Equilibrium Dynamics in the Thallium(III)–Bromide System in Acidic Aqueous Solution. A ^{205}Tl NMR Study
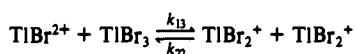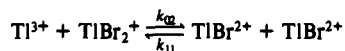
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Abstract: Kinetics of ligand exchange in the thallium(III)–bromide system in aqueous 3 M perchloric acid solution was studied by measuring ^{205}Tl NMR line widths at 25 °C. Three types of parallel second-order reaction paths were found to be dominant. For the reactions

$$\text{TlBr}_m^{3-m} + {}^*\text{TlBr}_n^{3-n} \underset{k_{nm}}{\rightleftharpoons} {}^*\text{TlBr}_m^{3-m} + \text{TlBr}_n^{3-n}$$

the rate constants are $k_{01} = 2.8 \times 10^4$ (1.25×10^4 at 10 °C), $k_{12} = 7.5 \times 10^4$, $k_{23} = 8.2 \times 10^6$, and $k_{34} = 2.3 \times 10^7$ M^{-1} s^{-1}. For the reactions

$$\text{Tl}^{3+} + \text{TlBr}_2^+ \underset{k_{11}}{\overset{k_{02}}{\rightleftharpoons}} \text{TlBr}^{2+} + \text{TlBr}^{2+}$$

$$\text{TlBr}^{2+} + \text{TlBr}_3 \underset{k_{22}}{\overset{k_{13}}{\rightleftharpoons}} \text{TlBr}_2^+ + \text{TlBr}_2^+$$

$k_{02} = 7.1 \times 10^5$, $k_{11} = 6.1 \times 10^3$, and $k_{13} = 2.4 \times 10^7$ M^{-1} s^{-1} ($k_{22} = 2.3 \times 10^5$ M^{-1} s^{-1}, calculated by use of equilibrium constants), and for the complex formation (anation) reactions

$$\text{TlBr}_n^{3-n} + \text{Br}^- \xrightarrow{k'_{n(n+1)}} \text{TlBr}_{n+1}^{2-n}$$
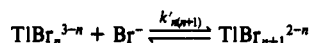
$k'_{01} < 10^{10}$, $k'_{12} = 5.8 \times 10^9$, $k'_{23} = 5.6 \times 10^{10}$, $k'_{34} = 1.5 \times 10^9$, and $k'_{45} \sim 6 \times 10^6$ M^{-1} s^{-1}. The first and the second types of exchange dominate at low bromide to thallium ratios, (Br$_{\text{tot}}$/Tl$_{\text{tot}}$) = $R \le 2$, whereas the third one becomes dominant at higher R values. The activation parameters for the reaction represented by k_{01} are $\Delta H^{\ddagger} = 38$ kJ mol^{-1} and $\Delta S^{\ddagger} = -32$ J mol^{-1} K^{-1}. A mechanism for this reaction is suggested to be a dissociatively activated interchange process. The present results are discussed and compared to the corresponding data for the thallium(III) chloride system. One important result of the present study is the estimation of the rate of water exchange for the hydrated thallium(III) ion, $k \sim 3 \times 10^8$ s^{-1}, which has not been possible to obtain by any other experimental method. "Specific interaction theory" calculation has been performed for the TlBr$_n^{3-n}$ complexes in order to check the validity of the used equilibrium constants; values of the appropriate specific interaction coefficients are given.

