The Reactions of (Trichlorostannato)rhodates(III) with Trichlorostannate(II) in Hydrochloric Acid Solutions

Shigemi Iwasaki,* Takashi Nagai, Eiichi Miki, Kunihiko Mizumachi, and Tatsujiro Ishimori
Department of Chemistry, College of Science, Rikkyo University, Nishi Ikebukuro 3, Toshima-ku, Tokyo 171

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(Trichlorostannato)rhodate(III) complexes, $[(CH_3)_4N]_3[RhCl_n(SnCl_3)_{6-n}]$ (n=2, 3, and 4), reacted with tin(II) in hydrochloric acid solutions to form a purple species. This purple species is assumed to be $[Rh^I(SnCl_3)_5]^{4-}$. The formation reaction of the purple species involved two independent paths, fast and slow paths. The main path was the fast one, in which the reactant mixture was in equilibria among $[RhCl_3(SnCl_3)_3]^{3-}$, $[RhCl_2(SnCl_3)_4]^{3-}$, $[RhCl(SnCl_3)_5]^{3-}$, and probably $[Rh(SnCl_3)_6]^{3-}$. The reaction orders in the formation of the purple species were 1, 2, and −2 with respect to the concentrations of the total rhodium(III) complexes, $SnCl_3^-$, and Cl^- respectively. The absorpton spectra of the reactant mixture showed an interaction absorption between $[RhCl_2(SnCl_3)_4]^{3-}$ and $SnCl_3^-$.

A series of six-coordinated (trichlorostannato)rhodate(III) complexes, $[(CH_3)_4N]_3[RhCl_n(SnCl_3)_{6-n}]$, where n=2, 3, and 4, have been prepared by Kimura.[1] The presence of $[RhCl(SnCl_3)_5]^{3-}$ (the pentakis complex) was confirmed in tin(II)–hydrochloric acid solutions by the use of Sn-119 NMR.[2] The complexes react with an excess of tin(II) in a hydrochloric acid solution to form a purple solution. In this paper, tentatively assuming the purple species in the solution to be $[Rh^I(SnCl_3)_5]^{4-}$, we will report an equilibrium mixture of the (trichlorostannato)rhodates(III) in tin(II)–hydrochloric acid solutions and the formation of the purple species from the equilibrium mixture.

Experimental

Materials. The rhodium(III)–trichlorostannato complexes (the rhodium(III) complexes), $[(CH_3)_4N]_3[RhCl_n(SnCl_3)_{6-n}]$, where n=2 and 3, were prepared by the methods of Kimura.[1] Reagents of a special grade were used.

Reaction Solution. The reaction solution was prepared by dissolving $[(CH_3)_4N]_3[RhCl_3(SnCl_3)_3]$ (the tris complex) or $[(CH_3)_4N]_3[RhCl_2(SnCl_3)_4]$ (the tetrakis complex) in a freshly prepared tin(II)–hydrochloric acid solution to give 2×10^{-4} mol dm^{-3}. The concentrations in the tin(II)–hydrochloric acid solution were adjusted to $[H^+]_{total}+[Li^+]_{total}=3.0$ mol dm^{-3}, $[Cl^-]_{total}+[ClO_4^-]_{total}=3.4$ mol dm^{-3}, and $[Sn^{II}]_{total}+[Zn^{II}]_{total}=0.2$ mol dm^{-3} by using zinc chloride, lithium chloride, and perchloric acid solutions respectively. In order to avoid the air oxidation of Sn^{II} in the reaction solution, a quartz cell was filled with the reaction solution and stoppered without any empty space, the stopper was then wrapped two-fold with polyethylene sheets. The concentration of Sn^{II} in the cell did not decrease more than a few per cent within 2 or 3 d. The total concentrations of Sn^{II} and Rh^{III} were determined in each run.

Measurements. The spectral change in the reaction solution was measured with a HITACHI 340 spectrophotometer equipped with a thermospacer cell compartment. The temperature of the reaction solution in the cell was thermostated at 25.0±0.3, 40.0±0.1, and 55.0±0.3 °C. A micro-computer was connected to the spectrophotometer to memorize the absorption curves at predetermined times and to calculate the rate constants by the method of least squares.

