Kinetics and Mechanism of the Reaction Between Thallium(III) and Thiocyanate Ion in Aqueous Perchloric Acid Solutions

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A study of the reaction between thallium(III) and thiocyanate ion in aqueous $HClO_4$ (0.2—2.0 mol dm^{-3}) solutions has shown the complex $[Tl(SCN)]^{2+}$ to be reactive, yielding final products possibly through a dimer. Two other complexes, $[Tl_2(SCN)]^{5+}$ and $[HTl(SCN)_2]^{2+}$ are also formed but are not reactive. In the presence of excess of SCN^- the observed rate law is as in equation (i) where

$$-d[Tl^{III}]/dt = k[Tl^{III}]^2/(1 + K_2[H^+][SCN^-])^2 \qquad \text{(i)}$$

K_2 is the complex-formation constant for $[HTl(SCN)_2]^{2+}$; k and K_2 were found to be 2.2 ± 0.2 dm^3 mol^{-1} s^{-1} and 24 ± 1 dm^6 mol^{-2} respectively at 20 °C and I = 2.0 mol dm^{-3}. In the presence of excess of Tl^{III} the observed rate law is as in equation (ii) where K_1 is the complex-formation constant for $[Tl_2(SCN)]^{5+}$; k and K_1 were found to be 2.1 ± 0.2 dm^3 mol^{-1} s^{-1} and 45 ± 5 dm^3 mol^{-1}.

$$-d[Tl^{III}]/dt = k[SCN^-]_T^2/(1 + K_1[Tl^{III}])^2 \qquad \text{(ii)}$$

Oxidation of anionic reductants by thallium(III) is invariably preceded by complex formation between them, and in some cases three or four complexes[1,2] are formed. Thallium(III)–oxygen bonding has been reported with nitrite.[3] We became interested in the oxidation of thiocyanate since it has two available co-ordination sites and we wished to know the number of complexes formed between thiocyanate and thallium(III). Thiocyanate forms complexes with iron(III),[4] chromium(VI),[5] cerium(IV),[6] manganese(III),[7] vanadium(V),[8] *etc.* and in all cases reduction of the metal ions also takes place.

In a study of the reaction of Tl^{III} with thiocyanate Treindl and Fico[9] reported several undefined complexes amongst which $[Tl_2(SCN)]^{5+}$ was considered reactive. No mechanism was given and the reaction under conditions when $[Tl^{III}]_0 > [SCN^-]_0$ (zero subscript indicating initial concentration) was not studied. An extended study under the above condition seemed to us worthwhile in order to determine the complexes formed and their reactivity. Incidently this is the only reaction of thallium(III) found to be second order under certain conditions.

Experimental

Stock solution of thallium(III) perchlorate[10] and lithium perchlorate[11] were prepared as described earlier. BDH AnalaR KSCN was used. Thallium(III) was standardized iodometrically[12] and KSCN was standardized argentometrically.[13] Solutions were prepared in twice distilled water, the second distillation being from permanganate solution.

Kinetic experiments were carried out in a temperature-controlled water-bath at 20 ± 0.1 °C usually by measuring Tl^{III} iodometrically;[12] for low concentrations a colorimetric[14] method was employed. The reaction was quenched by mixing aliquots with a solution of HCl whereby strong chloro-complexes[15] of Tl^{III} are formed which are not reactive. The order of mixing of the reactants had no effect on the rate.

Initial rates determined by the plane-mirror method[16] were used to calculate the orders in $[Tl^{III}]$ and $[SCN^-]$. Subsequently, linear plots (up to 80% completion of reaction) of $[Tl^{III}]^{-1}$ *versus* time were made when $[SCN^-]_0 \gg [Tl^{III}]_0$ to calculate pseudo-second-order rate constants (k_2). The observed rate law is $-d[Tl^{III}]/dt = A[Tl^{III}]^2$ (where A = constant depending on various concentrations). The use of initial rates was preferred since the reaction is complicated. The results were reproducible to ±5%.

For reactions when $[Tl^{III}]_0 \gg [SCN^-]_0$, an attempt was made to follow the kinetics by determining thiocyanate ion argentometrically,[13] but the method failed due to interference from thallium(III) present in the system. A spectrophotometric method also failed since thallium(III)[10] and thiocyanate[17] both absorb in the same range. Hence the kinetics was followed iodometrically, also under this condition, and only initial rates were determined, but these results were reproducible to ±10%. when $[SCN^-]_0 \gg [Tl^{III}]_0$ the maximum change in $[SCN^-]$ was less than 1% and the change in $[Tl^{III}]$ was 80—85%. When $[Tl^{III}]_0 \gg [SCN^-]$ the maximum change in $[Tl^{III}]$ was less than 15% and the change in $[SCN^-]$ was 60—65%.

