complex is formed in a second rapid equilibrium step which is assumed to be non-rate-determining.

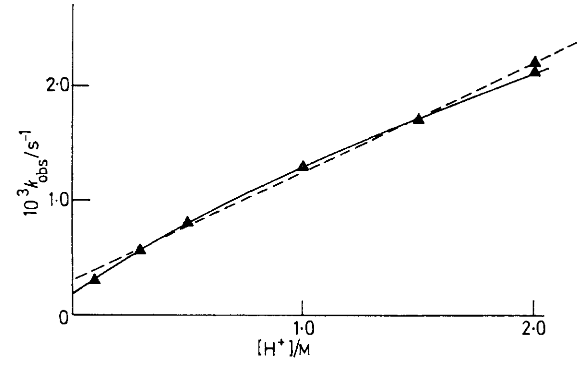


FIGURE 4 The dependence of k_{obs} on $[H^+]$ for the reaction of Cl^- with the μ-amido-μ-hydroxo-complex at 25.0 °C, $I = 2.0$M ($NaClO_4$)

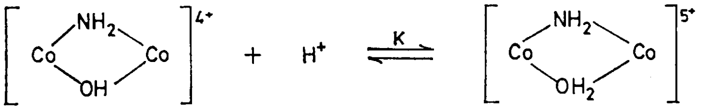
DISCUSSION

The identification of a reaction between NCS^- and perchloric acid has enabled us to eliminate one of the stages previously reported in the reaction of the μ-amido-μ-hydroxo-complex with NCS^-, thus permitting the assignment of a simpler mechanism. It is now clear, in keeping with related studies,[2] that hydroxo-bridge cleavage is the rate-determining process with the term k_1 dominant. A reaction sequence (2) and (3) applies, where the second stage, (3), is as far as we can ascertain rapid. There is no evidence for build-up of an aquothiocyanato or μ-thiocyanato-intermediate. In the related studies with chloride [7] and bromide,[8] formation of a bishalogeno-product is not as favourable thermodynamically, and such species are only detected when $[HCl] > 0.5$M or $[HBr] > 1.7$M. The major products for conditions $I = 2.0$M are the μ-halogeno rather than the aquohalogeno-species.[2] If a μ-thiocyanato-species is formed in the thiocyanate reaction it can only be present in very low concentrations. The replacement of a terminal aquo-ligand in, for example, the conversion of the μ-amido-bisaquo- to the μ-amido-μ-hydroxo-complex, or of the μ-amido-aquochloro- to the μ-amido-μ-chloro- or μ-amido-bischloro-complex, is known to be fast in comparison to bridge cleavage,[1,7,8] and is consistent with the assignment of reaction (3) as a fast step.

The $[H^+]$-independent term, k_2 in (1), has also been encountered in other hydroxo-bridge cleavage studies in the presence of chloride [7] and bromide.[8] The term k_2 is too small in the present study to allow precise values to be determined.

We now consider in detail the dependencies on $[NCS^-]$ and $[H^+]$ as illustrated in Figures 2 and 3. We are hesitant about invoking a more complex dependence on $[NCS^-]$ to explain the sigmoidal dependence illustrated in Figure 2, since deviations from linearity over the complete range are small. Our approach in determining activation parameters has been to accept the concentration dependencies in (4) which are strictly valid for $[NCS^-] \geqslant 0.5$M. The non-linear $[H^+]$ dependence (see Figure 3) must be taken into account, and a good fit to (4) is obtained over the whole $[H^+]$ range.

There are three possible explanations of the $[H^+]$ dependence in (4), but at present we are unable to distinguish between these. Firstly protonation of free thiocyanate may be involved. Literature values show a quite alarming spread ($10^{-3.6}$ to $10^{1.0}$ l mol^{-1}),[9] and the magnitude of K obtained in the present study can be accommodated within such a range. However this would also require a less than first-order dependence on $[NCS^-]$. A second possibility is that the assumption of equivalent activity coefficients for NCS^- and ClO_4^- may not be strictly valid when $[NCS^-]$ is varied over such a wide range (0.1 to 2.0M). Thirdly protonation of the μ-amido-μ-hydroxo-complex [see equation (5)], may account for the observed $[H^+]$ dependence.



(5)

All previous studies have led us to believe that the equilibrium (5) lies to the left with $K < 0.07$ l mol^{-1}.[10] However from the studies with chloride we now report a *possible* value of $K = 0.18 \pm 0.04$ l mol^{-1} at 25 °C. Furthermore, close examination of existing data with bromide [8] permits a value $K = 0.10 \pm 0.11$ l mol^{-1} to be fitted at 25 °C. The curvature is hardly perceptible in the latter case and at other temperatures is not apparent. As a result a value of $K < 0.02$ l mol^{-1} was previously suggested for the latter study. Only a very small change in absorption spectrum (250—500 nm) of the μ-amido-μ-hydroxo-complex is observed in 2M-$HClO_4$ as compared to water. If $K = 0.38$ l mol^{-1} then *ca.* 45% of the μ-aquo-species should be present under such conditions, and more significant spectrophotometric changes would be expected. The implication is that very little of the μ-aquo-species is formed in perchlorate media, equili-

---

[8] S.-W. Foong and A. G. Sykes, *J.C.S. Dalton*, 1974, 1453.