Kinetic Measurements. Figure 1 shows a typical example of the spectral change in the reaction solution. The absorptions at 402 and 560 nm were used independently for the kinetic analyses. Since Sn^{II}, Cl^-, and H^+ were in a large excess of the rhodium(III) complex, the pseudo-first-order method was used for the analyses. Because the absorption at 560 nm originated only from the product, the purple species, the change in the absorption at 560 nm(A_{560}) was used to determine the pseudo-first-order rate constant ($k_{obsd}(560)$) according to Eq. 1:

$$d(A_{560})/dt = k_{obsd}(560)\cdot(A_{560,\infty} - A_{560}). \qquad (1)$$

When absorption curves during the reaction were corrected for the contribution of the purple species, the absorption curves showed a maximum around 402 nm. The corrected absorption at 402 nm(A_{402}) was assumed to be proportional to the total concentration of the rhodium(III) complexes, which were in rapid equilibria with each other; A_{402} was also used to determine the pseudo-first-order rate constant, $k_{obsd}(402)$, according to Eq. 2:

$$-d(A_{402})/dt = k_{obsd}(402)\cdot(A_{402}). \qquad (2)$$

The spectral change at 402 nm was much greater than that at any other wavelength.

To determine the dependences of k_{obsd} on $[Sn^{II}]$ and $[H^+]$, $[Sn^{II}]_{total}$ was changed over the range of 0.02—0.06 mol dm^{-3} and $[H^+]_{total}$, over that of 0.25—3.0 mol dm^{-3}. The total concentration of Cl^- was changed over the range of 1.8—4.5 mol dm^{-3}. However, since the formation of the purple species was inhibited somewhat by the presence of perchloric acid, and since the reaction proceeded in a different way for $[HClO_4] > 1.8$ mol dm^{-3}, lithium chloride was added to the reaction solution, ignoring the increase in ionic strength in the cases of $[Cl^-]_{total} > 3.4$ mol dm^{-3}.

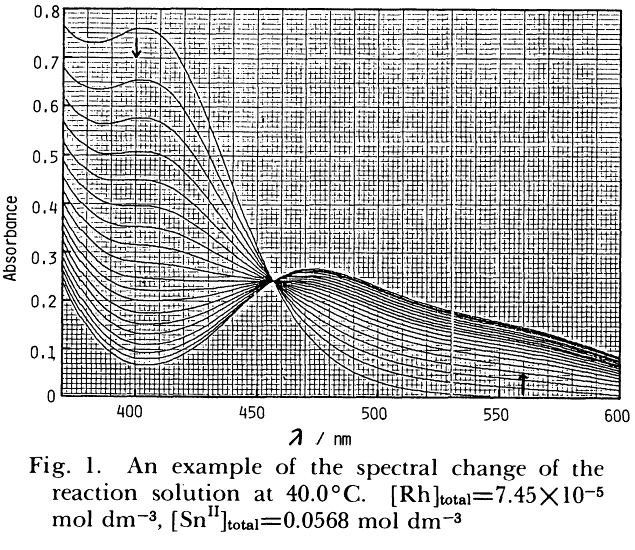

Fig. 1. An example of the spectral change of the reaction solution at 40.0 °C. $[Rh]_{total}=7.45\times10^{-5}$ mol dm^{-3}, $[Sn^{II}]_{total}=0.0568$ mol dm^{-3}

Results and Discussion

Reaction Product. The spectrum of the purple solution has been well established. The purple species can be assumed to be $[Rh(SnCl_3)_5]^{3-}$ (the rhodium(I) complex) on the basis of the complex salt obtained from the purple solution, $[Rh^{III}(NH_3)_6]_3[Rh^{I}(SnCl_3)_4(SnCl_4)]$-$[SnCl_6]\cdot 4H_2O$,[3] and on the basis of Sn-119 NMR studies of the Rh^{III}–Sn^{II} system in a hydrochloric acid solution.[2]

Reactants. Figure 2 shows an example of the conventional plots of the change in the absorptions at 402 and 560 nm. Two independent reaction paths, fast and slow ones, were generally observed under the conditions of $[Sn^{II}]_{total} > 0.02$ mol dm^{-3}. The formation of the rhodium(I) complex through the slow path was only a few per cent, and its rate constant could not be determined accurately. Therefore, data on the slow path were used mainly for determining accurately the pseudo-first-order rate constant of the fast path.