Most of the reactions when $[Tl^{III}]_0 \approx [SCN^-]_0$ were rapid and the kinetics was followed by a modified method. Several identical reaction mixtures were prepared, allowed to react separately for predetermined times, and analysed iodometrically. No aliquots were withdrawn in this method.

Spectrophotometric measurements were made on a Cecil CE 599 Universal automatic scanning instrument. The following details were used in calculating concentrations in 2.0 mol dm^{-3} $HClO_4$: Tl^{III}, peak at 199 nm, ε = 4 100 (1 900 at 214 nm); Tl^{I}, peak at 214 nm, ε = 4 400; SCN^-, peak at 196, ε = 4 500 (2 700 dm^3 mol^{-1} cm^{-1} at 214 nm).

Results

Stoicheiometry.—Excess of Tl^{III} was determined iodometrically[12] and excess of SCN^- argentometrically.[13] The ratio $\Delta[Tl^{III}]/\Delta[SCN^-]$ was found to be 3 ± 0.05:1, and confirmed by spectrophotometric measurements. The cyanide concentration was determined by titrating against Ni^{2+} by the method of Huditz and Flaschka[18] but $\Delta[SCN^-]/\Delta[CN^-]$ varied between 1.0 and 1.5:1. Sulphate ion was tested

Table 1. Thiocyanate dependence of the reaction between Tl^{III} and SCN^- at different $[Tl^{III}]$ under the conditions $[SCN^-]_0 \gg [Tl^{III}]_0$, $[HClO_4] = 2.0$ mol dm^{-3}, $I = 2.0$ mol dm^{-3}, 20 °C, $C = 2.2$ dm^3 mol^{-1} s^{-1}, and $D = 48$ dm^3 mol^{-1}

$[SCN^-]_0$/ mol dm^{-3}	k_2/dm^3 mol^{-1} s^{-1} for $[Tl^{III}]_0$		
	0.001	0.002	0.003 mol dm^{-3}
0.04	1.02	1.00	0.95
0.06	0.42	0.42	—
0.08	0.28	0.28	0.28
0.10	0.19	0.19	—
0.12	0.13	0.13	0.13
0.14	—	0.11	0.10
0.16	0.089	0.091	0.094
0.18	—	0.067	0.068
0.20	—	0.047	0.050
0.24	—	0.041	0.041
0.28	—	—	0.027
0.32	—	—	0.020

Table 2. Thiocyanate dependence of the reaction between Tl^{III} and SCN^- at different $[H^+]$ when $[SCN^-]_0 \gg [Tl^{III}]_0$, $[Tl^{III}]_0 = 2.0 \times 10^{-3}$ mol dm^{-3}, $I = 2.0$ mol dm^{-3}, 20 °C, $C = 2.2$ dm^3 mol^{-1} s^{-1}, and $D = 48$ dm^3 mol^{-1}

$[SCN^-]_0$/ mol dm^{-3}	k_2/dm^3 mol^{-1} s^{-1} for $[HClO_4]$		
	0.5	1.0	2.0 mol dm^{-3}
0.06	3.0	1.27	0.42
0.08	—	0.98	0.28
0.10	1.5	0.62	0.19
0.15	0.93	0.35	
0.20	0.67	0.18	0.047

Table 3. Thiocyanate and thallium(III) dependence in the $Tl^{III} + SCN^-$ reaction in the presence of excess of Tl^{III}, $[HClO_4] = 2.0$ mol dm^{-3}, $I = 2.0$ mol dm^{-3}, 20 °C, $E = 2.2$ dm^3 mol^{-1} s^{-1}, and $F = 4.8$ dm^3 mol^{-1}

$[SCN^-]_0 = 0.001$ mol dm^{-3}					
$[Tl^{III}$/mol dm^{-3}	0.06	0.05	0.04	0.03	0.02
$10^6 v_0$/mol dm^{-3} s^{-1}	0.15	0.205	0.28	0.45	0.72
$[SCN^-]_0 = 0.002$ mol dm^{-3}					
$[Tl^{III}]_0$/mol dm^{-3}	0.0616	0.0482	0.038	0.0298	
$10^6 v_0$/mol dm^{-3} s^{-1}	0.58	0.90	1.20	1.90	
$[SCN^-]_0 = 0.003$ mol dm^{-3}					
$[Tl^{III}]_0$/mol dm^{-3}		0.055		0.045	
$10^6 v_0$/mol dm^{-3} s^{-1}		1.60		2.25	

