13000, Office of Basic Energy Sciences, Division of Chemical Sciences, and the National Institutes of Health, Biotechnology Resource Program, Division of Research Resources. We thank Drs. M. K. Eidsness and S. P. Cramer for their assistance with early experiments.

Registry No. S, 7704-34-9; K_2SO_4, 7778-80-5; tetramethylene sulfone, 126-33-0; diphenyl sulfone, 127-63-9; dibenzothiophene sulfone, 1016-05-3; tetramethylene sulfoxide, 1600-44-8; 2-methylthiophene, 554-14-3; benzothiophene, 95-15-8; dibenzothiophene, 132-65-0; methionine, 63-68-3; thianthrene, 92-85-3; dioctyl sulfide, 2690-08-6; tetramethylthiophene, 14503-51-6; benzyl phenyl sulfide, 831-91-4; 2-naphthalenethiol, 91-60-1; cysteine, 52-90-4; diphenyl disulfide, 882-33-7; thiohemianthraquinone, 68629-85-6.

Equilibrium Dynamics in the Thallium(III)–Chloride System in Acidic Aqueous Solution

Istvan Banyai[1] and Julius Glaser*

Contribution from The Royal Institute of Technology (KTH), Department of Inorganic Chemistry, S-100 44 Stockholm, Sweden. *Received August 9, 1988*

Abstract: Kinetics of ligand exchange in the thallium(III)–chloride system in aqueous three molar perchloric acid solution was studied by measuring ^{205}Tl NMR line widths at 25 °C. The rate constants for the reactions

$$TlCl_m^{3-m} + {}^*TlCl_n^{3-n} \xrightleftharpoons{k_{mn}} {}^*TlCl_m^{3-m} + TlCl_n^{3-n}$$

are $k_{01} = 4.5 \times 10^4$ (7.8×10^3 at 0 °C), $k_{12} = 5.2 \times 10^4$ (1.5×10^4), $k_{23} = 2.7 \times 10^7$ (3.3×10^6), $k_{34} < 3 \times 10^7$ M^{-1} s^{-1}; for the reaction

$$Tl^{3+} + TlCl_2^{+} \xrightleftharpoons{k_{02}} 2TlCl^{2+}$$

$k_{02} = 6.4 \times 10^5$ M^{-1} s^{-1} (1.7×10^5), and for the anation reactions

$$TlCl_n^{3-n} + Cl^- \xrightleftharpoons{k'_{n(n+1)}} TlCl_{n+1}^{2-n}$$

$k'_{01} < 1 \times 10^8$, $k'_{12} = 3.3 \times 10^8$ (2.4×10^8), $k'_{23} = 1.3 \times 10^9$, and $k'_{34} = 4.7 \times 10^8$ M^{-1} s^{-1}. The first type of exchange dominates at low chloride to thallium ratios $(Cl_{tot}/Tl_{tot}) = R \leq 2$, the second type is only observed when the species Tl^{3+} and $TlCl_2^+$ are present, whereas the third one dominates at all higher R values. The activation parameters for the reaction represented by k_{01} are $\Delta H^\ddagger = 49$ (±2) kJ mol^{-1} and $\Delta S^\ddagger = +12$ (±0.3) J mol^{-1} K^{-1}. A mechanism for this reaction is suggested to be a dissociatively activated interchange process. The activation parameters for the reaction represented by k'_{34} are $\Delta H^\ddagger = 6.6$ kJ mol^{-1} and $\Delta S^\ddagger = -107$ J mol^{-1} K^{-1}. An associatively activated interchange mechanism for this reaction is proposed. The stability constant for the complex $TlCl_5^{2-}$ was estimated to be $K_5 = [TlCl_5^{2-}]/\{[TlCl_4^-][Cl^-]\} \approx 0.5$ M^{-1}.

The complexes formed in the thallium(III)–chloride system are among the strongest metal-ion–chloride complexes, and their equilibria have been extensively studied.[2-8] There is information on their structures both in solid and in solution.[9-13] However, there are only a few results on the kinetics of the complex formation and ligand exchange reactions of the thallium(III) ion.[14-17] The reason is probably that these reactions are rather fast not only on the traditional kinetic time scale but also on the NMR time scale of common NMR nuclei, e.g., ^{1}H or ^{35}Cl.[16]

Although there is a lot of data for the ligand and solvent exchange for the octahedral three-valent metal ions,[18] an investigation of dynamics in the thallium(III)–chloride system seems to be interesting. Structural studies showed that the geometry of thallium–halide complexes is different depending on the number of coordinated ligands.[12,13] In aqueous solution the aquated thallium(III) ion, the pentaaqua monochloro, and tetraaqua dichloro complexes are probably octahedral, the trichloro complex is tetrahedral or trigonal bipyramidal or both in equilibrium, but the fourth complex is clearly tetrahedral. These changes in the structure should influence the ligand exchange kinetics.

In the case of Al^{3+}, Ga^{3+}, and In^{3+} the mechanism of solvent exchange shows a trend to turn from a dissociatively into associatively activated process when the ionic radius increases.[19] Although the mechanism of solvent exchange is sometimes different from the mechanism of ligand exchange, in many cases similar trends have been observed. Kawai et al. studied the complex formation between Ga^{3+}, In^{3+}, and Tl^{3+} and semi-xylenol orange[14] and later between Tl^{3+} and 4-(2-pyridylazo)resorcinol,[15] by stopped-flow technique and found that the second-order rate

---

(1) Permanent address: Department of Physical Chemistry, Lajos Kossuth University, H-4010 Debrecen, Hungary.

(2) Lee, A. G. *The Chemistry of Thallium*; Elsevier: Amsterdam, 1971; pp 44–91, and references therein.

(3) Ahrland, S.; Grenthe, I.; Johansson, L.; Noren, B. *Acta Chem. Scand.* **1963**, *17*, 1567.

(4) Ahrland, S.; Johansson, L. *Acta Chem. Scand.* **1964**, *18*, 2125.

(5) Woods, M. J. M.; Gallagher, P. K.; Hugus, Z. Z.; King, E. L. *Inorg. Chem.* **1964**, *3*, 1313.

(6) Kul'ba, F. Y.; Mironov, V. E.; Mavrin, I. F. *Zh. Fiz. Khim.* **1965**, *39*, 2595.

(7) Glaser, J.; Biedermann, G. *Acta Chem. Scand.* **1986**, *A40*, 331.

(8) Glaser, J.; Henriksson, U. *J. Am. Chem. Soc.* **1981**, *103*, 6642.

(9) Davies, E. D.; Long, D. A. *J. Chem. Soc. A* **1968**, 2050.

(10) Biedermann, G.; Spiro, T. G. *Chem. Scr.* **1971**, *1*, 155.

(11) (a) Spiro, T. G. *Inorg. Chem.* **1965**, *4*, 731. (b) *Ibid.* **1967**, *6*, 569.

(12) Glaser, J.; Johansson, G. *Acta Chem. Scand.* **1982**, *A36*, 125.

(13) Glaser, J. *Acta Chem. Scand.* **1982**, *A36*, 451.

(14) Kawai, Y.; Takahashi, T.; Hayashi, K.; Imamura, T.; Nakayama, H.; Fujimoto, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1417.

(15) Funada, R.; Imamura, T.; Fujimoto, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1535.

(16) Lincoln, S. F.; Sandercock, A. C.; Stranks, D. R. *Aust. J. Chem.* **1975**, *28*, 1901.

(17) Henriksson, U.; Glaser, J. *Acta Chem. Scand.* **1985**, *A39*, 355.

(18) Wilkins, R. G. *The Study of Kinetics and Mechanism of Reactions in Transition Metal Complexes*; Allyn and Bacon: Boston, 1974.

(19) van Eldik, R. *Inorganic High Pressure Chemistry Kinetics and Mechanisms*; Elsevier: Amsterdam, 1986.

0002-7863/89/1511-3186\$01.50/0

constants for the $Tl(OH)^{2+}$ species are of the same order of magnitude for both ligands. This observation was explained assuming that the rate-determining step is dissociation of a water molecule from the coordination sphere of $Tl(OH)^{2+}$. For Tl^{3+}, the rate constants were, unfortunately, not possible to identify.

Lincoln et al.[16] studied chloride exchange between the free chloride and $GaCl_4^-$, $InCl_4(H_2O)_2^-$, and probably $TlCl_6^{3-}$, respectively, by measuring ^{35}Cl NMR relaxation time in solutions containing very high chloride excess, [HCl] = 7 and 11 M. For the $GaCl_4^-$ species associative mechanism was suggested while for $InCl_4(H_2O)_2^-$ dissociative activation seemed to be probable. In the case of $TlCl_6^{3-}$ only a lower limit for the pseudo-first-order rate constant was estimated. Recently, Henriksson and Glaser[17] observed separate ^{205}Tl NMR signals for Tl^{3+} and $TlCl^{2+}$ in acidic aqueous solution which shows that the chloride exchange between these two species is slow on a time scale defined by the difference between their chemical shifts. For higher complexes ($n \geq 2$) one signal was observed, but the line width was found to be controlled by chemical exchange. These observations allowed to determine lifetimes for the chloride and bromide exchange between the different Th(III)–halide complexes.

In the present paper we present kinetic results for the Tl(III)–chloride system in aqueous 3 M $HClO_4$ solution based on ^{205}Tl NMR line width measurements. The total metal ion concentration was varied between 5×10^{-4} and 5×10^{-2} M and the ligand/metal ratio between 0 and 7.