The complexes formed in the thallium(III)–bromide system are among the strongest metal ion–bromide complexes, and their equilibria have been extensively studied by different authors in various media (e.g., refs 2–5). Strong complexes were found with the composition TlBr$_n^{3-n}$ up to $n = 4$. The stability of the complexes with $n = 5$ and 6 was found to be very low, usually the stepwise stability constant log $K_n < 0$ (except a few papers that suggested log $K > 2$[6,7]). There is information on the structure of the complexes both in solution[5,8] and in solid.[9] The X-ray and ^{205}Tl NMR structural studies in solution indicate that the coordination number in the aqua, first, and second complexes is six, including the water molecules in the inner coordination sphere. The third complex, TlBr$_3$, contains probably two coordinated

molecules of water while the fourth complex, TlBr$_4^-$, is clearly tetrahedral and hence does not contain water ligands.[5,8]

There are only a few kinetic studies for the thallium(III) complexes, probably because the ligand-exchange reactions are rather fast. Fujimoto et al. investigated the complex formation between Tl^{3+} and semixylenol orange and 4-(2-pyridylazo)res-orcinol by a stopped-flow technique.[10] Only the reaction of Tl(OH)$^{2+}$ ion was identified and the dissociation of a water

Table I. Rate Constants for Different Exchange Reactions for TlX$_n^{3-n}$ at 25 °C

	for X = Br		for X = Cl	
	k_{mn}/M^{-1} s^{-1}	k_{mn}^{rds}/s^{-1}	k_{mn}/M^{-1} s^{-1}	k_{mn}^{rds}/s^{-1}
	Reactions 1 and 2			
k_{01}	$(2.8 \pm 0.5) \times 10^4$	4×10^8	4.9×10^4	6×10^8
k_{02}	$(7.1 \pm 2.1) \times 10^5$	2×10^8	6.4×10^5	1×10^8
k_{11}	$(6.1 \pm 1.3) \times 10^3$		9.4×10^3	
k_{12}	$(7.5 \pm 0.7) \times 10^4$	6×10^6	5.2×10^4	4×10^6
k_{13}	$(2.4 \pm 0.6) \times 10^7$	8×10^6		
k_{23}	$(8.2 \pm 1.7) \times 10^6$	3×10^7	2.7×10^7	9×10^7
k_{34}	$(2.3 \pm 0.5) \times 10^7$	8×10^7	$<3 \times 10^7$	
	Reaction 3			
k'_{01}	$<10^{10}$			
k'_{12}	$(5.8 \pm 1.5) \times 10^9$	1×10^9	3.2×10^8	6×10^7
k'_{23}	$(5.6 \pm 1.9) \times 10^{10}$	6×10^{10}	1.3×10^9	1×10^9
k'_{34}	$(1.5 \pm 0.7) \times 10^9$	5×10^9	4.7×10^8	2×10^9

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4704 *J. Am. Chem. Soc., Vol. 112, No. 12, 1990*

Bányai and Glaser

molecule from the $Tl(OH)^{2+}$ was assumed to be the rate-determining step. Lincoln et al. reported that the rate of ligand exchange between $TlCl_6^{3-}$ and the free Cl^- was fast on the ^{35}Cl NMR time scale and only a lower limit of the rate constant was estimated.[11]

The fact that the equilibrium and structural data are available led us to study the ligand-exchange kinetics in this system in order to obtain mechanistic information through comparison of the kinetic to the structural information.

In our previous papers we stated that the high-field ^{205}Tl NMR is a powerful technique to determine the rate constants of the very fast ligand-exchange reactions of $Tl(III)$.[5,12] Studying in detail the ligand exchange of $TlCl_n^{3-n}$ species in 3 M $HClO_4$ we have identified three types of reaction paths.[12] The first one proceeds without net chemical change:

$$TlCl_m^{3-m} + *TlCl_n^{3-n} \xrightleftharpoons{k_{mn}} *TlCl_m^{3-m} + TlCl_n^{3-n} \quad (1)$$
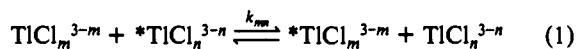
where $m = n + 1$. The rate constants k_{01}, k_{12}, and k_{23} and the lower limit for k_{34} have been determined at 25 °C (cf. Table I). The second reaction path involves net chemical change:

$$Tl^{3+} + TlCl_2^+ \xrightleftharpoons[k_{11}]{k_{02}} 2TlCl^{2+} \quad (2)$$
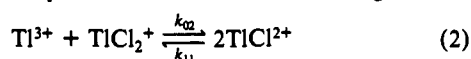
with the rate constants k_{02} and k_{11} (Table I). These types of exchange reactions dominate at lower chloride to thallium ratios, $(Cl^-_{tot}/[Tl^{3+}]_{tot}) = R \leq 2$; throughout the text R has the same meaning. Taking into account the structures of the species and the determined activation parameters, a dissociatively activated interchange process was suggested as the mechanism for the reactions 1 and 2.