qualitatively only since Tl^I and SCN^- interfered in the quantitative analysis. The thallium(I) concentration was estimated spectrophotometrically and $\Delta[Tl^{III}]/\Delta[Tl^I]$ found to be 1.0 ± 0.1 : 1. All these results show that the reaction occurs as in equation (1). Thallium(I) thiocyanate was not precipitated

$$3Tl^{III} + SCN^- + 4H_2O \longrightarrow 3Tl^I + HCN + SO_4^{2-} + 7H^+ \quad (1)$$

in any of the stoicheiometric experiments since the concentrations of thallium(III) and thiocyanate employed were of the order of $\approx 10^{-3}$ mol dm^{-3}. In kinetics experiments a slight turbidity was obtained only when $[SCN^-]$ was larger than 0.2 mol dm^{-3}.

The same reaction products were obtained in the oxidations of thiocyanate by Cr^{VI},[5] Ce^{IV},[6] V^V,[8] Ir^{IV},[19] $[Os(phen)_3]^{3+}$ (phen = 1,10-phenanthroline) and $[Os(bipy)_3]^{3+}$ (bipy = 2,2′-bipyridyl),[20] and $[Fe(bipy)_3]^{3+}$, and $[Fe(phen)_3]^{3+}$.[21] Thiocyanogen is reported to be the product in oxidations by manganese(III),[7] iron(III)[22] (in acetonitrile), and cobalt(III)[23] (in acidic perchlorate). However, it may be an intermediate in other reactions too, and readily hydrolyzes[24] to yield SO_4^{2-} and HCN in aqueous acidic solutions [equation (2)].

Table 4. Initial rates of the reactions when $[Tl^{III}]_0 \approx [SCN^-]_0$, $[HClO_4] = 2.0$ mol dm^{-3}, $I = 2.0$ mol dm^{-3}, 20 °C

10^3 $[SCN^-]$/ mol dm^{-3}	10^5 v_0/ mol dm^{-3} s^{-1} for $[Tl^{III}]_0$				
	0.001	0.002	0.003	0.004	0.005 mol dm^{-3}
0.2	0.024	0.022	0.016	0.014	0.012
0.4	0.09	0.082	0.066	0.055	0.049
0.8	0.37	0.31	0.27	0.23	0.20
1.0	0.70	0.50	0.45	0.40	0.36
2.0	0.50	2.8	2.1	1.6	1.4
3.0	0.45	2.0	5.4	4.8	3.4
4.0	—	—	5.0	10.0	8.0
5.0	—	—	—	9.0	16
6.0	—	—	—	7.5	14

$$3(SCN)_2 + 4H_2O \longrightarrow 5SCN^- + HCN + SO_4^{2-} + 7H^+ \quad (2)$$

Thallium(III) *Dependence*.—Since the reaction is complex this dependence was studied in the presence of a large excess of SCN^-. When $[SCN^-]_0 > 60[Tl^{III}]_0$ plots of $[Tl^{III}]$ *versus* time were made to calculate initial rates (v_0) for different $[Tl^{III}]_0$, (1—5) × 10^{-3} mol dm^{-3}, and these were then plotted against $[Tl^{III}]^2$. This gave a straight line passing through the origin, the slope being found to be 0.184 ± 0.02 dm^3 mol^{-1} s^{-1} by the least-squares method. Thus the observed rate law is $-d[Tl^{III}]/dt = k_2[Tl^{III}]^2$ where k_2 is the pseudo-second-order rate constant. Subsequently, second-order plots of $[Tl^{III}]^{-1}$ *versus* time were made and k_2 was found to be 0.18 ± 0.012 dm^3 mol^{-1} s^{-1} at $[SCN^-]_0 = 0.2$ mol dm^3, $[HClO_4] = 1.5$ mol dm^{-3}, and 20 °C.

Thiocyanate Dependence.—The results of the variation of excess of SCN^- (minimum $[SCN^-]_0/[Tl^{III}]_0$ was 60 taking into consideration the stoicheiometry of reaction) are given in Table 1. The rate decreases and tends to zero with increasing $[SCN^-]$. The observed rate equation is $k_2 = C/(1 + D[SCN^-])^2$ where C and D are constants depending on various concentrations. Some more results at two more $[H^+]$ are given in Table 2. However, the thiocyanate dependence is quite different when $[Tl^{III}]_0 \gg [SCN^-]_0$. From Table 3 the order in $[SCN^-]$ appears to be two and the observed rate law is as in equation (3).