Some of the kinetic results at 40.0 °C are listed in Table 1. In each run, $k_{obsd}(560)$ agrees with $k_{obsd}(402)$ within the limits of experimental error. This supports the assumption on the absorption at 402 nm in the Experimental section. When the absorption curves during the reaction were corrected for the contributions of the rhodium(I) complex and of the reaction mixture involved in the slow path and were expressed as the molar absorption curves with respect to the total rhodium(III) complexes involved in the fast path, all the absorption curves gave almost the same curve in a kinetic run except during the last period of the reaction. However, the curve did not agree with the absorption curves of the tris complex nor with that of the tetrakis complex, and it varied with such reaction conditions as $[Sn^{II}]_{total}$.

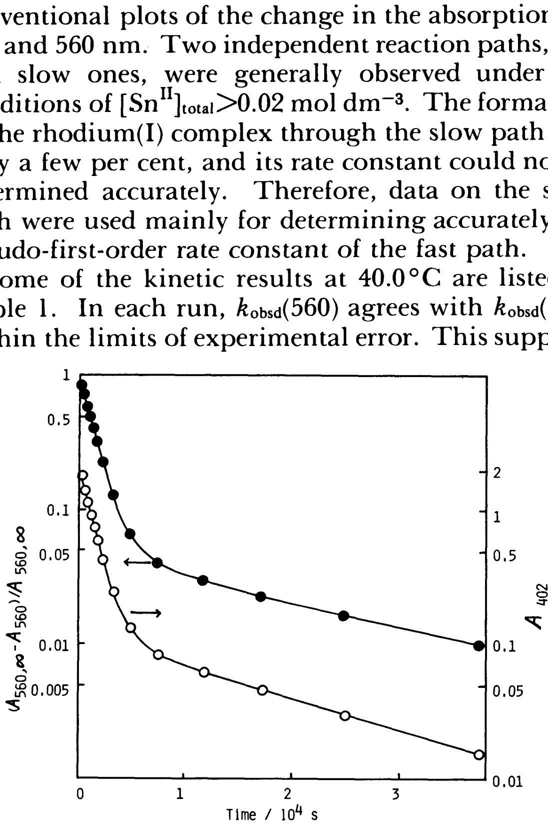

Fig. 2. The change in the absorptions at 402 and 560 nm.
log A_{402} vs. time(○), and log $(A_{560,\infty}-A_{560})/A_{560,\infty}$ vs. time(●). $[(CH_3)_4N]_3[RhCl_3(SnCl_3)_3]$ was dissolved at 55.0 °C. $[Rh]_{total} = 1.96 \times 10^{-4}$ mol dm^{-3}, $[Sn^{II}]_{total} = 0.0574$ mol dm^{-3}.

It is reasonable to consider that equilibria among the rhodium(III) complexes are present in relation to $[Sn^{II}]_{total}$, that one of the rhodium(III) complexes is the true reactant, and also that the equilibria are established rapidly enough for the rate of the reaction. The total rhodium(III) complexes in equilibria will hereafter be called "the yellow species" (Y); especially, the yellow species involved in the fast reaction path will be abbreviated as Y_I. The mean molar-absorption coefficients of Y_I, $\varepsilon(Y_I)$ were much greater than the molar-absorption coefficients of $[(CH_3)_4N]_3[RhCl_3(SnCl_3)_3]$ (the tris complex) or $[(CH_3)_4N]_3[RhCl_2(SnCl_3)_4]$ (the tetrakis complex), as is shown in Fig. 3. Furthermore, the absorptions of the pentakis and the hexakis complex are not expected to be large enough to explain the absorptions of Y_I. The molar-absorption coefficients of Y_I can be explained on the basis of the interaction absorption between $SnCl_3^-$ and the tetrakis complex, Y_4. The interaction absorption, IA, per mole of Y_4 can be defined as Eq. 3:

$$IA = \varepsilon(Y_I) - \varepsilon(Y_4), \tag{3}$$

where $\varepsilon(Y_I)$ is the mean molar-absorption coefficient of Y_I, and $\varepsilon(Y_4)$ is the molar-absorption coefficient of the tetrakis complex. Plots of IA at 402 nm vs. $[SnCl_3^-]$ are shown in Fig. 4. The values of $[SnCl_3^-]$ were calculated as will be described below. In Fig. 4, there is a linear relationship by which the straight line passes through the point of origin, the molar-absorption coefficient of Y_4. The relationship held at the other wavelengths as well. It is certain that these relationships are caused by the interaction absorption. It is also indicated that the tetrakis complex is the predominant species among the