Experimental Section

Materials. About 1 M solution of $Tl(ClO_4)_3$ was obtained by anodic oxidation of $TlClO_4$ solution.[20a,b] Stock solutions containing 0.1 M total thallium were prepared at total chloride/total thallium ratio 0, 4, and 7. The total hydrogen ion concentration was 3 M, the ionic medium was $I = 3$ M $\{H^+,(ClO_4^- + Cl^-)\}$. The samples for measurements were prepared by mixing the different stock solutions and diluting with 3 M perchloric acid in order to obtain different total thallium concentrations.

Analysis. Tl(I) was determined by titration with 0.1 M solution of $KBrO_3$ using methyl orange as indicator. Total thallium content was obtained by reducing Tl(III) with SO_2, boiling off the SO_2 excess, and titrating with 0.1 M $KBrO_3$.[21] Chloride content was determined by the Volhard method after reducing Tl(III) to Tl(I) with SO_2, removing excess SO_2 by boiling, and cooling the solution. Prior to back-titration with KSCN, nitrobenzene was added in order to protect the precipitated AgCl.[22]

Acid concentration of Tl(III) solutions was determined by titration with NaOH after adding excess of solid NaCl to the analyzed solution. In this way, the concentrations of acid, Tl(I) and Tl(III) could be determined one after the other in the same sample.

NMR Measurements. ^{205}Tl NMR spectra have been recorded at 230.8 MHz and at a probe temperature of 25 ± 0.5 °C using a Bruker AM400 spectrometer. In order to obtain activation parameters some spectra have been recorded at different temperatures from 0 °C up to 60 °C. The NMR parameters were chosen so that approximately quantitative spectra could be obtained, typically: flip angle ~25° (15 μs), pulse repetition time ≈ 0.1 s, sweep width ~60000 Hz, number of scans = 5000–30000. The chemical shifts are reported in ppm toward higher frequency with respect to an aqueous solution of $TlClO_4$ extrapolated to infinite dilution. The accuracy of the measured line widths is about 10% and that of the chemical shifts about 0.1–1 ppm depending on the line width.

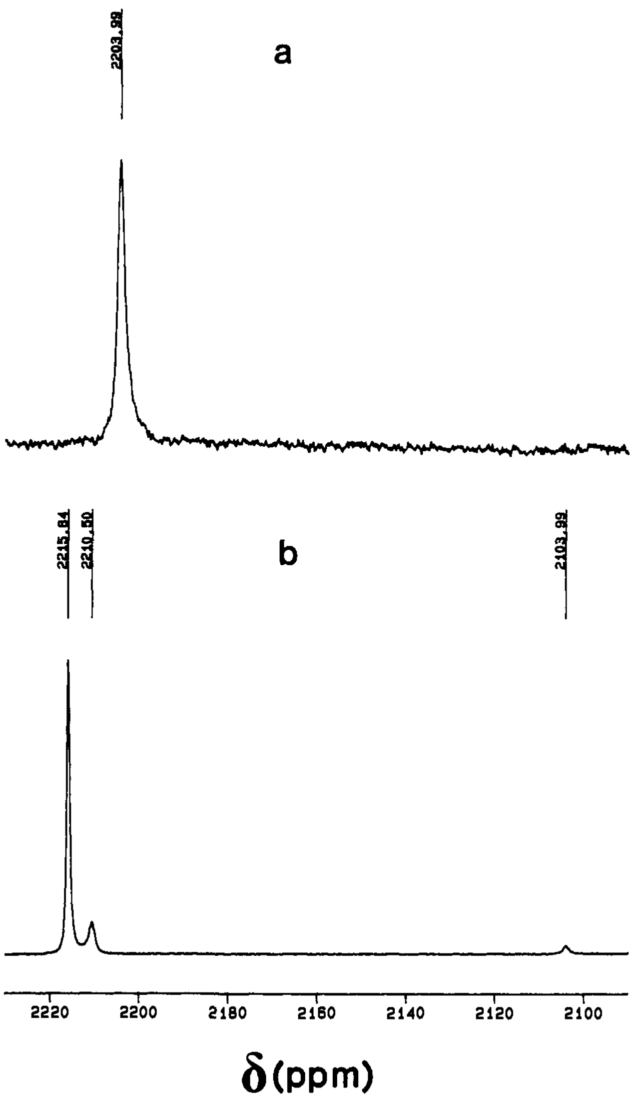


Figure 1. ^{205}Tl NMR spectra at $R = 1.12$ and $[Tl]_{tot} = 0.02$ M: (a) at 25 °C and (b) at 0 °C. The chemical shifts are reported in ppm toward higher frequency with respect to an aqueous solution of $TlClO_4$ extrapolated to infinite dilution.

Results and Calculations

Determination of Chemical Shifts. The individual chemical shifts for the aqua and first complexes were measured directly from the spectra. For the chemical shift of the second complex a value was reported to be very close to that of the first one.[8] Since fast exchange is expected between them,[17] the accurate determination of their chemical shifts is critical from kinetic point of view because 1 ppm error in the chemical shift can mean more than 20% error in the NMR time scale and consequently high error in the rate constants. At the total ligand/metal ratio $R = 1.12$ (throughout the text, R is used for the total chloride to the total thallium mole ratio) all the three above-mentioned species are present in measurable concentrations as can be calculated from the stability constants.[5] At 25 °C only one ^{205}Tl NMR signal is observed for 0.020 M solution (the intensity of aqua signal is very low and the peak is very broad because of chemical exchange), but at 0 °C three signals appear (cf. Figure 1). From this spectrum the chemical shift of the second complex was found to have 5.2 ppm lower value than that of the first one. The chemical shift difference between the first and the second complex was also measured at higher R values at 0 °C and was found to be constant and equal to 5.2 ppm until $R = 1.7$, indicating that this value is not affected by exchange processes. On the other hand, it was also found that the chemical shift difference between the zeroth and first complexes is constant when the temperature is varied from 0 °C up to 60 °C. On the basis of these facts we have accepted that the chemical shift difference between the second and the first complex is 5.2 ppm at 25 °C, i.e., the same value as found at 0 °C. For the third and fourth complexes the individual chemical shifts were calculated with the following equation:

$$^{i}\delta_{obsd} = \sum {}^{i}p_n \delta_n \qquad (1)$$

where $^{i}\delta_{obsd}$ is the experimental chemical shift for the experimental point i, $^{i}p_n$ is the molar fraction, and δ_n is the chemical shift of

---

(20) (a) Biedermann, G. *Arkiv Kemi* **1953**, *5*, 441. (b) Glaser, J. Thesis, The Royal Institute of Technology (KTH), Stockholm, Sweden, 1981. (c) Glaser, J. *Acta Chem. Scand.* **1979**, *A33*, 789. (d) Glaser, J. *Acta Chem. Scand.* **1980**, *A34*, 75. (e) Glaser, J. *Acta Chem. Scand.* **1980**, *A34*, 141. (f) Glaser, J.; Johansson, G. *Acta Chem. Scand.* **1981**, *A35*, 639.

(21) Noyes, A. A.; Hoard, J. L.; Pitzer, K. S. *J. Am. Chem. Soc.* **1935**, *57*, 1231.

(22) Kolthoff, I. M.; Sandell, E. B. *Textbook of Quantitative Inorganic Analysis*; Macmillan: New York, 1961; p 546.

Table I. ^{205}Tl NMR Chemical Shifts[a] and Nonexchange Line Widths for $TlCl_n^{3-n}$ Complexes in 3 M $HClO_4$, at 25 °C

n (in $TlCl_n^{3-n}$)	δ^c (ppm)	$\Delta\nu_{1/2}^0$ (this work)[b] (Hz)	δ (ref 8)[c]
0	2093 (±1)	25 (11)	2086 (±1)
1	2204 (±1)	48 (5)	2198 (±4)
2	2199 (±1)	~25	2201 (2)
3	2435 (4)	~45	2412 (5)
4	2648 (5)	~25	2645 (2)
5	2022 (±20)[d]		2022 (±20)[d]

[a] The chemical shifts are reported in ppm toward higher frequency with respect to an aqueous solution of $TlClO_4$ extrapolated to infinite dilution. Numbers in parentheses with ± are maximum errors of measurements, otherwise standard deviations obtained from least-squares calculations. [b] Contains magnetic field inhomogeneity. [c] In (3 M $HClO_4$ + 1 M $NaClO_4$), 27 °C. [d] Determined by measuring wide line ^{205}Tl NMR for powder samples.

the nth complex. The p_n values were calculated using the stability constant (β_n) values published by Woods et al. for the same ionic medium.[5] δ_n values were determined by least-squares method using the experimental chemical shifts in the range $1.8 < R < 7$. In this region the chemical exchange can be considered fast enough for eq 1 to be valid. The chemical shift values are given in Table I and compared to the values determined earlier.[8] From the tendency of the change of the chemical shift with ligand/metal ratio it has been found that the fifth complex also forms in the system when $R > 6$. Since there is no stability data for this species in three molar perchloric acid we estimated it from our measurements using the chemical shift value determined by Glaser and Henriksson for the solid $Na_2TlCl_5{\cdot}12H_2O$[8] and applying eq 1 for the calculation. The best fitting was obtained for log β_5 equal to 18.02, that is for log $K_5 = -0.3$.