$$-d[Tl^{III}]/dt = E[SCN^-]^2/(1 + F[Tl^{III}])^2 \quad (3)$$

Unfortunately a wide range of concentration of SCN^- could not be employed since no suitable method for its determination in presence of other constituents is available. Incidentally, Table 3 also shows the thallium(III) dependence when $[Tl^{III}]_0 \gg [SCN^-]_0$. The rate decreases with increasing $[Tl^{III}]$. This aspect of the reaction was completely missed by the previous workers.[9]

Some results when $[Tl^{III}]_0 \approx [SCN^-]_0$ are given in Table 4. For any set of concentrations, in a vertical column or in a horizontal line, the rate is a maximum when $[Tl^{III}]_0 = [SCN^-]_0$ and the observed rate law under this condition

Table 5. Effect of hydrogen ion on the rate of the Tl^{III} + SCN^- reaction at $[Tl^{III}]_0 = 2.0 \times 10^{-3}$ mol dm^{-3}, $[SCN^-]_0 = 0.2$ mol dm^{-3}, $I = 2.0$ mol dm^{-3}, 20 °C, $P = 2.2$ dm^3 mol^{-1} s^{-1}, and $Q = 4.8$ dm^3 mol^{-1}

$[HClO_4]$/mol dm^{-3}	0.2	0.3	0.5	1.0	1.5	2.0
k_2/dm^3 mol^{-1} s^{-1}	1.96	1.02	0.66	0.18	0.10	0.047

$[Tl^{III}]_0 = 0.04$ mol dm^{-3}, $[SCN^-]_0 = 0.001$ mol dm^{-3}, $I = 2.0$ mol dm^{-3}, 20 °C

$[HClO_4]$/mol dm^{-3}	0.5	1.0	1.5	2.0
$10^6\ v_0$/mol dm^{-3} s^{-1}	0.26	0.28	0.24	0.28

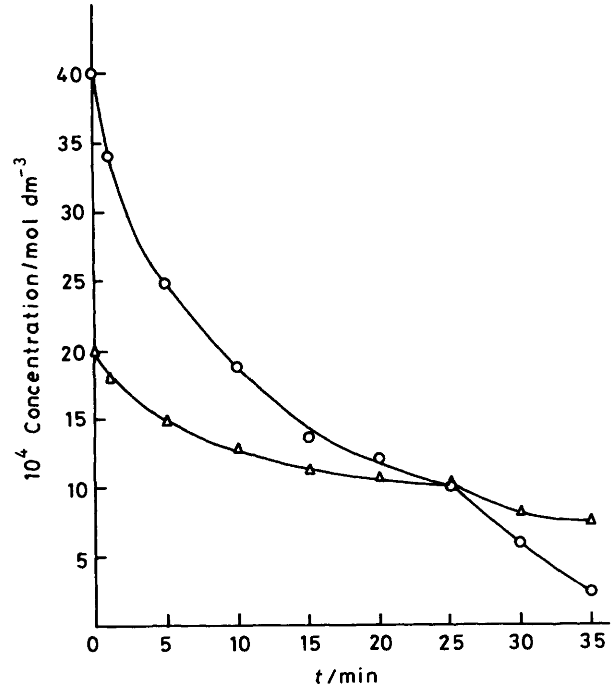

Figure 1. Plots of the concentrations of Tl^{III} (initially 4.0×10^{-3} mol dm^{-3}) (○) and SCN^- (initially 2.0×10^{-3} mol dm^{-3}) (△) *vs.* time at $[HClO_4] = 2.0$ mol dm^{-3} and 20 °C

appears to be $-d[Tl^{III}]/dt = A[Tl^{III}]_0^2$ or $A[SCN^-]_0^2$. A typical plot when $1 < [Tl^{III}]_0/[SCN^-]_0 < 3$ is shown in Figure 1. This clearly shows that the concentration of reactive species of thallium(III) which controls the rate, significantly changes during the course of reaction and it is not simply the decrease in $[Tl^{III}]$. The reaction becomes rapid at a particular stage, *i.e.* when $[Tl^{III}] = [SCN^-]$.

Effect of Ionic Strength.—The ionic strength was varied by use of $LiClO_4$. The rate decreases about 100 times upon increasing I from 1.0 to 3.5 mol dm^{-3} in a typical run involving $[Tl^{III}] = 2.0 \times 10^{-3}$, $[SCN^-] = 0.2$, and $[HClO_4] = 0.5$ mol dm^{-3} at 20 °C.