Table 1. The pseudo-first-order rate constants at 40.0±0.1 °C

Complex[a]	$[Sn^{II}]_{total}$	$k_{obsd}(560)$	$k_{obsd}(402)$
(M=[(CH$_3$)$_4$N])	mol dm^{-3}	10^{-4} s^{-1}	10^{-4} s^{-1}
$M_3[RhCl_3(SnCl_3)_3]$	0.0197	0.442±0.001	0.401±0.006
	0.0280	1.42±0.00	1.41±0.00
	0.0288	1.38±0.16	1.27±0.01
	0.0449	3.08±0.01	3.03±0.01
	0.0568	5.23±0.09	5.19±0.04
$M_3[RhCl_2(SnCl_3)_4]$	0.0173	0.424±0.003	0.425±0.002
	0.0256	0.968±0.004	0.974±0.005
	0.0378	2.37±0.01	2.50±0.03
	0.0587	6.13±0.61	5.82±0.35

a) The complex used to prepare the reaction solution. Reaction solution: [HCl]=3.0 mol dm^{-3}. $[Sn^{II}]+[Zn^{II}]=0.2$ mol dm^{-3}.

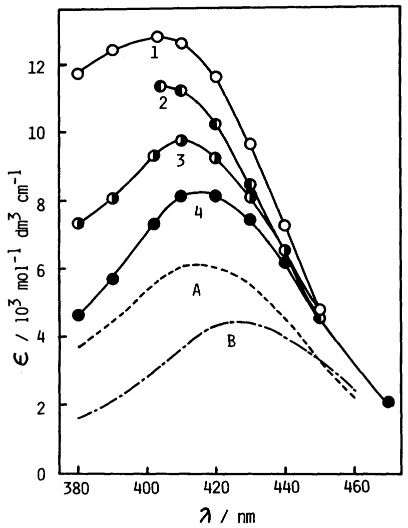

Fig. 3. The mean molar absorption coefficient of Y_I. $[(CH_3)_4N]_3[RhCl_3(SnCl_3)_3]$ was dissolved at 40.0 °C in Sn^{II} solutions of various concentration of Sn^{II}: $[Sn]_{total}$/mol dm^{-3}; (1) 0.0568, (2) 0.0449, (3) 0.0280, (4) 0.0197. Spectrum of $[RhCl_2(SnCl_3)_4]^{3-}$ (A), and that of $[RhCl_3(SnCl_3)_3]^{3-}$ (B) were taken from Ref. 1.

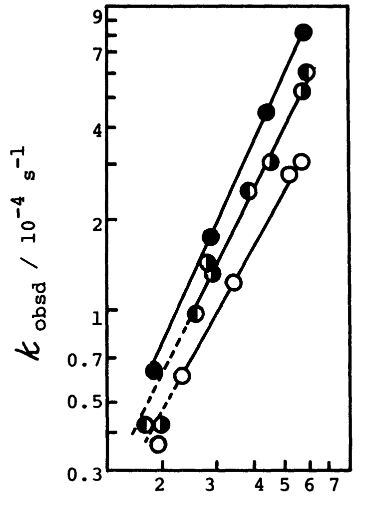

Fig. 5. The effect of $[Sn^{II}]_{total}$ on k_{obsd}.
○: 25.0 °C, the starting materials (s.m.)=the tris complex, ◑: 40.0 °C, s.m.=the tris complex, ◐: 40.0 °C, s.m.=the tetrakis complex, ●: 55.0 °C, s.m.=the tris complex.

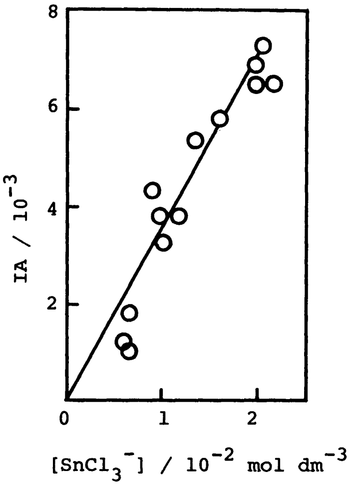

Fig. 4. The interaction absorption between the tetrakis complex and $SnCl_3^-$. $K_a(HSnCl_3)=2$. The absorptions at 402 nm were used.

rhodium(III) complexes in these reaction solutions.