Determination of Empirical Rate Equations. $0 < R < 1.0$. For chloride/metal ratios $0 < R < 1.0$ the exchange between Tl^{3+} and $TlCl^{2+}$ is slow on the actual time scale. Hence, measured line widths for each of the signals can be written as[23]

$$\Delta\nu_{1/2} = 1/(\pi T_2^{\text{exp}}) \tag{2}$$

where $\Delta\nu_{1/2}$ is the measured line width and $1/T_2^{\text{exp}}$ is a sum of three terms

$$1/T_2^{\text{exp}} = 1/T_2 + 1/T_2^{\text{inh}} + 1/\tau_{\text{ex}} \tag{3}$$

containing the transverse relaxation time, the inhomogeneity of the magnetic field, and the chemical exchange contribution. In eq 3 only $1/\tau_{\text{ex}}$ depends on the concentration of different species present in solution. Thus, the measured line widths of the signals of Tl^{3+} and $TlCl^{2+}$ contain pseudo-first-order rate constants for all reactions in which these species take part. At first approximation these reactions can be of zero or of first order for other species present, that is

$$\Delta\nu_{1/2} = \Delta\nu_{1/2}^0(i) + c_i + \sum_{j=0}^{n} c'_{ij}[\text{Cl}^-] + \sum_{j=0}^{n} c_{ij}p_j \tag{4}$$

where $\Delta\nu_{1/2}^0(i) = 1/T_2 + 1/T_2^{\text{inh}}$ (nonexchange line width for the ith complex), p_j is the molar fraction of the jth complex, c denotes constants which are proportional to the rate constants, index i means that the equation belongs to the signal of the ith complex, index j indicates the complex species to which the rate is proportional, and c'_{ij} denotes rate constants of the reactions for which the rates are proportional to the ith complex and the free ligand concentration yielding the jth complex. Equation 4 can be applied to obtain the constants c by least-squares analysis in the case of experiments when the total thallium concentration is constant but R is varied. Equation 4 can also be modified for least-squares analysis of experiments when the ligand/metal ratio is constant but the total thallium concentration is varied. Since the complexes formed in this system are very strong, at constant R the free chloride concentration and the relative populations of different coordinated species are constant independent of the total thallium concentration. Introducing these conditions into eq 4

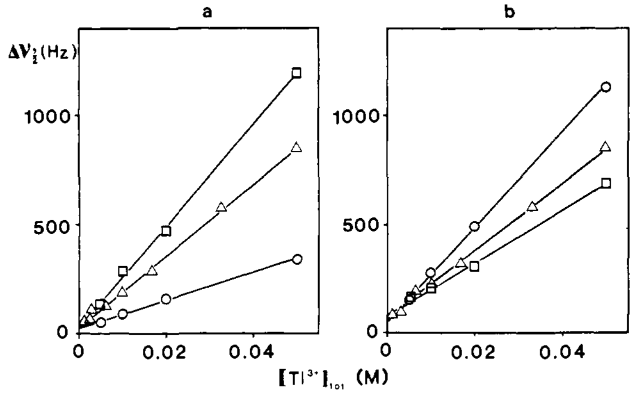


Figure 2. Dependence of line width of Tl^{3+} (a) and $TlCl^{2+}$ (b) on $[\text{Tl}]_{\text{tot}}$ at $R = 0.24$ (○), $R = 0.5$ (△), $R = 0.7$ (□). $T = 25$ °C.

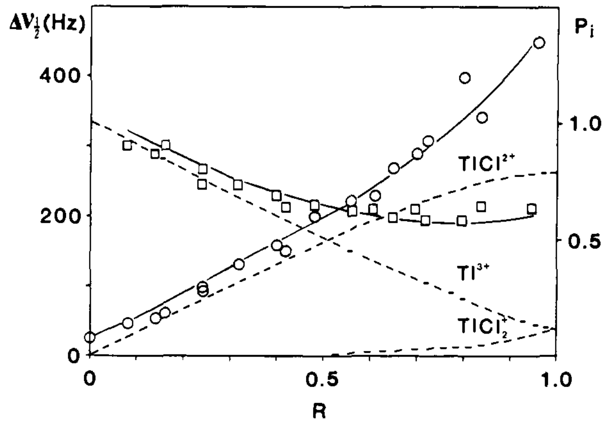


Figure 3. Dependence of line widths (○ of Tl^{3+} and □ of $TlCl^{2+}$) and molar fractions (dashed line) of complexes on total ligand/metal ratio at $[\text{Tl}]_{\text{tot}} = 0.01$ M. Full line represents line widths calculated by using the rate constants in Table II. $T = 25$ °C.

$$\Delta\nu_{1/2} = I_R + S_R[\text{Tl}]_{\text{tot}} \tag{5}$$

where $I_R = \Delta\nu_{1/2}^0(i) + c_i + \sum_{j=0}^{n} c'_{ij}[\text{Cl}^-]$, $S_R = \sum_{j=0}^{n} c_{ij}p_j$, and the index R indicates the total ligand/metal ratio.

The dependence of line widths on the total thallium concentration at different R values has been found to be linear (cf. Figure 2). The intercepts for line widths of the aqua complex do not depend on R which means that no free chloride contributed reaction occurs in the exchange process of the aqua complex, that is $c'_{01} = 0$. The mean value of the intercepts is 25 ± 11 which is very close to the measured line width for the aqua complex in absence of chloride ions (22 ± 3 Hz). Consequently, it can be assumed that the nonexchange line width for the aqua complex, i.e., $\Delta\nu_{1/2}^0(0) = 25$ Hz. For the $TlCl^{2+}$ signal the intercepts increase slightly with increasing R, but the change is not significant enough in order to calculate c'_{12}. The intercept for $TlCl^{2+}$ at $R = 0.24$ is accepted as $\Delta\nu_{1/2}^0(1) = 48 \pm 5$ Hz for the monochloro complex. From Figure 2 it can also be seen that the slopes strongly depend on the total ligand/metal ratio indicating the presence of exchange reactions with contribution of complexed species.

In order to obtain the constants c_{ij} the line width versus R data have been considered at constant $[\text{Tl}]_{\text{tot}}$ (cf. Figure 3). From the line widths of the Tl^{3+} signal, using the nonexchange line width determined above from the total concentration dependences, the values of parameters $c_{01} = 314 \pm 20$ and $c_{02} = 2043 \pm 330$ have been found by the least-squares method on the basis of eq 4. For the line widths of the $TlCl^{2+}$ signal two sets of parameters have given a fitting with approximately the same goodness. In the first set $c_{01} = 258 \pm 8$, $c_{11} = 68 \pm 16$, and $c_{12} = 917 \pm 230$ are supposed to describe the system; in the second set $c_{01} = 254 \pm 9$, $c_{11} = 49 \pm 18$, but instead of c_{12} (which corresponds to reaction 23, vide

---

(23) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982; pp 1–29.

Table II. Rate Constants for Different Exchange Reactions at 25 °C

	rate constants ($M^{-1}\ s^{-1}$)	used in the model ($M^{-1}\ s^{-1}$)
k_{01}	$(4.9 \pm 0.4) \times 10^4$,[a] $(4.1 \pm 0.3) \times 10^4$[b]	4.5×10^4
k_{02}	$(6.4 \pm 1.1) \times 10^5$	6.4×10^5
k_{11}	$(9.4 \pm 2.7) \times 10^3$	
k_{12}	$(5.1 \pm 0.4) \times 10^4$,[c] $(5.3 \pm 0.3) \times 10^4$[d]	5.2×10^4
k_{23}	$(2.7 \pm 0.7) \times 10^7$	2.7×10^7
k'_{12}	$(3.3 \pm 0.4) \times 10^8$,[c] $(3.1 \pm 0.5) \times 10^8$[d]	3.2×10^8
k'_{23}	$(1.3 \pm 0.2) \times 10^9$	1.3×10^9
k'_{34}	$(4.7 \pm 1.3) \times 10^8$	4.7×10^8

[a] From the peak of the aqua complex. [b] From the peak of the first complex. [c] From $R = 1.3$. [d] From $R = 1.5$.

infra) we obtain $c'_{12} = (2.4 \pm 0.5) \times 10^8$ (corresponds to reaction 24). Since the constants indexed 12 belong to an exchange between $TlCl^{2+}$ and $TlCl_2^+$ and are only determined by some experimental points at $R > 0.7$, it is difficult to choose between the two sets.

For the exchange between the aqua and first complexes the following reactions can be proposed on the basis of the calculations above:

$$Tl^{3+} + {}^*TlCl^{2+} \overset{k_{01}}{\rightleftharpoons} {}^*Tl^{3+} + TlCl^{2+} \tag{6}$$

This is a reaction without any net chemical change but with change in the magnetic environment of the thallium nuclei.

This work deals with a chemical system in equilibrium. Hence, the concentrations are not changing in time, and all terms of the type $d[TlCl_n^{3-n}]/dt$ are equal to zero. However, in order to calculate the connections between the dynamics in the investigated solutions and the NMR spectra we will use usual rate equations of the type $d[TlCl_n^{3-n}]/dt = k[A][B]...+...$ etc. but with a different meaning. The left side of such an equation will represent the rate of the microscopic change of the concentrations of the different species. Thus, the rate corresponding to reaction 6 is

$$d[Tl^{3+}]/dt = 2k_{01}[Tl^{3+}][TlCl^{2+}] \tag{7}$$

because one aqua complex forms in the forward and one in the back reaction. The rate constant k_{01} can be calculated from c_{01} by using eq 2 and 4 as $k_{01} = c_{01}\pi/(2[Tl]_{tot})$. From c_{02} the following exchange path can be proposed

$$Tl^{3+} + TlCl_2^+ \underset{k_{11}}{\overset{k_{02}}{\rightleftharpoons}} 2TlCl^{2+} \tag{8}$$

which leads to net chemical change. The rate equation is

$$-d[Tl^{3+}]/dt = k_{02}[Tl^{3+}][TlCl_2^+] \tag{9}$$

and the value of $k_{02} = c_{02}\pi/[Tl]_{tot}$. The rate constants are given in Table II.