The third type of ligand exchange was found to be the anation reaction of the thallium complexes:

$$TlCl_n^{3-n} + Cl^- \xrightleftharpoons{k'_{n(n+1)}} TlCl_{n+1}^{2-n} \quad (3)$$
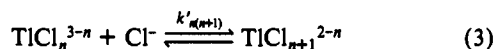
with the rate constants k'_{01} (higher limit only), k'_{12}, k'_{23}, and k'_{34} (cf. Table I). An associatively activated interchange process was proposed for the anation mechanism.

Mechanistic conclusions are usually based on comparison of the information available on the investigated system to the appropriate data on the same metal ion and other ligands, as well as to the corresponding data on other, but similar metal ions. Unfortunately, kinetic and mechanistic information on thallium-(III) and its neighbors in the periodic table is very limited or practically nonexistent in the literature. Therefore, in order to verify the above cited proposals for the mechanisms, a systematic study of $Tl(III)$ halide and pseudo-halide complexes was considered to be appropriate. Since the equilibrium and structural information on the $Tl(III)$–bromide system is available, the kinetic study of this system by means of ^{205}Tl NMR seemed to be a logical following step and is presented in this paper.

Experimental Section

Materials. About 1 M aqueous solution of $Tl(ClO_4)_3$ was obtained by anodic oxidation of $TlClO_4$ solution.[13] Stock solutions containing 0.1 M total thallium and the total bromide/total thallium ratios 0 and 5, respectively, were prepared from the solutions of $Tl(ClO_4)_3$, HBr, and $HClO_4$. The total hydrogen ion concentration was 3 M and the ionic medium throughout this study was $I = 3$ M $\{H^+, (ClO_4^- + Br^-)\}$. The samples for measurements were prepared by mixing the stock solutions in different proportions and diluting with 3 M perchloric acid in order to obtain different total thallium concentrations (typically, $[Tl]_{tot} = 0.050$ M).

Analysis. Acid concentration of $Tl(III)$ solutions was determined by titration with NaOH after adding excess of solid NaCl to the analyzed solution. $Tl(I)$ was determined by titration with a 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 $KBrO_3$.[14] In this way, the concentrations of acid,

$Tl(I)$, and $Tl(III)$ could be determined one after the other in the same sample. Bromide 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.[15]

NMR Measurements. The ^{205}Tl NMR spectra were recorded at 230.8 MHz at a probe temperature of 25 ± 0.5 °C with a Bruker AM400 spectrometer. The magnetic field was unlocked; field drift was found to be negligible. The samples were contained in 10-mm (outer diameter) spinning sample tubes. In order to obtain activation parameters, some spectra have been recorded at different temperatures from 10 to 60 °C. Typical NMR parameters were as follows: flip angle, $\sim 15°$ (15 μs), pulse repetition time, 0.1 s, sweep width, 125 kHz, 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. Since the chemical shifts for aqueous solutions of different $Tl(I)$ salts extrapolate to the same value at infinite dilution,[16] this value corresponds to the chemical shift of the free hydrated Tl^+ ion. The accuracy of the measured line widths is $\sim 10\%$ and that of the chemical shifts ~ 0.1–1 ppm, depending on the line width.