The interaction absorption in Sn^{II}-Sn^{IV} in a hydrochloric acid solution[4] has been assumed to occur through a Cl^- bridge between Sn^{II} and Sn^{IV}.[5] The Mössbauer spectra of the rhodium(III) complexes suggested that the cooridnating Sn atoms were rather more similar to Sn^{IV} than to Sn^{II}.[1] Accordingly, the interaction absorption between $[RhCl_2(SnCl_3)_4]^{3-}$ and $SnCl_3^-$ in the reaction solution can be considered to occur with an associated species such as $[(SnCl_3)_3Cl_3RhSnCl_3\text{--}SnCl_3]^{4-}$.

Rate Law. In Fig. 5, the logarithm of the means of $k_{obsd}(560)$ and $k_{obsd}(402)$, namely, k_{obsd}, are plotted against the total concentration of Sn^{II}. In the figure, the k_{obsd}'s for the reaction solutions prepared by dissolving the tris complex or the tetrakis complex are distributed on the same line. This also confirms the idea regarding the yellow species in the equilibria. The slopes of the lines were 1.82±0.02 at 25.0 °C, 2.03±0.06 at 40.0 °C, and 2.31±0.02 at 55.0 °C. The slopes increased with an increase in the temperature.

The slope for the plot of log k_{obsd} *vs.* log $[Cl^-]_{total}$ at 40.0 °C was −2.0. Since the total concentration of Sn^{II} could not be kept absolutely constant in the series of experiments, the rate constants, k_{obsd}'s, obtained were corrected according to the dependence on the concentration of Sn^{II} described above. As perchlorate ions inhibited the progress of the formation of the rhodium(I) complex, the concentration of Cl^- was not changed over a wide range; the ionic strengths of the reaction solutions used ranges from 3.60 to 4.68 mol dm^{-3}. In order to examine the effect of the ionic strength, the solutions with the following compositions were compared: Soln A; [LiCl]=2.75 mol dm^{-3}, [HCl]=0.25 mol dm^{-3}, $[Cl^-]_{total}$=3.4 mol dm^{-3}, $[Sn^{II}]_{total}$= 0.038 mol dm^{-3}, $[Zn^{II}]_{total}$=0.16 mol dm^{-3}, I(ionic strength)=3.6 mol dm^{-3}. Soln B; $[CaCl_2]$= 1.375 mol dm^{-3}, [HCl]=0.25 mol dm^{-3}, $[Cl^-]_{total}$= 3.4 mol dm^{-3}, $[Sn^{II}]_{total}$=0.038 mol dm^{-3}, $[Zn^{II}]_{total}$= 0.16 mol dm^{-3}, I=4.98 mol dm^{-3}. The A and B solutions had the same concentrations of Cl^- and Sn^{II}, but different ionic strengths. The k_{obsd} was 6.7×10^{-4} s^{-1} for the A solution and 7.0×10^{-4} s^{-1} for the B. Consequently, the variation in the ionic strength to such an extent had little effect on k_{obsd}. The dependence was −1.95±0.04 for $[Cl^-]_{total}$ in the range from 2.55 to 4.47 mol dm^{-3}.

The slope for the plot of log k_{obsd} *vs.* log $[H^+]_{total}$ at 40.0 °C was −0.40±0.03. The corrections for slight variations in $[Sn^{II}]_{total}$ were made similarly to the case of the $[Cl^-]$ dependency.

A kinetic run was carried out in the presence of 1600 times as much $[Sn^{IV}]$ as $[Rh^{III}\text{ complex}]_{total}$. The observed rate constant for the fast reaction path, k_{obsd}, was not influenced by the presence of $[Sn^{IV}]$; this suggested that the redox equilibrium, $Rh^{III}+$

$Sn^{II} \rightleftarrows Rh^{I} + Sn^{IV}$,was not involved in the processes before the rate-determining step.