From line widths of $TlCl^{2+}$ the constant c_{01} belongs to reaction 6, and from Table II it can be seen that the calculated rate constant agrees with the previously calculated value of k_{01}. Considering the reaction 8, c_{11} can be proportional to the rate constant of the reverse path. The rate equation is

$$d[Tl^{3+}]/dt = -\tfrac{1}{2} d[TlCl^{2+}]/dt = k_{11}[TlCl^{2+}]^2 \tag{10}$$

that is

$$d[TlCl^{2+}]/dt = 2k_{11}[TlCl^{2+}]^2 \tag{11}$$

and $k_{11} = c_{11}\pi/(2[Tl]_{tot})$ where $c_{11} = 60$ as an average value of the two sets. Certainly, there should be a connection between k_{02} and k_{11} determined by equilibrium constants

$$k_{02}/k_{11} = [TlCl^{2+}]^2/[Tl^{3+}][TlCl^{2+}] = \beta_1^2/\beta_2 \tag{12}$$

From our experimental rate constants $k_{02}/k_{11} = 66$, while from the potentiometric equilibrium data[5] $\beta_1^2/\beta_2 = 53$ which is a good agreement taking into account that the standard deviations of the determined rate constants are ~15% for k_{02} and ~25% for k_{11}. Finally, the slopes of line width for the zeroth and first chloride complexes, respectively, vs $[Tl]_{tot}$ can be calculated from the rate constants at different ratios with eq 5. At $R = 0.24$, $S_{R^0}{}^{calcd} = 7200$ (experimental $= 6462 \pm 250$) and $S_{R^1}{}^{calcd} = 23\,100$ ($22\,060 \pm 184$); at $R = 0.5$, $S_{R^0}{}^{calcd} = 15\,200$ ($16\,450 \pm 300$) and $S_{R^1}{}^{calcd} = 17\,800$ ($16\,630 \pm 176$); at $R = 0.7$, $S_{R^0}{}^{calcd} = 24\,800$ ($23\,410 \pm 852$) and $S_{R^1}{}^{calcd} = 12\,900$ ($12\,407 \pm 420$). Thus, the agreement with the measured values seems to be excellent.

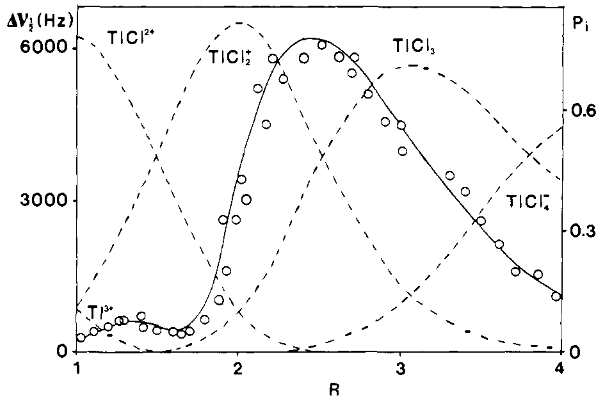


Figure 4. Dependence of line widths (○) and molar fractions (dashed line) of $TlCl_n^{3-n}$ complexes on total ligand/metal ratio at $[Tl]_{tot} = 0.02$ M. Full line represents line widths calculated by using the rate constants in Table II. $T = 25$ °C.

$R > 1$. When the total ligand/metal ratio is higher than 1 (at 25 °C) always one signal appears in the spectra indicating occurrence of fast exchange on the time scale determined by the chemical shifts of the different thallium complexes. The dependence of line widths and the molar fractions of the complexes on R is shown in Figure 4.

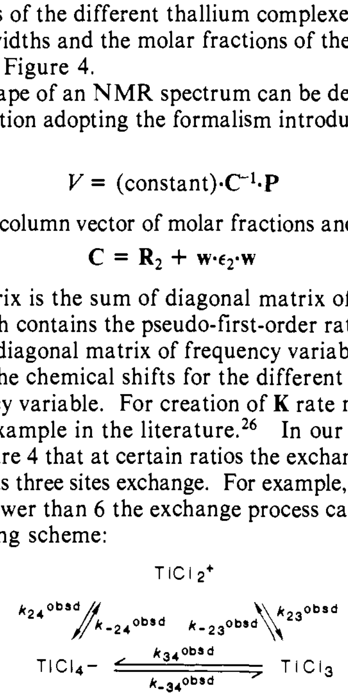
The bandshape of an NMR spectrum can be described by the following equation adopting the formalism introduced by Reeves and Shaw[25]

$$V = (\text{constant})\cdot\mathbf{C}^{-1}\cdot\mathbf{P} \tag{13}$$

where **P** is the column vector of molar fractions and **C** is a matrix

$$\mathbf{C} = \mathbf{R}_2 + \mathbf{w}\cdot\epsilon_2\cdot\mathbf{w} \tag{14}$$

where $\mathbf{R}_2$ matrix is the sum of diagonal matrix of $\Delta\nu_{1/2}{}^0(i)$ and **K** matrix which contains the pseudo-first-order rate constants, $\epsilon_2 = \mathbf{R}_2^{-1}$, **w** is a diagonal matrix of frequency variable $\mathbf{w}_j = x - \Omega_j$, where Ω_j are the chemical shifts for the different species, and x is the frequency variable. For creation of **K** rate matrix there is an excellent example in the literature.[26] In our case it can be seen from Figure 4 that at certain ratios the exchange system can be considered as three sites exchange. For example, at ratio higher than 2.5 but lower than 6 the exchange process can be described by the following scheme:



For this scheme the rate equation is

$$d[TlCl_j]/dt = \mathbf{K}[TlCl_j] \tag{15}$$

where the left hand side is the column vector of exchange rate, $[TlCl_j]$ is the column vector of concentrations, and the form of **K** rate matrix is the following:

$$\mathbf{K} = \begin{vmatrix} -(k_{23}{}^{obsd} + k_{-24}{}^{obsd}) & k_{-23}{}^{obsd} & k_{24}{}^{obsd} \\ k_{23}{}^{obsd} & -(k_{34}{}^{obsd} + k_{-23}{}^{obsd}) & k_{-34}{}^{obsd} \\ k_{-24}{}^{obsd} & k_{34}{}^{obsd} & -(k_{24}{}^{obsd} + k_{-34}{}^{obsd}) \end{vmatrix}$$

with the usual connection between the rate constants $p_i k_{ij} = p_j k_{-ij}$. From eq 13 and 14 it follows that the line width in this case is

---

(24) Piette, L. H.; Anderson, W. A. *J. Chem. Phys.* **1959**, *30*, 899.
(25) Reeves, L. W.; Shaw, K. N. *Can. J. Chem.* **1970**, *48*, 3641.
(26) Chan, S. O.; Reeves, L. W. *J. Am. Chem. Soc.* **1973**, *95*, 670.

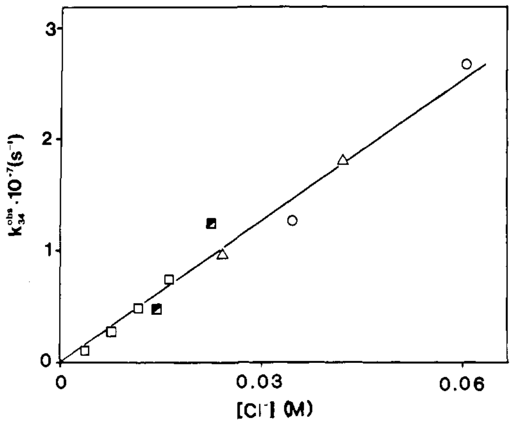


Figure 5. Dependence of the pseudo-first-order rate constant k_{34}^{obsd} (cf. eq 17) on free chloride concentration at $[Tl]_{tot}$ = 0.005 M (■), $[Tl]_{tot}$ = 0.01 M (□), $[Tl]_{tot}$ = 0.02 M (△), $[Tl]_{tot}$ = 0.03 M (○). T = 25 °C.

determined by three pseudo-first-order rate constants, three chemical shifts, and three values of $\Delta\nu_{1/2}^0$. Actually, in our system no direct exchange of the type

$$TlCl_2^+ + {}^*TlCl_4^- \overset{k_{23}}{\rightleftharpoons} TlCl_2^+ + {}^*TlCl_4^-$$

has been found to occur. The chemical shifts values are known. The $\Delta\nu_{1/2}^0$ values for the different complexes can be estimated in the following way. At 0.05 and 0.03 M total thallium concentration at $R = 7$ it was found that the line width is 25 Hz independently of the composition; that is, the exchange is very fast. Since at these circumstances 90% of the thallium in the solution is present in the form of $TlCl_4^-$, we can assume that for the species $TlCl_4^-$ $\Delta\nu_{1/2}^0(4) \sim 25$ Hz. In very concentrated thallium solutions at $R = 2$ where the relative population of the second complex is about 80% the line width was found to be 25 Hz. Similarly, at $R = 3$ the third complex constitutes 70% of the total thallium, and the line width of the signal at high $[Tl]_{tot}$ values is 40 Hz. From these experiments we accepted $\Delta\nu_{1/2}^0(2) \sim 25$ Hz for $TlCl_2^+$ and $\Delta\nu_{1/2}^0(3) \sim 40$ Hz for $TlCl_3$. Since the experimental line widths are usually higher than 400 Hz, the error introduced by these estimations is within the uncertainty of the measured line widths.