Results and Calculations

Data Treatment. The analysis of ^{205}Tl NMR data for dynamic purposes is described in some detail in our previous paper. Here, only a short summary is presented in order to make the calculations and the discussion understandable for the reader. The band shape of an absorption mode NMR spectra can be calculated, deducing from the exchange modified Bloch equations, as follows:

$$V(x) = \gamma H_1 M_0 C^{-1} \cdot P \quad (4)$$

x is frequency variable, γ is the gyromagnetic ratio, H_1 is the strength of the magnetic field, M_0 is the total magnetization, and P is the column vector of molar fractions of magnetically active n sites present.[17a] C is a quadratic matrix:

$$C = R_2 + w \cdot \epsilon_2 \cdot w \quad (5)$$

where w is a diagonal matrix of independent variable $w_n = x - \Omega_n$, where Ω_n is the chemical shift of the nth site and $\epsilon_2 = R_2^{-1}$. R_2 matrix is the sum of a diagonal matrix with elements of the nonexchange line widths $\Delta\nu_{1/2}^0(n)$ and the rate matrix, K, of the exchange system. The $\Delta\nu_{1/2}(n)$ parameter contains the transverse relaxation time, $1/T_2(n)$, the inhomogeneity of the magnetic field, and in practice also the line-broadening parameter used to obtain less noisy NMR spectra. The K rate matrix is a quadratic matrix containing the linear combination of pseudo-first-order rate constants, k_{mn}^{obs}, attributed to the chemical exchange between the sites m and n.[17b] For example, the definition of pseudo-first-order rate constants for the $Tl(III)$–Br^- system comes from eq 6, where the left-hand side of the equation is the column vector

$$d[TlBr_n^{3-n}]/dt = K \cdot [TlBr_n^{3-n}] \quad (6)$$

of exchange rates with $n + 1$ elements (e.g., the first element, $n = 0$, corresponds to the aqua complex and $n = N$ is the last element) and $[TlBr_n^{3-n}]$ is the concentration vector for the magnetic sites. Since (pseudo-) first-order reactions considered as the elements of the K matrix are independent of the concentration units, the molar fractions, p_n, can be substituted into eq 6 in order to compare to eq 4. Considering that there is chemical exchange between all sites, the diagonal elements K_{mn} of the matrix K are

$$K_{mn}(m = n) = -\sum_{n=0}^{n=N} k_{mn}^{obs}(m \neq n) \quad (7a)$$

and the off-diagonal elements are

$$K_{mn}(m \neq n) = k_{nm}^{obs} \quad (7b)$$

$$p_m \xrightleftharpoons[k_{nm}^{obs}]{k_{mn}^{obs}} p_n \quad (8)$$

Certainly, the microscopic reversibility requires that $k_{mn}^{obs} p_m =$

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Dynamics in the Tl(III)-Bromide System

J. Am. Chem. Soc., Vol. 112, No. 12, 1990 4705

Table II. ^{205}Tl NMR Chemical Shifts[a] and Nonexchange Line Widths for TlBr$_n$$^{3-n}$ Complexes in 3 M HClO$_4$, at 25 °C[b]

n (in TlBr$_n$$^{3-n}$)	δ/ppm	$\Delta\nu_{1/2}$[c]/Hz	δ^{sd}/ppm
0	2093.6 (±1)	~15	2086 (±1)
1	1575 (±1)	~35	1538 (±3)
2	782 (±1)	~35	766 (±2)
3	1158 (4)	~35	1184 (5)
4	1312 (2)	~35	1318 (2)
5	−800[e]		

[a] The chemical shifts are reported in ppm toward higher frequency with respect to an aqueous solution of TlClO$_4$ extrapolated to infinite dilution. [b] Numbers in parentheses with ± are maximum errors of measurements; others are standard deviations obtained from least-squares calculations. [c] Contains magnetic field inhomogeneity. [d] In 3 M HClO$_4$ + 1 M NaClO$_4$. 27 °C. [e] Estimated value (see text).

$k_{nm}^{obs}p_n$, so that K is symmetrical and the sum of the elements in each column is 0.