[9] See ' Stability Constants of Metal–Ion Complexes,' *Chem. Soc. Special. Publ., nos.* 17 *and* 25.

[10] See *e.g.* M. B. Stevenson, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 1059.

brium constant $\leqslant 0.38$ l mol^{-1}, and that more extensive protonation occurs in the presence of other anions. Such a scheme would require other denominator terms however, unless ion-pairing to the binuclear complex is complete under all conditions studied.

The mechanistic implications of the studies on hydroxo-bridge cleavage of the μ-amido-μ-hydroxo-complex have already been discussed.[6] The value of $k_1 = 4.7 \times 10^{-4}$ l mol^{-1} s^{-1} at 25 °C and activation parameters $\Delta H^{\ddagger}_1 = 17.5 \pm 0.4$ kcal mol^{-1} and $\Delta S^{\ddagger}_1 = -14.7 \pm 1.4$ cal K^{-1} mol^{-1} are in extremely good agreement with data for other bridge-cleavage reactions with 1— anions. Since the denominator terms in [H$^+$] obtained with chloride and bromide only marginally affect the values of k_1, previous comments on these studies remain unchanged.

Finally, Buckingham *et al.*[11] have obtained clearcut evidence for a less than first-order dependence on anion concentration in their study of the hydroxo-bridge cleavage of the μ-hydroxo-bis[penta-amminecobalt(III)] complex in the presence of chloride. This effect was only detected by working at low hydrogen-ion concentrations, conditions under which it is not possible to work with the μ-amido-μ-hydroxo-complex due to the slowness of hydroxo-bridge cleavage, and the incidence of ammonia loss which proceeds at a comparable rate.[4] They have interpreted their data at higher [H$^+$] in terms of a complex multi-term concentration dependence. We note that under these conditions a simpler dependence, k_1-[H$^+$][NCS$^-$],[3] applies for bridge cleavage in the presence of thiocyanate (anion dependent path). Using this simpler equation k_1 values for bridge cleavage in the presence of chloride and methanesulphonate are within 10% of those obtained using the more complex dependence. We feel, therefore, that more detailed concentration dependences which might be invoked in connection with the present study are unlikely to affect the main features of the interpretation already made.[6] The data obtained for hydroxo-bridge cleavage of the μ-hydroxo-bis[penta-amminecobalt(III)] complex (k_1 term, l^2 mol^{-2} s^{-1} at 25 °C) in the presence of NCS$^-$ (0.137),[3] Cl$^-$(0.303),[11] and $CH_3SO_3^-$ (0.061) [11] are adequately described by an S_N1 mechanism of the non-limiting kind.

EXPERIMENTAL

The preparation of the perchlorate salt of the μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] complex was as described previously.[4] Sodium thiocyanate (Hopkin and Williams, Reagent Grade) was recrystallised once from ethanol. Lithium thiocyanate (B.D.H., Laboratory Reagent) was recrystallised three times from water. The iron content of the AnalaR 72% perchloric acid was $<5 \times 10^{-5}$ %. In an attempt to inhibit a red-brown colour formation in these studies, perchloric acid was prepared from lithium perchlorate (which gave no colour with NCS$^-$) by passing a 2M solution down an Amberlite IR-120 ion-exchange column which had been acidified using 5M-HCl. The perchloric acid eluted from the column still gave rise to red-brown colour on being mixed with NaNCS. The procedure for kinetic runs was that a solution containing perchloric acid and thiocyanate ($I = 2.00$M) was thermostatted for 20 min in a 1-cm cell. A small volume of the complex solution in dilute acid was then injected to initiate the reaction. The side reaction due to perchloric acid and thiocyanate was minimised by adopting this procedure. Reactions were monitored on a Unicam SP 800 recording spectrophotometer. For runs with [NCS$^-$] $\geqslant$ 0.5M absorbance (O D$_\infty$) readings were measured in all but the slowest run (at [H$^+$] = 0.02M), when the Guggenheim treatment [12] was used. For runs at [NCS$^-$] $\leqslant$ 0.4M, k_{obs} was evaluated from the initial slope of OD against time plots, and the total absorbance change calculated using relevant absorption coefficients.

[4/1873 *Received*, 13*th September*, 1974]

---

[11] D. A. Buckingham, W. Marty, and A. M. Sargeson, *Inorg. Chem.*, 1974, **13**, 2165. We are most grateful for correspondence from Drs. A. M. Sargeson and W. Marty.

[12] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanisms,' J. Wiley, New York, 2nd edn., 1961, p. 49.