At R values higher than 4 it was assumed that only the exchange between the third and the fourth complex affected the line widths. Consequently, it can be considered as two sites exchange. All experimental spectra have been successfully fitted as Lorentzian curve. For this case Piette and Anderson deduced an approximate formula to obtain pseudo-first-order rate constants directly from the experimental line widths[24]

$$k_{34}^{obsd} = 4\pi p_3 p_4^2(\delta\nu)^2/\left[\Delta\nu_{1/2} - p_3\Delta\nu_{1/2}^0(3) - p_4\Delta\nu_{1/2}^0(4)\right] \tag{16}$$

where $\delta\nu$ is the difference between the individual chemical shifts of third and fourth complex in Hz. Assuming first-order dependence of k_{34}^{obsd} (calculated by eq 16) on the free chloride concentration (k'_{34}) and on the concentration of the $TlCl_4^-$ species (k_{34}) the following equation can be deduced to express the change of k_{34} as a function of the free chloride and $[Tl^{3+}]_{tot}$

$$k_{34}^{obsd} = k'_{34}[Cl^-] + k_{34}K_4[Tl^{3+}]_{tot}[Cl^-](1 + K_4[Cl^-])^{-1} \tag{17}$$

where $K_4 = \beta_4/\beta_3$ and $[Tl^{3+}]_{tot} = [TlCl_3] + [TlCl_4^-]$. However, the plot of k_{34}^{obsd} versus free chloride shows a linear dependence with zero intercept independent of $[Tl^{3+}]_{tot}$ (cf. Figure 5). Hence, there is no significant contribution of exchange with direct collision of $TlCl_3$ and $TlCl_4^-$, and from the slope of the straight line in Figure 5, k'_{34} can be calculated.

Thus, the dominant exchange path between $TlCl_3$ and $TlCl_4^-$ is

$$TlCl_3 + Cl^- \underset{k'_{-34}}{\overset{k'_{34}}{\rightleftharpoons}} TlCl_4^- \tag{18}$$

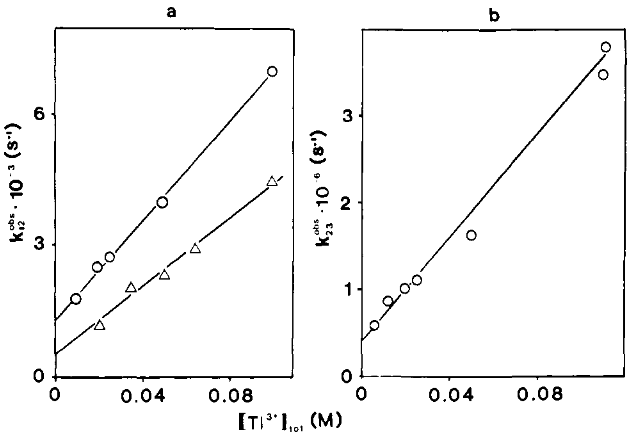


Figure 6. Dependence of k_{12}^{obsd} (a, cf. eq 22) and k_{23}^{obsd} (b, cf. eq 19) on $[Tl]_{tot}$ at R = 1.3 (a,△), R = 1.5 (a,○), and R = 2.52 (b). T = 25 °C.

Supposing maximum 10% contribution to the line width of the reaction path with direct collision of $TlCl_3$ and $TlCl_4^-$ one can find an upper limit for $k_{34} < 3 \times 10^7$ M^{-1} s^{-1}.

In order to obtain the rate constants for the exchange between $TlCl_2^+$ and $TlCl_3$ the dependence of the line width on the total thallium concentration has been considered at R = 2.52 using eq 13–15 in the following way. In the **K** rate matrix, $k'_{34}[Cl^-]$ has been substituted for k_{34}^{obsd}, and k_{23}^{obsd} values have been varied until the experimentally measured line width was obtained. The k_{23}^{obsd} values found show linear dependence on the total thallium concentration as can be seen in Figure 6. The following equation is suggested to describe this function:

$$k_{23}^{obsd} = 2k_{23}p_3[Tl]_{tot} + k'_{23}[Cl^-] \tag{19}$$

that is, the following exchange paths can be said to be dominant:

$$TlCl_2^+ + {}^*TlCl_3 \overset{k_{23}}{\rightleftharpoons} TlCl_3 + {}^*TlCl_2^+ \tag{20}$$

and

$$TlCl_2^+ + Cl^- \underset{k'_{-23}}{\overset{k'_{23}}{\rightleftharpoons}} TlCl_3 \tag{21}$$

Since the complex distribution as well as the free ligand concentration in the system change less than 8% when the total thallium concentration changes from 0.012 to 0.05 M, the free chloride concentration and the molar fraction of the third complex can be considered approximately constant. Accepting this assumption k'_{23} has been calculated from the intercept and k_{23} from the slope of the straight line in Figure 6 as (1.3 ± 0.2) × 10^9 M^{-1} s^{-1} and (2.7 ± 0.7) × 10^7 M^{-1} s^{-1}, respectively. By using these values of the rate constants the dependence of the line width on the total ligand/metal ratio at 0.02 M total thallium concentration has been calculated by eq 5 for $2.5 \le R \le 4$. The agreement between the calculated and experimental line widths is rather good, as can be seen in Figure 4.

For $1 < R < 2.5$ four site exchange, involving complexes from the aqua up to the third complex, has been considered when eq 5 was used in order to find the rate constants for the exchange between $TlCl^{2+}$ and $TlCl_2^+$. At first the dependence of line width on $[Tl]_{tot}$ has been described at R = 1.32 and 1.52 in the same way as at R = 2.52 by using the rate constants which have already been determined. At both ratios linear dependence was found for k_{12}^{obsd} vs $[Tl]_{tot}$ as it is shown in Figure 6, that is

$$k_{12}^{obsd} = 2k_{12}p_2[Tl]_{tot} + k'_{12}[Cl^-] \tag{22}$$

Hence, the following reaction paths are proposed to be dominant:

$$TlCl^{2+} + {}^*TlCl_2^+ \overset{k_{12}}{\rightleftharpoons} TlCl_2^+ + {}^*TlCl^{2+} \tag{23}$$

and

$$TlCl^{2+} + Cl^- \underset{k'_{-12}}{\overset{k'_{12}}{\rightleftharpoons}} TlCl_2^+ \tag{24}$$

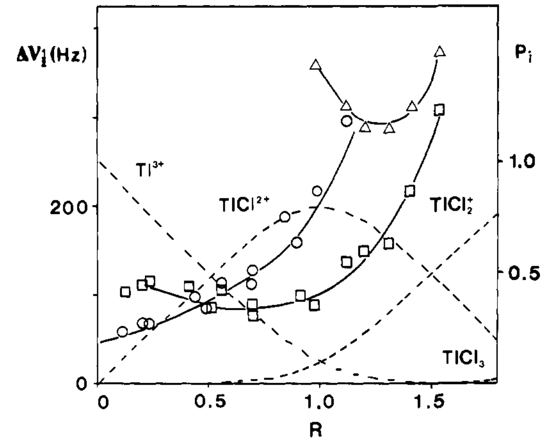


Figure 7. Dependence of the line width of Tl^{3+} (○), $TlCl^{2+}$ (□), and $TlCl_2^+$ (△) signals and molar fractions of complexes (dashed line) on the total ligand/metal ratio at $[Tl]_{tot} = 0.02$ M at 0 °C. The full line represents line widths calculated by using the rate constants in Table III.

Table III. Rate Constants for Different Exchange Reactions at 0 °C

	values ($M^{-1}\ s^{-1}$)		values ($M^{-1}\ s^{-1}$)
k_{01}	$(7.8 \pm 2.3) \times 10^3$	k_{23}	$(3.3 \pm 0.8) \times 10^6$
k_{02}	$(1.7 \pm 0.2) \times 10^5$	k'_{12}	$(2.4 \pm 1.2) \times 10^8$
k_{12}	$(1.5 \pm 0.6) \times 10^4$		

The rate constants are $k_{12} = (5.3 \pm 0.3) \times 10^4$ and $(5.1 \pm 0.4) \times 10^4$ $M^{-1}\ s^{-1}$ and $k'_{12} = (3.1 \pm 0.5) \times 10^8$ and $(3.3 \pm 0.4) \times 10^8$ $M^{-1}\ s^{-1}$ for $R = 1.32$ and $R = 1.52$, respectively. By using average values of the rate constants, dependence of line width on R at $[Tl]_{tot} = 0.02$ M has been described as it is shown in Figure 4. Summarizing, Figures 3, 4, and 5 show that our model reflects the principal character of the system with the rate constants collected in Table II.

Measurements at 0 °C. From Figure 1 it can be seen that the exchange reactions between Tl^{3+}, $TlCl^{2+}$, and $TlCl_2^+$ at 0 °C and at $[Tl]_{tot} = 0.02$ M are so slow that the signals of all species present can be observed separately (up to the ratio 1.7). It allows us to calculate the rate constants directly from the line width data by eq 2–4.

In Figure 7, dependence of the line width and the population of the different complexes is shown as a function of R. In order to calculate the distribution curves at 0 °C the enthalpies of formation for the different species have been used.[5] At $R = 1.3$ the total concentration dependence of the line width has also been measured (cf. Figure 8). Analyzing the dependence of the line width of the aqua complex on R by least-squares method, the values of $\Delta\nu_{1/2}{}^0(0) = 50 \pm 18$ Hz, k_{01} and k_{02} have been determined (cf. Table III).

Since slow exchange takes place in the measured range of R the linewidth of $TlCl^{2+}$ is expectably determined by five parameters, i.e., $\Delta\nu_{1/2}{}^0(1)$, k_{01}, k_{11}, k_{12}, and k'_{12} using the same letters as at 25 °C. Independent parameter fitting for all five parameters have been unsuccessful because of the small number and the high relative error of the experimental data. However, there is a possibility to determine k_{12} independently from the total concentration dependence at R = 1.3. From eq 5 the slopes of the straight lines (cf. Figure 8) are

$$S_{R^1} = c_{01}p_0 + c_{11}p_1 + c_{12}p_2 \qquad (25)$$

and

$$S_{R^2} = c_{02}p_{02} + c_{12}p_1 + c_{23}p_3 \qquad (26)$$

From eq 25 using c_{01} and $c_{11} = 2c_{02}\beta_2/\beta_1{}^2$ values determined above, c_{12} and consequently k_{12} can be calculated. The numeric value of k_{12} is 1.4×10^4 $M^{-1}\ s^{-1}$. Assuming that at $R = 1.3$ the term $c_{23}p_3$ is negligible, from eq 26 k_{12} has been found to be 1.6×10^4 $M^{-1}\ s^{-1}$ in good agreement with the previous value. Now, using k_{01}, k_{11}, and k_{12} the values $\Delta\nu_{1/2}{}^0(1) = 27 \pm 6$ Hz and k'_{12} have been determined by least-squares analysis on the basis of eq 4. The rate constants are given in Table III.