If one determines the chemical shifts, Ω_m (δ_n in ppm units) and knows the equilibrium populations p_n (i.e., if the overall stability constants, β_n, are known) the elements of the matrix K can be determined by comparison of the measured and the calculated NMR spectra by means of eq 4. If the chemical-exchange reactions are slow at the time scale defined by the chemical shift difference of the exchanging magnetic sites, the solution of eq 4 will result in as many Lorentzian peaks having line widths at half height $\Delta\nu_{1/2}(n)$, as the number of magnetic sites being dominant. In this case, the pseudo-first-order rate constants can be calculated directly by using eq 9:[18]

$$\left[\Delta\nu_{1/2}(m) - \Delta\nu_{1/2}^{0}(m)\right]\pi = \sum_{n=0}^{n=N} k_{mn}^{obs} \quad (9)$$

The positions of the peaks correspond to the individual chemical shifts of the participating thallium species. If the exchange is fast on that time scale, only one peak will be obtained with chemical shift determined by the individual chemical shifts of all the exchanging species. The line widths of this peak, $\Delta\nu_{1/2}$, is determined by all elements of the exchange matrix K. In this case the characteristic points of the experimental spectra can be compared to that of the calculated ones giving k_{mn}^{obs} values.

The dependence of the obtained k_{mn}^{obs} values on the equilibrium concentrations of the different species gives the empirical rate equations in the form (only first-order terms are considered[12])

$$k_{mn}^{obs} = k_0 + \sum_{m=0}^{m=N} k_{mn}[\text{TlBr}_n^{3-n}] + \sum_{n=m}^{n=m+1} k'_{mn}[\text{Br}^-] \quad (10)$$

Determination of the Chemical Shifts. The individual chemical shifts of the aqua, first, and the second complexes were determined directly from the spectra (slow-exchange regime). For the third and fourth complexes the individual chemical shifts were calculated by using the following equation

$$^l\delta_{obs} = {}^lp_3\delta_3 + {}^lp_4\delta_4 \quad (11)$$

where $^l\delta_{obs}$ is the experimental chemical for the experimental point i, ^lp_n is the molar fraction, and δ_n is the individual chemical shift. $^l\delta_{obs}$ were measured in the range $2.5 < R < 4.8$ where the exchange was considered to be fast enough for eq 11 to be valid. The results are given in Table II and are compared to the values determined earlier.[5a] In the calculations, experimental β_n (n = 1–4) values obtained for 3 M LiClO$_4$ ionic medium were used[19] since it has been shown that these values are valid in 3 M HClO$_4$ ionic medium (cf. ref 20). The validity of these stability constants for the present measurements is considered in some detail in the Discussion. No change was found in the experimental chemical shifts in the range $4.2 < R < 4.8$ at [Tl^{3+}]$_{tot}$ = 0.05 M, indicating that complexes higher than TlBr$_4^-$ do not form in appreciable concentration.
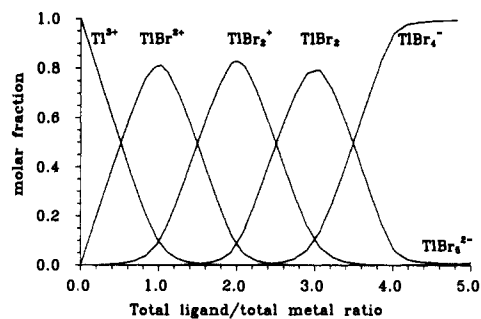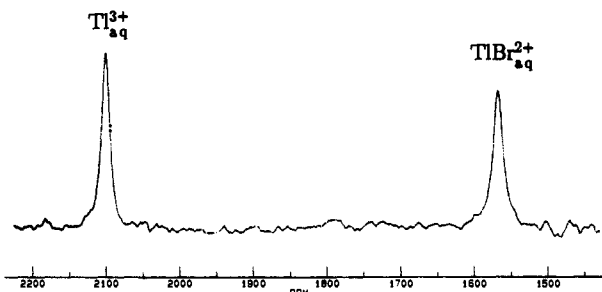
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Figure 1. Distribution of thallium(III) bromide complexes as a function of R. [Tl]$_{tot}$ = 0.05 M. 25 °C.