These results for the fast reaction path at 40.0 °C can be summarized as in Eq. 4:

$$k_{obsd} \propto [Sn^{II}]^{2.0}_{total}\,[Cl^-]^{-2.0}_{total}\,[H^+]^{-0.4}_{total}\,[Sn^{IV}]^{0}_{total}\,. \tag{4}$$

We attemped to express the rate law in terms of the concentrations of definite species instead of the total concentrations. Since $SnCl_3^-$ behaved as a ligand, the concentraion of $SnCl_3^-$ was used in place of the total concentraion of Sn^{II}. In the calculation, the formation constants of $ZnCl^+$, $ZnCl_2$, and $ZnCl_3^-$,⁶⁾ and of $SnCl^+$, $SnCl_2$ and $SnCl_3^-$,⁷⁾ and the acid-dissociation constants of $HZnCl_3$ and $HSnCl_3$ were taken into account. The present experiments were carried out at temperatures different from those in the literature; the differences were corrected by using the thermodynamic data in the literature to estimate the formation constants of the zinc-chloro and tin-chloro complexes. Although hydrogen trichlorostannate(II), $HSnCl_3$, has been reported to be a weak acid, ⁸⁾ the dissociation constant, $K_a(HSnCl_3)$, has not been measured. Therefore, $K_a(HSnCl_3)$ was assumed to be 0.1, 1, 2, 5, 10, and ∞. On the other hand, since the value of $K_a(HZnCl_3)$ previously reported⁹⁾ was considered to be too small, $K_a(HZnCl_3)$ was measured at $[Cl^-]_{total}=3$ mol dm^{-3} and found to be 4.9 ± 1.5 at 40.0 °C (I=3.0 mol dm^{-3}) by the potentiometric-titration method. By the use of these values, the dependencies were expressed at 40.0 °C as follows:

$$\begin{array}{rrl}
K_a(HSnCl_3) = & 0.1 & k_{obsd} \propto [SnCl_3^-]^{2.0}[Cl^-]^{-1.8}[H^+]^{1.2} \\
 & 1 & [SnCl_3^-]^{2.0}[Cl^-]^{-1.9}[H^+]^{0.3} \\
 & 2 & [SnCl_3^-]^{2.0}[Cl^-]^{-2.0}[H^+]^{0.1} \\
 & 5 & [SnCl_3^-]^{2.0}[Cl^-]^{-2.1}[H^+]^{-0.1} \\
 & 10 & [SnCl_3^-]^{2.0}[Cl^-]^{-2.1}[H^+]^{-0.2} \\
 & \infty & [SnCl_3^-]^{2.0}[Cl^-]^{-2.2}[H^+]^{-0.3}.
\end{array} \tag{5}$$

In the range of $K_a(HSnCl_3)$ values described above, the rate of the fast reaction path was always second-order with respect to the concentration of $SnCl_3^-$. When $K_a(HSnCl_3)$ was set at 2, the rate constant, k_{obsd} was almost independent of the hydrogen concentration. It was possible that H^+ participated only in the acid-dissociation equilibrium of $HSnCl_3$. The kinetic order of the concentration of Cl^- was in the range from −1.8 to −2.2. In the experiments concerning the effect of the Cl^- concentration on the fast reaction path, the concentration of Cl^- was somewhat changed. In the case of $K_a(HSnCl_3)=2$, the reaction order of $[Cl^-]$ was an integer, −2.0. It is probable that $K_a(HSnCl_3)=2$.

Reaction Routes. Several reaction routes were possible and so were considered. However, none of them could be chosen as the most probable one, because the reactant involved in the rate-determining step was not identified. As examples, two possible reaction routes are shown in Scheme 1.

In Route (1), the yellow species involved in the fast reaction path, Y_I, are considered to be an equilibrium mixture of the tris (Y_3), the tetrakis (Y_4), the pentakis (Y_5), and the hexakis(Y_6) complex. The rate-determining step is assumed to be the reaction of Y_6; it is assumed not to involve $SnCl_3^-$. The construction of a model of the hexakis complex shows that six trichlorostannato(II) ligands can coordinate to the rhodium(III) atom when the Cl–Sn–Cl angles are small enough.