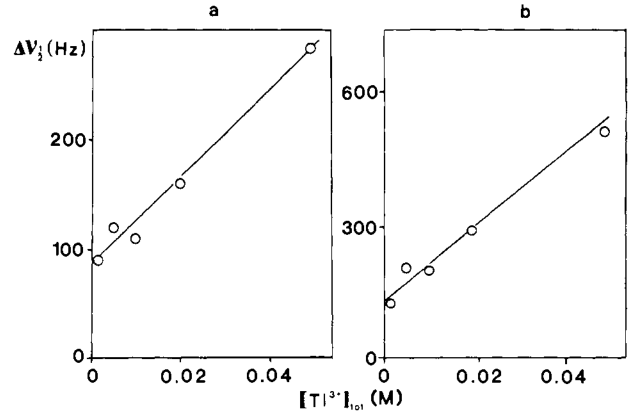


Figure 8. Dependence of the line widths of $TlCl^{2+}$ (a) and $TlCl_2^+$ (b) signals on $[Tl]_{tot}$ at $R = 1.3$ at 0 °C.

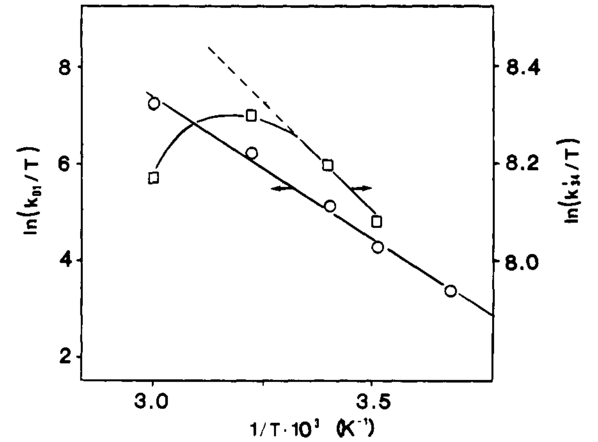


Figure 9. Arrhenius plot of the rate constant dependence on the temperature: (○) for k_{01}; (□) for k'_{34}.

There is a possibility to check the $\Delta\nu_{1/2}{}^0(1)$ and k'_{12} values because from eq 5 the intercept of total concentration dependence of the line width of $TlCl^{2+}$ should be equal to $I_{R^1} = (\Delta\nu_{1/2}{}^0(1) + k'_{12}\ [Cl^-]/\pi)$. The calculated value of I_{R^1} is 97 Hz; the experimentally found value is 84 ± 17 Hz.

The line width of $TlCl_2^+$ versus R data are expectably determined by five parameters $(\Delta\nu_{1/2}{}^0(2) + k'_{-12})$, k_{02}, k_{12}, k_{23}, and k'_{23}, of which only the first and the last two are unknown. The least-squares parameter fitting has shown that the dependence of the line width on R (for $R \leq 1.7$) can be approximated by assumption of k_{23} rather than k'_{23} giving the numerical values $(\Delta\nu_{1/2}{}^0(2) + k'_{-12}/\pi) = 89 \pm 15$ Hz and $k_{23} = (3.3 \pm 0.8) \times 10^6$ $M^{-1}\ s^{-1}$.

Plotting the line width of $TlCl_2^+$ vs $[Tl]_{tot}$ at $R = 1.3$, a straight line is obtained (cf. eq 5 and Figure 8b), and the intercept can be deduced as $K_{R^2} = (\Delta\nu_{1/2}{}^0(2) + k'_{-12}/\pi)$. The numeric value of this parameter has been found to be 117 ± 19 Hz, compared to the value obtained from R dependence (89 ± 15 Hz); it seems to be a reasonable agreement.

It is also possible to calculate the value of k'_{-12} as $k'_{-12} = k'_{12}\beta_1/\beta_2 = 440 \pm 220$ s^{-1} considering the β values without error. It can be seen that dividing this value by π one can obtain 140 Hz which is larger than the sum $(\Delta\nu_{1/2}{}^0(2) + k'_{-12}/\pi)$; that is negative value would be obtained for $\Delta\nu_{1/2}{}^0(2)$. The probable reason for this irresonable result is the high uncertainty of k'_{12} determined from R dependence.

The Temperature Dependence. At the ratios 0.4 and 6, respectively, we have only one dominant exchange path. Therefore, studying the temperature dependence there is a possibility to calculate activation parameters and by this way to obtain more knowledge about the mechanisms. In Figure 9, the temperature dependence of k_{01} is shown in an Arrhenius plot. The activation

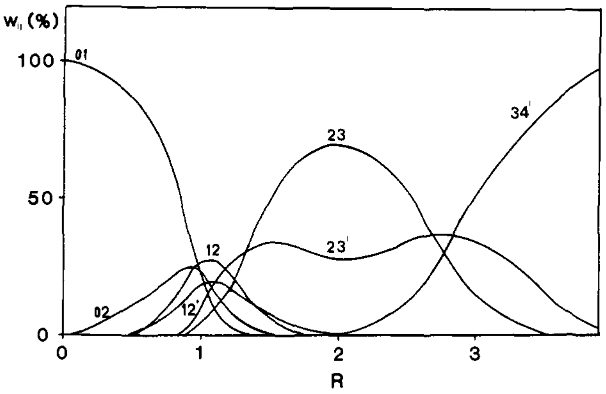


Figure 10. Percentage contribution of different parallel exchange paths (w_{ij}, numbered by the indices of rate constants) to the total exchange rate $w_{ij} = \sum_{i,j}(2k_{ij}[\mathrm{TlCl}_i][\mathrm{TlCl}_j] + k'_{ij}[\mathrm{TlCl}_i][\mathrm{Cl}^-])$. T = 25 °C.

enthalpy is 49 ± 2 kJ mol^{-1}, and the activation entropy is +12 ± 0.3 J mol^{-1} K^{-1}.

At ratio 6, it can be seen from Figure 9 that the line width becomes relaxation-controlled when the temperature is increased above 40 °C. Approximate activation parameters for the reaction represented by k'_{34} are $\Delta H^* \simeq 6.6$ kJ mol^{-1} and $\Delta S^* \simeq -107$ J mol^{-1}.

Furthermore, there is a possibility to obtain approximate activation parameters for the remaining reactions at 25 °C and 0 °C. These values are certainly very rough but may be of some (though limited) value for discussion of the mechanism(s) (see below). For the reaction paths characterized by k_{02}, $\Delta H^* \sim 32$ kJ mol^{-1} and $\Delta S^* \sim -27$ J K^{-1}; k_{12}, $\Delta H^* \sim 33$ kJ mol^{-1} and $\Delta S^* \sim -45$ J K^{-1}; k'_{12}, $\Delta H^* \sim 7.6$ kJ mol^{-1} and $\Delta S^* \sim -56$ J K^{-1}; k_{23}, $\Delta H^* \sim 51.2$ kJ mol^{-1} and $\Delta S^* \sim 69$ J K^{-1}.

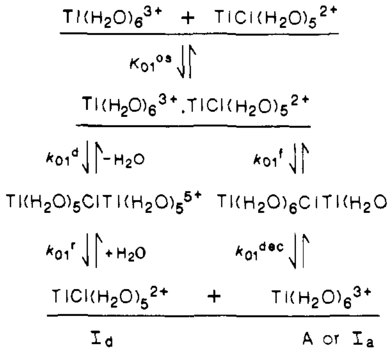
Discussion

By the above interpretation of the experimental results seven reaction paths are suggested to be dominant in the Tl^{3+}–Cl^- system depending on the concentrations of the components (cf. Figure 10). The reaction paths denoted k_{mn} (cf. reactions 6, 20, and 23) are the type of chemical exchange reactions in which no net chemical change occurs. This reaction type can be called self-exchange using the nomenclature introduced for a similar type of electron-transfer reactions.[19] Reaction 8 also represents an exchange between complex species, but the microscopic process includes net chemical change. Usually, this type of ligand exchange reactions cannot be observed because of their low rate constants compared to the anation reactions such as reactions 18, 21, and 24 (Table II). In the present case the high stability of the coordinated species results in a very small concentration of the free ligand at lower ligand/metal ratios and allows the self-exchange reactions to become dominant. Moreover, anation reaction of Tl^{3+} has not been observed.

In Figure 10, relative participation of the different parallel exchange paths *in the total exchange rate* is plotted as a function of the total ligand/metal ratio. It can be seen that at 0.7 ≤ R ≤ 1.5 six parallel paths exist with comparable rate. Certainly, the contribution of these exchange paths *to the values of the line widths* is different because beside the rate constants the chemical shift differences between the complexes which are present affect the line width governed by fast-exchange regime.[23]

Model calculations have shown that the line width values at 0.7 ≤ R ≤ 1.5 are determined by exchange of all species except TlCl_4^- and are very sensitive for the difference in the chemical shifts between TlCl^{2+} and TlCl_2^+, which are the dominant species at these ratios. For example, when the value of the chemical shift of TlCl_2^+ is lowered by 1 ppm, k_{12} and k'_{12} can be found to be higher by 50% and 20%, respectively. Since the chemical shift of TlCl_2^+ has been extrapolated from 0 °C, 0.3 ppm uncertainty is a reasonable assumption so that the accuracy of rate constants for the exchange between TlCl^{2+} and TlCl_2^+ is lower than the calculated standard deviations show. This fact is taken into account in the further discussion.