Figure 2. ^{205}Tl NMR spectra at R = 0.5 and [Tl]$_{tot}$ = 0.05 M at 25 °C. The chemical shifts are reported in ppm toward higher frequency with respect to an aqueous solution of TlClO$_4$ extrapolated to infinite dilution.
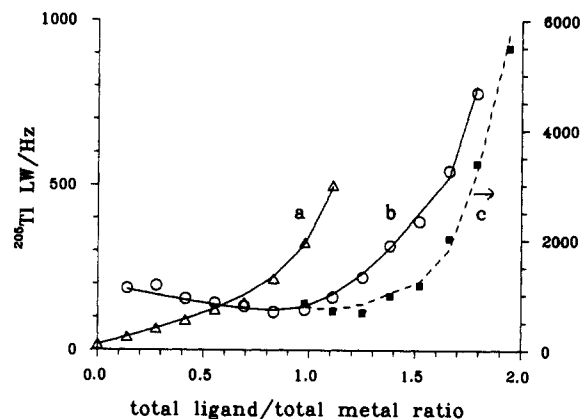
Figure 3. Dependence of line widths of (a) Tl^{3+} (b) TlBr^{2+}, and (c) TlBr$_2^+$ on total ligand/metal ratio at [Tl]$_{tot}$ = 0.02 M. Lines represent line widths calculated by using rate constants in Table I. T = 25 °C.

Table III. Overall Stability Constants, β_n, for the TlBr$_n$$^{3-n}$ Complexes in 3 M HClO$_4$, at 25 °C

n (in TlBr$_n$$^{3-n}$)	log β_n ref 19	log β_n this work	log β_n calcd[a]	specific interactn coeff used in calcn of β_n[b]
0				ϵ(Tl^{3+}, ClO$_4^-$) = 0.65$_6$[c]
1	9.28		9.31	ϵ(TlBr^{2+}, ClO$_4^-$) = 0.53$_9$
2	16.7		16.8	ϵ(TlBr$_2^+$, ClO$_4^-$) = 0.64$_3$
3	22.1	21.9	22.0	ϵ(TlBr$_3$) = 0.57$_5$
4	25.7	25.7	26.1	(ϵ(TlBr$_4^-$, H$^+$) = 0.70
				ϵ(TlBr$_4^-$, Na$^+$) = 0.59
5		~24.7[d]		

[a] By means of the specific interaction theory; see text. [b] Other ϵ values used in the calculation: ϵ(H$^+$, Br$^-$) = 0.16, ϵ(Na$^+$, Br$^-$) = 0.05. For details of the calculation, see text. [c] From ref 22. [d] Estimated; see text.