Variation of Hydrogen-ion Concentration.—The hydrogen-ion concentration was varied by use of $HClO_4$ at a constant ionic strength of 2.0 mol dm^{-3} adjusted with $LiClO_4$. The results are given in Table 5. There is a significant decrease in the rate with increasing $[H^+]$ and the observed rate equation is $k_2 = P/(1 + Q[H^+])^2$ where P and Q include other concentration variables. Some of these results have already been given in Table 2. The reaction rate is independent of $[H^+]$ in the range 0.5—2.0 mol dm^{-3} under the condition $[Tl^{III}]_0 \gg [SCN^-]_0$.

Discussion

As mentioned in the Introduction, most of the redox reactions of Tl^{III} are accompanied by complex formation between the metal ion and the substrate and as expected there is kinetic evdence for at least three complexes in the present system. Table 4 shows that it is most rapid at the ratio $[Tl^{III}]/[SCN^-] = 1:1$. For any set of comparable concentrations of the reactants under the condition $[Tl^{III}]_0 > [SCN^-]_0$, a situation arises during the course of reaction when $[Tl^{III}] = [SCN^-]$. This must happen since each mol of SCN^- requires 3 mol of Tl^{III} for oxidation. The reaction becomes rapid at this stage as can be seen from Figure 1.

The above characteristics indicate the formation of a reactive 1:1 complex of Tl^{III} and SCN^-. The orders of two with respect to $[Tl^{III}]$ and $[SCN^-]$, each in isolation, may suggest a total order of four. However, on doubling both $[Tl^{III}]$ and $[SCN^-]$ under the condition when they are equal the rate does not increase by a factor of 16; it just increases four fold as is obvious from Table 4. Thus, Tl^{III} and SCN^- do not participate as such in the reaction. There must be a complex with a kinetic order of two, which may be reactive. This could be $[Tl(SCN)]^{2+}$.

For any reaction mixture of Tl^{III} and SCN^- in 1:1 ratio, the rate decreases on increasing or decreasing the concentration of any of the two reactants. This is possible only when the reactive 1:1 complex is partially converted into less reactive or unreactive $Tl_x(SCN)^{3x-1}$ or $Tl(SCN)_x^{3-x}$ where $x > 1$. For simplicity we may regard these complexes as $[Tl_2(SCN)]^{5+}$ and $[Tl(SCN)_2]^+$ or 2:1 and 1:2 complexes respectively.

Generally in oxidations of SCN^- with metal ions the thiocyanate dependence has been found to be complex[5,6,19,20] and the order in $[SCN^-]$ varies between 1 and 2 or between 2 and 3. The order of two has been found in its oxidation with iron(III) complexes.[21] The present study is complex not only with respect to SCN^-, but also with respect to Tl^{III}, and this could be known only when $[SCN^-]$ was comparable and less than $[Tl^{III}]$.

Although an estimate of the complex-formation constants for the 2:1 and 1:2 complexes has been made kinetically, this was not possible for the 1:1 complex. However, since the initial rates at $[Tl^{III}]_0 = [SCN^-]_0$ for different concentrations are proportional to $[Tl^{III}]^2$ or $[SCN^-]^2$ the formation constant for the complex $[Tl(SCN)]^{2+}$ appears to be large compared to those for the other two complexes. The order of two in $[Tl(SCN)^{2+}]$ suggests that the composition of the complex may be $[Tl_2(SCN)_2{}^{4+}]$ or that it is a dimer, $[\{Tl(SCN)\}_2]^{4+}$ as in equilibrium (4). There is no other evidence for the dimer

$$2[Tl(SCN)]^{2+} \rightleftharpoons [\{Tl(SCN)\}_2]^{4+} \qquad (4)$$

formation, but other systems such as those of Co^{III},[25] Fe^{III},[26] *etc.* are known to possess reactive dimeric species.

U.V. Spectrophotometry of the Reaction Mixture.—Some useful information is obtainable from this study under the condition $[Tl^{III}] \gg [SCN^-]$. In the initial stages of the reaction (0.5, 2, 5, and 10 min) peaks at 199, 231, and 250 nm are obtained (reference 2.0 mol dm^{-3} $HClO_4$). The last two peaks ultimately disappear and a peak (214 nm) characteristic of Tl^I appears. The peak at 199 nm corresponds to Tl^{III} and those at 231 and