Yellow Species: $Y = Y_I + Y_{II}$

Fast path

Route (1) $K_4 \qquad K_5 \qquad K_6$

$$Y_I{:}\,Y_3 \underset{Cl^-}{\overset{L^-}{\rightleftarrows}} Y_4 \underset{Cl^-}{\overset{L^-}{\rightleftarrows}} Y_5 \underset{Cl^-}{\overset{L^-}{\rightleftarrows}} Y_6;\ Y_6 \xrightarrow{\text{r.d.s.}} [Rh^{I}L_5]^{4-} + Sn^{IV}Cl_3^{+}$$

Route (2)

$$Y_I{:}\,Y_3 \underset{Cl^-}{\overset{L^-}{\rightleftarrows}} Y_4 \underset{Cl^-}{\overset{L^-}{\rightleftarrows}} Y_5 \underset{Cl^-}{\rightleftarrows} [Rh^{III}L_5]^{2-} \overset{L^-}{\rightleftarrows} [L_4RhSnCl_3\text{--}\,\text{--}SnCl_3]^{3-};\ Y_5'\text{–}SnCl_3$$

$$Y_5'\text{–}SnCl_3 \xrightarrow{\text{r.d.s.}} [Rh^{I}L_5]^{4-} + Sn^{IV}Cl_3^{+}$$

Slow path $Y_{II} \longrightarrow [Rh^{I}L_5]^{4-}$

Scheme 1. Possible reaction routes. $L = SnCl_3$, $Y_3 = [RhCl_3L_3]^{3-}$, $Y_4 = [RhCl_2L_4]^{3-}$, $Y_5 = [RhClL_5]^{3-}$, $Y_6 = [RhL_6]^{3-}$. r.d.s. represents rate-determining step. $K_4 = [Y_4][Cl^-]/[Y_3][L^-]$, $K_5 = [Y_5][Cl^-]/[Y_4][L^-]$, $K_6 = [Y_6][Cl^-]/[Y_5][L^-]$.

On the basis of the reaction Route (1) (in Scheme 1), k_{obsd} is expressed as follows:

$$k_{obsd} = \frac{k_1K_4K_5K_6[SnCl_3^-]^3}{[Cl^-]^3 + K_4[SnCl_3^-][Cl^-]^2 + K_4K_5[SnCl_3^-]^2[Cl^-] + K_4K_5K_6[SnCl_3^-]^3}. \tag{6}$$

In Eq. 6, the first term of the denominator is attributed to the tris complex(Y_3); the second term, to the tetrakis complex(Y_4); the third term, to the pentakis complex (Y_5), and the fourth term, to the hexakis complex(Y_6). When the tetrakis complex is the predominant species in the equilibrium mixture(Y_I), the following relationship is derived:

$$k_{obsd} = k_1K_5K_6[SnCl_3^-]^2[Cl^-]^{-2}. \tag{7}$$

This is in agreement with the derived rate law when $K_a(HSnCl_3)$ is assumed to be 2 in Eq. 5. In Fig. 5, the k_{obsd}'s obtained at low $[SnCl_3^-]$ values are found somewhat below the line with a slope of 2, which suggests that, in the reaction solution with a low $[SnCl_3^-]$, small amounts of the tris complex are present together with the major species, the tetrakis complex.

Route (2) (in Scheme 1) also satisfies the observed rate law when the tetrakis complex is predominant in the reactant mixture. The intermediate, Y_5'-$SnCl_3$, can be assumed because it is similar to the intermediate⁵⁾ in the exchange reaction of Sn^{II} and Sn^{IV} in hydrochloric acid solutions.

As to the temperature effect on the reaction, the slope of log k_{obsd} *vs.* log$[Sn^{II}]_{total}$ increased with the increase in the temperature, as may be seen from Fig. 5. This is explained by the shift of the equilibria among the rhodium(III) complexes due to the temperature; that is, at a higher temperature the tetrakis complex dissociates to the tris complex, whereas at a lower temperature the pentakis complex comes to be formed.¹⁰⁾

It was found that the formation of the purple species was generally accelerated by light irradiation. When $[(CH_3)_4N]_3[RhCl_4(SnCl_3)_2]$ was used as the starting material, the reaction was complicated and was greatly accelerated by light irradiation.

From this study, it was found clearly that the equilibria concerning the rhodium(III)–trichlorostannato complexes were rapidly established in the process of the formation reaction of the rhodium(I) complex. The reduction of the rhodium(III) complexes was not involved in the equilibria. It has been stated that anionic complexes of Rh^{III} are kinetically labile.11) Our results were consistent with this view.

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