However, at [Tl^{3+}]$_{tot}$ = 0.25 M, a slight decrease of the measured chemical shift was found for R increasing between 4.2 and 7, which indicates that higher complexes may be present. Although the equilibrium concentration of these complexes is probably very low at [Tl^{3+}]$_{tot}$ = 0.05 M, they can have kinetic effect (vide infra). The values of the used equilibrium constants are given in Table III, and the distribution of the complexes is shown in Figure 1.
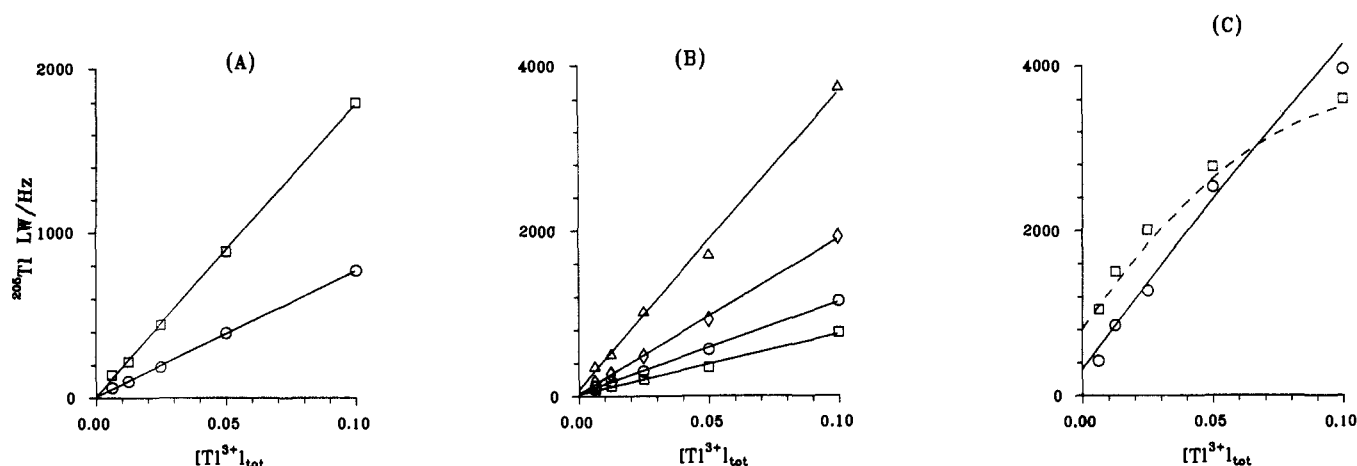
Figure 4. Dependence of line widths on total thallium concentration. (A) for Tl^{3+} at $R = 0.42$ (O) and at $R = 0.78$ (□): (B) for $TlBr^{2+}$ at $R = 0.78$ (□). $R = 0.42$ (O), $R = 1.33$ (◇), and $R = 1.55$ (△): and (C) for $TlBr_2^+$ at $R = 1.33$ (O) and $R = 1.55$ (□). $T = 25$ °C.

Determination of Empirical Rate Equations. At $0 < R < 1.7$ the peaks of the aqua, first, and second complexes appeared separately and their chemical shifts did not change with changing R, indicating that the exchange is slow on the time scale determined by the chemical shift differences between them. An example of a ^{205}Tl NMR spectrum is shown in Figure 2. The change of $\Delta\nu_{1/2}(n)$ values as a function of R is shown in Figure 3.

For the line width of the aqua complex the following empirical equation was found to be valid by means of the least-squares analysis:

$$\Delta\nu_{1/2}(0) = c_0 + c_{01}[TlBr^{2+}] + c_{02}[TlBr_2^+] \quad (12)$$

for $[Tl^{3+}] = 0.01$ M. The constants have the following values: $c_0 = 18 \pm 5$, $c_{01} = (1.47 \pm 0.12) \times 10^4$, and $c_{02} = (2.27 \pm 0.62) \times 10^5$. The value of c_0 is very close to the measured nonexchange line width of the aqua complex, $\Delta\nu_{1/2}{}^0(0) = 15$ Hz. c_{01} can be attributed to the exchange reaction

$$Tl^{3+} + {}^*TlBr^{2+} \underset{k_{01}}{\overset{k_{01}}{\rightleftharpoons}} {}^*Tl^{3+} + TlBr^{2+} \quad (13)$$
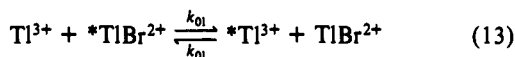
with the rate

$$-d[Tl^{3+}]/dt = 2k_{01}[Tl^{3+}][TlBr^{2+}] \quad (14)$$

where the factor 2 takes into account that one aqua complex participates in the forward and one in the reverse reaction. Consequently, by use of eqs 9, 12, and 14, the rate constant $k_{01} = \pi c_{01}/2$. c_{02} can originate from the reaction between the aqua and second complex:

$$Tl^{3+} + TlBr_2^+ \underset{k_{11}}{\overset{k_{02}}{\rightleftharpoons}} 2TlBr^{2+} \quad (15)$$