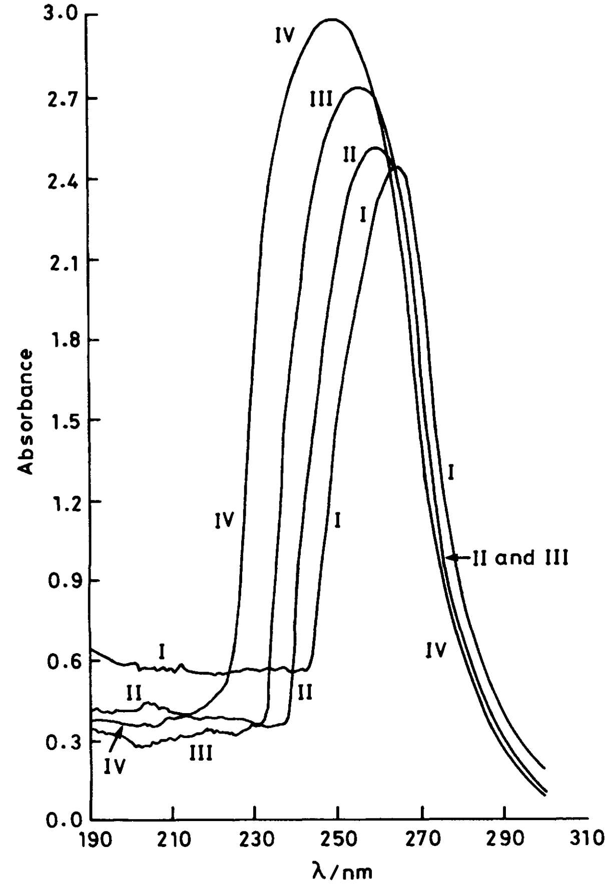

Figure 2. Spectra of mixtures of 5 × 10^{-4} mol dm^{-3} SCN^- and different [Tl^{III}] after 0.5 min: [Tl^{III}] = 0.035; (I), 0.025 (II), 0.015 (III), and 0.005 mol dm^{-3} (IV) at [$HClO_4$] = 2.0 mol dm^{-3}; reference Tl^{III} in 2.0 mol dm^{-3} $HClO_4$

250 nm must correspond to one or two intermediate species. The spectra (Figure 2) with different excesses of Tl^{III} show a peak between 266 and 250 nm which must correspond to a 1:1 complex intermediate. The spectra of one mixture with excess of Tl^{III} at different times are shown in Figure 3. The peak at 250 nm can be ascribed to a 1:1 complex on the basis of the spectra of Figure 2. Thiocyanogen was prepared as described[23] and its spectrum in glacial acetic acid gave a peak at 285 nm (reported[27] 288 nm). A 2.0 mol dm^{-3} $HClO_4$ solution of thiocyanogen (immediately) yielded a spectrum with a peak at 268 nm and a shoulder at 235 nm. Thus the peak at 233 nm (Figure 3) in the reaction mixture may correspond to thiocyanogen.

Mechanism of the Reaction.—Thus, on the basis of the stoicheiometry [Tl^{III}]/[SCN^-] of 3:1, a reactive 1:1 complex, unreactive 2:1 and 1:2 complexes, the order of two in [$Tl(SCN)^{2+}$], and inverse hydrogen-ion dependence when $[SCN]_0 \gg [Tl^{III}]_0$, the mechanism in equations (2) and (5)—(8) can be proposed. Hydrothiocyanic acid is reported[28] to be a strong acid and hence has not been considered.

$$Tl^{3+} + SCN^- \overset{K}{\rightleftharpoons} [Tl(SCN)]^{2+} \quad (5)$$

$$[Tl(SCN)]^{2+} + Tl^{3+} \overset{K_1}{\rightleftharpoons} [Tl_2(SCN)]^{5+} \quad (6)$$

$$[Tl(SCN)]^{2+} + SCN^- + H^+ \overset{K_2}{\rightleftharpoons} [HTl(SCN)_2]^{2+} \quad (7)$$