Scheme I



Second-order rate equations have been found for the self-exchange reactions. Consequently, both species should take part in the transition state(s). Formation of transition-state species can be imagined either by the decreasing or, more probably, by the increasing of the coordination number of the central thallium atom, because the ionic radius of $\mathrm{Tl}^{3+} \simeq 95$ pm and for the smaller In^{3+} ion (80 pm) transition state for water exchange reaction is obtained by the increasing of the coordination number (according to ref 19). On the other hand, the size of the coming ligand can also determine the mechanism. The following scheme shows these two possibilities for the reaction between the aqua and the monochloro complexes.

In Scheme I and throughout the discussion thallium(III) chloride complexes are assumed to coordinate water molecules according to the results obtained earlier by means of X-ray diffraction on solution,[12,13] on crystals,[20b–f] IR Raman,[9,11] and NMR data,[8] i.e., $\mathrm{Tl(H_2O)_6^{3+}}$, $\mathrm{TlCl(H_2O)_5^{2+}}$, $\mathrm{TlCl_2(H_2O)_4^+}$, $\mathrm{TlCl_3(H_2O)}$ or $\mathrm{TlCl_3(H_2O)_2}$, and $\mathrm{TlCl_4^-}$. The coordinated water molecules are always written in the formulas when they play an important role in the actual considerations, otherwise they are omitted for the sake of simplicity.

The left hand side reactions in Scheme I are analogous to a dissociatively activated ligand exchange mechanism, while the right hand side to an associatively activated one; but there are important differences. Since our rate equations are first order for both species which take part in the exchange reaction, the limiting dissociative mechanism (D) can be closed out. The interchange mechanisms, according to the Eigen–Wilkins mechanism,[27] proceed in two steps: the fast formation of an outer-sphere complex, described by an equilibrium constant K_{os}, followed by the rate-determining outer-sphere to inner-sphere interchange step, characterized by the rate constant k^{rds}.

In the case of $\mathrm{I_d}$ mechanism of simple ligand exchange the dissociation of the leaving ligand is thought as the rate-determining step (k_{01}^{d} in Scheme I). But in the present type of self-exchange the rearrangement and the decomposition of the intermediate (k_{01}^{r} in Scheme I) can also be imagined as the rate-determining step. In spite of this special property of self-exchange we shall use the symbol of dissociative interchange $\mathrm{I_d}$, for this mechanism.

In the case of the associative part of Scheme I, K_{os} rather represents the formation of activated complex (K^*) if the mechanism is limiting associative (A) and the rate-determining step is the formation of the seven-coordinated intermediate (k_{01}^{f}). Langford and Gray[28] call this mechanism limiting A if the kinetic test shows the presence of an intermediate of increased coordination number. When no intermediate species can be found, as in our case (unless the intermediates are very short-lived, which is not impossible), the mechanism is declared an interchange process. Consequently, the associative interchange, $\mathrm{I_a}$, (rather than A) seems to be the reasonable alternative taking into account k_{01}^{f} or k_{01}^{dec} as k^{rds} after the outer-sphere complex formation.

However, there are some arguments which rather support the $\mathrm{I_d}$ mechanism than the $\mathrm{I_a}$: (i) Positive values of activation entropy

---

[27] Wilkins, R. G.; Eigen, M. *Adv. Chem. Ser.* **1965**, *49*, 55.

[28] Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; W. A. Benjamin Inc.; New York, 1965.

found for the exchange reaction between the $Tl(H_2O)_6^{3+}$ and $TlCl^{2+}$ and roughly estimated for the self-exchange between $TlCl_2^+$ and $TlCl_3$ show that the transition state is less ordered than the initial one. (Rough estimation leads to a negative value of the activation entropy for the self-exchange between the $TlCl^{2+}$ and $TlCl_2^+$ as well as between Tl^{3+} and $TlCl_2^+$, but because of the uncertainty of this parameter it cannot be stated that the two latter exchange reactions are of the type of associative interchange in spite of the fact that the two former reactions are not. Here it should be emphasized that the activation parameters include an unknown contribution from the formation of the outer-sphere complex. In general, this fact lowers the predictive potential of the activation entropies. In this particular case, however, the opposite situation probably occurs: the formation of the outer-sphere complex is a kind of associative process and in spite of the complication arising from the rearrangement of the solvent molecules, the formation probably gives a negative contribution to the calculated activation entropies. Hence, if the calculated $\Delta S^{\ddagger}$ for the reaction is positive, the entropy contribution from the rate-determining step is certainly positive thus indicating a dissociative type of reaction mechanism.) (ii) The entering "ligand", which in this case is another complex species (e.g., $TlCl(H_2O)_5^{2+}$), is so large that its coordination as a seventh ligand seems less probable. In the light of above considerations the rate equation for the self-exchange reactions can be written as

$$\text{rate} = k^{\text{rds}}K_{\text{os}}[TlCl_n^{3-n}][TlCl_{n+1}^{2-n}] \tag{27}$$

that is the rate constants determined experimentally are the multiplication of the outer-sphere equilibrium constants and the rate constants of the rate-determining step (k^{rds}).

There is a possibility to estimate K_{os} values for the different direct exchange paths using the Bjerrum–Fuoss equation,[29] which assumes only electrostatic interactions to be present

$$K_{\text{os}} = 4\pi Na^3/3000 \exp(-Z) \tag{28}$$

where N is Avogadro's number, a is the encounter complex separation being 5 Å (one layer), and Z is the coulombic energy divided by kT. Following numerical values can be calculated: $K_{\text{os}}(0,1) = 7.5 \times 10^{-5}$ M and $k^{\text{rds}}(0,1) = 6 \times 10^8\ \text{s}^{-1}$; $K_{\text{os}}(0,2) = 4.7 \times 10^{-3}$ M and $k^{\text{rds}}(0,2) = 1.4 \times 10^8\ \text{s}^{-1}$; $K_{\text{os}}(1,2) = 1.2 \times 10^{-2}$ M and $k^{\text{rds}}(1,2) = 4 \times 10^6\ \text{s}^{-1}$; $K_{\text{os}}(2,3) = 3 \times 10^{-1}$ M and $k^{\text{rds}}(2,3) = 9 \times 10^7\ \text{s}^{-1}$. In the case of I_d mechanism k^{rds} should be within one order of magnitude of the rate constant of water exchange and should be independent of (or only slightly dependent on) the nature of the entering ligand.

Unfortunately, no experimental data are available in the literature for water exchange on Tl^{3+}, but there is an estimation of $k_{01}{}^{d} > 3 \times 10^9\ \text{s}^{-1}$ based on chloride substitution reactions of Fe^{3+} complexes.[30] Furthermore, Lincoln et al.[16] found by ^{35}Cl NMR measurements that the rate constant of Cl^- exchange reaction between $TlCl_6^{3-}$ and free chloride is larger than 1.3×10^6 and $1.6 \times 10^6\ \text{s}^{-1}$, in 7 and 11 M HCl, respectively. It can be accepted as a lower limit for the Tl–Cl bond breaking and thus for the rate constant for the rearrangement of the intermediate. The calculated rate constant for the rate-determining step of the self-exchange between Tl^{3+} and $TlCl^{2+}$, $k^{\text{rds}}(0,1) = 6 \times 10^8\ \text{s}^{-1}$, is lower than the lower limit estimated for the water exchange rate constant for the aqua complex.[30] Since both the lower limit of water exchange rate constant[30] and our calculations for $k_{01}{}^{d}$ contain simplifications, neither the difference nor the agreement is significant.

The same mechanism (I_d) is thought for the reaction between Tl^{3+} and $TlCl_2^+$ (eq 8) in spite of the (roughly estimated) negative value of the activation entropy. The numerical values of $k^{\text{rds}}(0,1)$ and $k^{\text{rds}}(0,2)$ are of the same order of magnitude. Since the chloride moves from one complex to another in a self-exchange reaction, the most probable picture of the transition state is a binuclear species containing chloride ligand between the two thallium atoms. It means that in the self-exchange reactions 6 and 8 the water should leave the aqua complex part of the ion pairs before the formation of the intermediates. That is, if the rate-determining step in these two reactions is the cleavage of the water–thallium bond, $k^{\text{rds}}(0,1)$ and $k^{\text{rds}}(0,2)$ should have the same or at least similar values. Thus, for the self-exchange reactions in which Tl^{3+} takes part, $k_{01}{}^{d}$ seems to be the rate-determining step.

In the self-exchange reaction between $TlCl^{2+}$ and $TlCl_2^+$ or between $TlCl_2^+$ and $TlCl_3$ a water molecule can leave both sides of the ion pairs yielding binuclear complexes with chloride bridge ligand. We assume higher rate constant values for the water exchange rate for these complexes than for that of the aqua complex because the water–thallium bond is longer[20b] and hence presumably more labile in the former complexes. It means that the rearrangement of the transition binuclear complex can become the rate-determining step instead of the dissociation of water. The extremely low value for the $k^{\text{rds}}(1,2)$ may be attributed to a very symmetric intermediate containing an axial $Cl^-–Tl^{3+}–Cl^-–Tl^{3+}–Cl^-$ bond sequence which can be imagined to be relatively inert. In the case of the self-exchange between $TlCl_2^+$ and $TlCl_3$ it is difficult to predict the structure of the intermediate because $TlCl_3$ can be trigonal bipyramidal or tetrahedral, but the sharp change in the structure may be the explanation for the large difference between the rate constants $k^{\text{rds}}(1,2)$ and $k^{\text{rds}}(2,3)$.