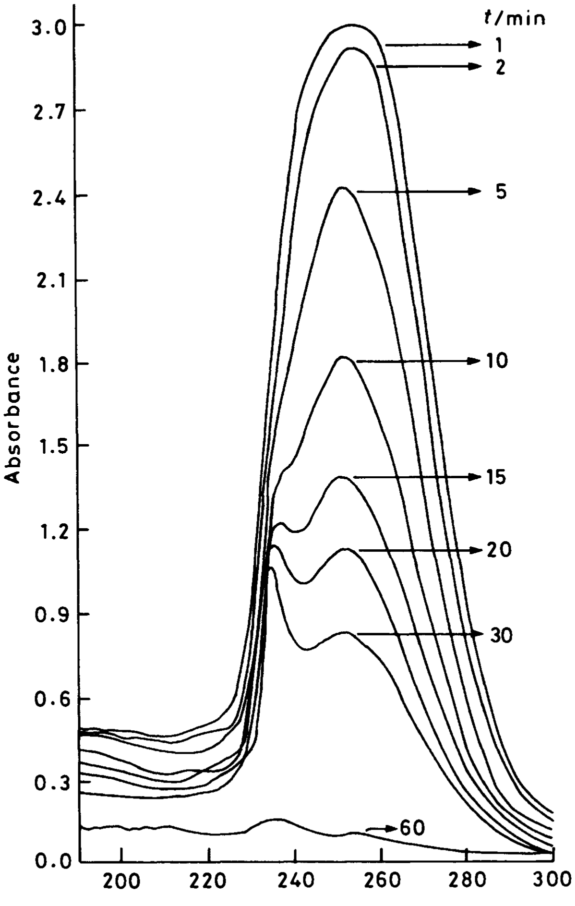

Figure 3. Absorption of a reaction mixture at different times. [Tl^{III}] = 5.0 × 10^{-3}; [SCN^-] = 5.0 × 10^{-4}; [$HClO_4$] = 2.0 mol dm^{-3}; reference is Tl^{III} + $HClO_4$

$$2[Tl(SCN)]^{2+} \overset{K_d}{\rightleftharpoons} \text{dimer} \xrightarrow{k'} Tl^I + Tl^{III} + (SCN)_2 \quad (8)$$

$$3(SCN)_2 + 4H_2O \xrightarrow{\text{fast}} 5SCN^- + HCN + SO_4^{2+} + 7H^+ \quad (2)$$

$$[Tl^{III}]_T = [Tl^{3+}] + [Tl(SCN)^{2+}] + 2[Tl_2(SCN)^{5+}] + [HTl(SCN)_2{}^{2+}] \quad (9)$$

$$[SCN^-]_T = [SCN^-] + [Tl(SCN)^{2+}] + [Tl_2(SCN)^{5+}] + 2[HTl(SCN)_2{}^{2+}] \quad (10)$$

(1) *Rate law when* $[SCN^-]_0 \gg [Tl^{III}]_0$, i.e. *when* [$Tl^{3+}$] *and* [$Tl_2(SCN)^{5+}$] *are almost zero.* Equations (11)—(14) may be derived where $k = k'K_d$. A plot of $k_2^{-\frac{1}{2}}$ *versus* $[H^+][SCN^-]$ (Figure 4) gives a straight line with non-zero intercept. The values of k and K_2 were found to be 2.2 ± 0.2 dm^3 mol^{-1} s^{-1} and 24 ± 1 dm^6 mol^{-2} respectively at 20 °C and I = 2.0 mol dm^{-3}.

$$[Tl^{III}]_T = [Tl(SCN)^{2+}] + [HTl(SCN)_2{}^{2+}] \quad (11)$$

$$\begin{aligned} -d[Tl^{III}]/dt &= k'\,[\text{dimer}] = k'K_d[Tl(SCN)^{2+}]^2 \\ &= k'K_d[Tl^{III}]_T{}^2/(1 + K_2[H^+][SCN^-])^2 \end{aligned} \quad (12)$$

$$\frac{-d[Tl^{III}]/dt}{[Tl^{III}]_T{}^2} = k_2 = k/(1 + K_2[H^+][SCN^-])^2 \quad (13)$$

$$k_2{}^{-\frac{1}{2}} = k^{-\frac{1}{2}} + k^{-\frac{1}{2}}K_2[H^+][SCN^-] \quad (14)$$

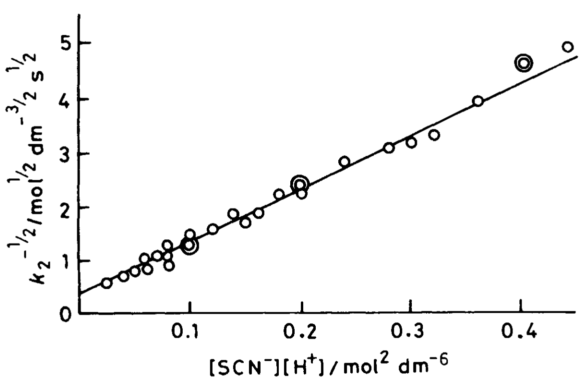

Figure 4. Plot of $k_2^{-\frac{1}{2}}$ *versus* [SCN$^-$][H$^+$] at [Tl^{III}] = 2.0 × 10^{-3}, I = 2.0 mol dm^{-3}, and 20 °C

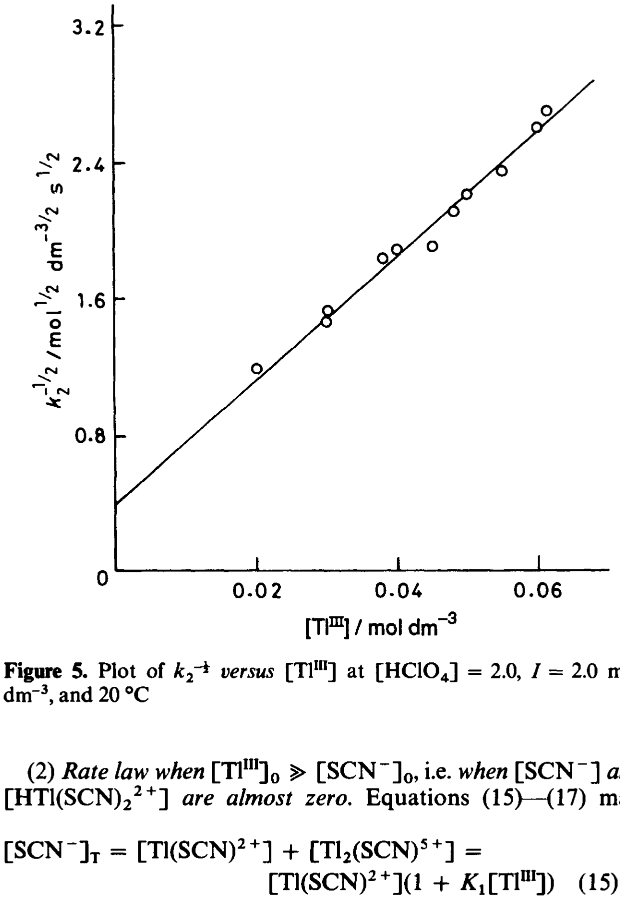

Figure 5. Plot of $k_2^{-\frac{1}{2}}$ *versus* [Tl^{III}] at [HClO$_4$] = 2.0, I = 2.0 mol dm^{-3}, and 20 °C

(2) *Rate law when* [Tl^{III}]$_0$ ≫ [SCN$^-$]$_0$, i.e. *when* [SCN$^-$] *and* [HTl(SCN)$_2{}^{2+}$] *are almost zero.* Equations (15)—(17) may

$$[\mathrm{SCN^-}]_\mathrm{T} = [\mathrm{Tl(SCN)^{2+}}] + [\mathrm{Tl_2(SCN)^{5+}}] = [\mathrm{Tl(SCN)^{2+}}](1 + K_1[\mathrm{Tl^{III}}]) \quad (15)$$

$$[\mathrm{Tl(SCN)^{2+}}] = [\mathrm{SCN^-}]_\mathrm{T}/(1 + K_1[\mathrm{Tl^{III}}]) \quad (16)$$

$$-\mathrm{d}[\mathrm{Tl^{III}}]/\mathrm{d}t = k'K_\mathrm{d}[\mathrm{Tl(SCN)^{2+}}]^2 = k'K_\mathrm{d}[\mathrm{SCN^-}]_\mathrm{T}{}^2/(1 + K_1[\mathrm{Tl^{III}}])^2 \quad (17)$$

be derived. A plot of $v_0^{-\frac{1}{2}}$[SCN$^-$] *versus* [Tl^{III}] (Figure 5) yields a straight line with non-zero intercept according to equation (17) and the values of k and K_1 were found to be 2.1 ± 0.2 dm^3 mol^{-1} s^{-1} and 45 ± 5 dm^3 mol^{-1} respectively. Similar values of k under the two conditions show the validity of the mechanism and the rate laws.

Thallium(III) complexes with contents of the reducing ligand larger than thallium(III), are often unreactive or less reactive. This has been reported in the oxidation of nitrite,[3] glycolic acid,[1] and benzilic acid.[2] The unreactivity has been ascribed [3] to the stabilization of the molecule owing to the formation of a ring structure. A similar structure for the 1:2 complex in the present case may perhaps be the reason for its not being reactive.

Our results differ from those of Treindl and Fico[9] in the following respects. (*i*) A study in the lower range of concentration of thiocyanate indicates the 1:1 complex to be reactive and the 2:1 complex [Tl$_2$(SCN)]$^{5+}$ is kinetically not reactive. (*ii*) Another unreactive complex has a 1:2 stoicheiometry and is not [Tl$_2$(SCN)$_2$]$^{4+}$. The latter or the dimer [{Tl(SCN)}$_2$]$^{4+}$ is the real reactive intermediate. Kinetically they are not distinguishable. (*iii*) The hydrogen-ion dependence, though of similar nature, was not discussed quantitatively in the previous study. (*iv*) No rate law was given in the previous study. (*v*) The previous study was made with TlCl$_3$ and since chloride ions form strong complexes with Tl^{III} and they inhibit the reaction, the system is less well defined.

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