Summarizing the above considerations and speculations on the self-exchange reactions, a synchronous mechanism is probable with I_d character. For the aqua complex the water dissociation can be the rate-determining step, whereas for the chloride-containing species the rearrangement of the intermediate can be the rate-determining step.

We have found only a few data for this type of self-exchange in the literature. Canon and Richards published self-exchange rate constants for the In^{3+} ion

$$In(H_2O)_6^{3+} + {}^*In(H_2O)_5X^{2+} \leftharpoondown {}^*In(H_2O)_6^{3+} + In(H_2O)_5X^{2+}$$

where X is F^-, Cl^-, Br^-, and I^-.[31] The rate constants decrease slightly from F^- to I^-, and the numeric values are, respectively, 5.9×10^4, 8.5×10^3, 8.6×10^3, and $2.2 \times 10^3\ \text{M}^{-1}\ \text{s}^{-1}$ at $I \sim 5$ and $T = 25$ °C. The authors have not discussed any details of the mechanism. Assuming dissociative interchange mechanism and estimating $K_{\text{os}} = 7 \times 10^{-5}$ M, k^{rds} values for F^-, Cl^-, Br^-, and I^- are 8.3×10^8, 1.2×10^8, 1.2×10^8, and $3.1 \times 10^7\ \text{s}^{-1}$, respectively. These values are close to our values for $k^{\text{rds}}(0,1) = 6 \times 10^8\ \text{s}^{-1}$ and $k^{\text{rds}}(0,2) = 1.4 \times 10^8\ \text{s}^{-1}$, but are considerably higher than the water exchange rate constant for the $In(H_2O)_6^{3+}$ determined by Geier to $2 \times 10^6\ \text{s}^{-1}$ at 12 °C and ionic strength $I = 0.1$ M.[32]

The preliminary data published earlier[17] show that the lifetime of thallium in the form of Tl^{3+} and $TlBr^{2+}$ at $R = 0.5$ is 5×10^{-4} s at 27 °C and in the ionic medium of (3 M $HClO_4$ + 1 M $NaClO_4$). From this value, assuming that only the self-exchange between Tl^{3+} and $TlBr^{2+}$ occurs, $k^{\text{rds}}(0,1)$ for the bromide system is $\sim 5 \times 10^8\ \text{s}^{-1}$, i.e., the same value as obtained above for $k^{\text{rds}}(0,1)$ for the chloride system, thus supporting our mechanistic conclusion. From the data in ref 17, 31, and 32 we can only conclude that more experimental data would be needed to consider the details of the self-exchange reactions. Certainly, a detailed analysis of the thallium(III)–bromide system can give more information for mechanistic conclusions. Therefore, we have started such a study, and the results will be published in the near future.

For the anation reaction paths

$$TlCl_n(H_2O)_p{}^{3-n} + Cl^- \xrightleftharpoons{k'_{n,n+1}} TlCl_{n+1}(H_2O)_q{}^{2-n} + (p-q)H_2O \tag{29}$$

two possibilities can also be drawn for example for the anation of the third complex (assumed to be tetrahedral).

The estimated activation enthalpies for the anation reactions are much smaller than those for the self-exchange reactions, and

---

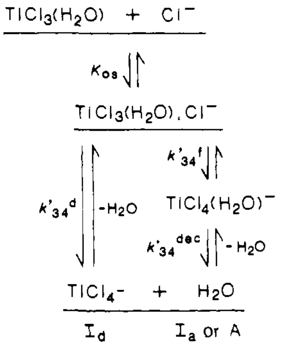
(29) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059.

(30) Sutin, N. *Ann. Rev. Phys. Chem.* **1966**, *17*, 119.

(31) Canon, T. H.; Richards, R. E. *Trans. Faraday Soc.* **1966**, *62*, 1378.

(32) Geier, G. *Z. Elektrochem.* **1965**, *69*, 617.

Scheme II



the activation entropies are negative in the former case indicating a different mechanism. The rate equations are of first order for complexed species and for the free ligand as well. These results and the relatively large size of the thallium(3+) ion support an associatively activated interchange mechanism (I_a).

The outer-sphere complex formation equilibrium can also be considered here and the rate constants for the rate-determining step can be calculated as $k'_{rds}(m,n) = k'_{mn}/K_{os}(m,n)$. The numerical values are as follows: $k'_{rds}(1,2) = 6.2 \times 10^7$ s^{-1} (K_{os} = 5), $k'_{rds}(2,3) = 1 \times 10^9$ s^{-1} (K_{os} = 1.3) and $k'_{rds}(3,4) = 1.6 \times 10^9$ s^{-1} (K_{os} = 0.3). For the anation of the aqua complex $k'_{rds}(0,1)$ must be less than 5×10^6 s^{-1} because one can show that k'_{01} must be smaller than 1×10^8 M^{-1} s^{-1} (assuming that the contribution of this reaction to the exchange rate between Tl^{3+} and $TlCl^{2+}$ is smaller than 10%).

The values of k'_{rds} for the anation of Tl^{3+} and $TlCl^{2+}$ are considerably lower than the rate constant of water exchange assumed above (between 1×10^8 and 6×10^8 s^{-1}); that is, the associative type mechanism seems to be probable. The rate constants can, alternatively, represent penetration of the ligand to the coordination sphere.[33] In the case of $TlCl_2^+$ and $TlCl_3$, either type of anation (I_a or I_d) can be imagined. The very high values of k'_{rds}, interpreted as $k'_{34}{}^{d}$, can be the consequence of the longer water–thallium bonds (in the case of $TlCl_2^+$ which is still octahedral). The associative anation is also possible because of the relatively large thallium ion and small chloride ion (especially in the case of $TlCl_3$ which is trigonal bipyramidal or tetrahedral).

Literature data for kinetics of complex formation of thallium is very scarce. In the case of $Tl(OH)(H_2O)_5^{2+}$ it was found that the rate constants of the complex formation with two very different ligands are of the same order of magnitude. The numerical values for 4-(2-pyridylazo)resorcinol[15] (LH_3^+) is 1.8×10^5 M^{-1} s^{-1} and for semixylenol orange[14] (H_4SXO^0) is 3×10^5 M^{-1} s^{-1}. On the basis of these results the reactions were suggested to be controlled by the "step of dissociation of the coordinated water molecule from aqua Tl(III) ion".[15] Since the reaction was found to be first order both for $Tl(OH)(H_2O)_5^{2+}$ and for the entering ligands and the entering ligands have different charge, consequently the outer-sphere complexes must have different K_{os}. Hence, the above cited statement may be questionable.

Considering that the solvent exchange reactions for Al^{3+}, Ga^{3+}, and In^{3+} turn from dissociative interchange to associative interchange in the named order for all studied cases,[19] I_a mechanism in the case of chloride anation (in the thallium(III) system) seems to be more probable. Lincoln et al.[16] proposed an associative interchange mechanism for chloride exchange on $GaCl_4^-$, and a dissociative interchange mechanism on $InCl_4^-$, although the authors did not eliminate the I_a mechanism in the latter case.

It is not reasonable to compare our data for the chloride anation to that for other three-valent metal ions, because detailed investigations are available only for transition metals.[19] The conclusion is that the nature of the mechanism strongly depends on the nature of the central ion.[19] However, Tl^{3+} ion is very different in its coordination character than the transition metals, and the ligand exchange data for Tl^{3+}, including the present ones, are too scarce to allow any meaningful comparisons.

Conclusions

The thallium(III)–chloride system is relatively complicated from the kinetic point of view since as much as seven exchange reaction paths have been shown to be of importance (cf. Figure 10). Fortunately, this problem can be solved because at selected *R* regions only one or two exchange reactions dominate. The "self-exchange" reactions of the type

$$Tl_{aq}{}^{3+} + {}^*TlCl_{aq}{}^{2+} \rightleftharpoons {}^*Tl_{aq}{}^{3+} + TlCl_{aq}{}^{2+}$$

(where two positively charged species collide) do not seem probable at first sight. However, the strong line broadening dependence on the total thallium concentration leaves no doubt that this is the dominating reaction type at low *R* values, where the free chloride ion concentration is extremely low, and, accordingly, the more common anation reactions are suppressed. Unfortunately, kinetic and especially mechanistic information for solutions containing Tl^{3+} ion (or other d^{10} ions) is very limited or practically nonexistent, and it is difficult to pursue more detailed discussion of our results.

In the light of previous results[34] and considering the present work it can be stated that ^{205}Tl NMR spectroscopy is a powerful technique to study ligand exchange reactions in Tl(III)–ligand systems, for example, for halide or pseudohalide ligands. Such investigations can give information necessary for a deeper analysis of mechanisms of exchange reactions of the Tl^{3+} ion. In general, metal ion NMR studies can provide valuable information about the dynamics of coordinated species in solution.

Acknowledgment. We are grateful to The Swedish Natural Sciences Research Council (NFR) for financial support and, together with The Knut and Alice Wallenberg Foundation, for providing funds for purchasing the NMR spectrometer. Financial support from The Swedish Institute toward I.B.'s stay in Stockholm is kindly acknowledged.

Registry No. Tl, 7440-28-0; Cl, 7782-50-5.

---

(33) Miceli, J.; Stuehr, J. *J. Am. Chem. Soc.* **1968**, *90*, 6967.

(34) Hinton, J. F.; Metz, K. R.; Briggs, R. W. *Annual Reports on NMR Spectroscopy*; Academic Press: London, 1982; Vol. 13A.