which leads to net chemical change. The rate is

$$-d[Tl^{3+}]/dt = k_{02}[Tl^{3+}][TlBr_2^+] \quad (16)$$

and $k_{02} = \pi c_{02}$. The rate constants are given in Table I. If R is constant, because of the high stability of the $TlBr_n{}^{3-n}$ complexes the molar fractions and the free ligand concentration are practically constant and independent of the total thallium concentration. For this case, by use of eqs 9 and 10, the dependence of the line width on the total thallium concentration can be written in the following form:

$$\Delta\nu_{1/2}(0) = \Delta\nu_{1/2}{}^0(0) + (c_{01}p_1 + c_{02}p_2)[Tl^{3+}]_{tot} \quad (17)$$

In fact, linear dependence was found between the experimental line width and the total thallium concentration (Figure 4A). The intercepts were calculated to be 12 ± 5 and 15 ± 7 Hz at $R = 0.42$ and 0.78, respectively. These values are close to the nonexchange line width measured in 0.01 M $Tl(ClO_4)_3$ solution. The slopes were found experimentally to be 7631 ± 100 at $R = 0.42$ and $17\,808 \pm 230$ at $R = 0.78$. These values are in good agree-

ment with the corresponding slopes calculated by using the rate constants obtained from the R dependence, 7680 and 18 100, respectively.

For the dependence of the line width of the $TlBr^{2+}$ signal on R (cf. Figure 3), the following empirical equation was found to be valid (by means of the least-squares method):

$$\Delta\nu_{1/2}(1) = c_0 + c_{10}[Tl^{3+}] + c_{11}[TlBr^{2+}] + c_{12}[TlBr_2^+] +$$
$$c_{13}[TlBr_3] + c'_{12}[Br^-] \quad (18)$$

with $c_0 = 40 \pm 14$, $c_{01} = (1.88 \pm 0.11) \times 10^4$, $c_{11} = 39 \pm 9$, $c_{12} = (4.6 \pm 0.4) \times 10^4$, $c_{13} = (7.5 \pm 1.9) \times 10^5$, and $c'_{12} = (1.8 \pm 0.4) \times 10^9$. The values of c_{13} and c'_{12} correlated very strongly and the minimum value of the least-squares sum could only be reached by step-by-step variation of c_{13}. The total thallium concentration dependence of the line width can be written as

$$\Delta\nu_{1/2}(1) =$$
$$c_0 + c'_{12}[Br^-] + (c_{10}p_0 + c_{11}p_1 + c_{12}p_2 + c_{13}p_3)[Tl^{3+}]_{tot} \quad (19)$$

It can be seen in Figure 4B that the linearity is confirmed by the experiment. The parameter c_0 is the nonexchange line width for $TlBr^{2+}$, $\Delta\nu_{1/2}{}^0(1) = c_0 = 35 \pm 14$ Hz. It is obvious that the parameter c_{10} belongs to the k_{01} value determined independently from eq 14. The parameter c_{11} could be attributed to the right-to-left reaction (15) for which the rate is

$$d[Tl^{3+}]/dt = -\tfrac{1}{2}d[TlBr^{2-}]/dt = k_{11}[TlBr]^2 \quad (20)$$

Keeping in mind that the line width of the $TlBr^{2+}$ signal is proportional to the exchange rate defined as $d[TlBr^{2+}]/dt$, the rate constant $k_{11} = c_{11}\pi/2$. Naturally, there should be a connection between k_{11} and k_{02} since

$$k_{02}/k_{11} = [TlBr^{2+}]^2/[Tl^{3+}][TlBr_2^+] = \beta_1{}^2/\beta_2 \quad (21)$$

From the literature[19] $\beta_1{}^2/\beta_2 = 72$ while $k_{02}/k_{11} = 116$; this seems to be a good agreement, taking into account the standard deviation values given for the rate constants. The parameter c_{12} can be associated with the exchange:

$$TlBr^{2+} + {}^*TlBr_2^+ \underset{k_{12}}{\overset{k_{12}}{\rightleftharpoons}} {}^*TlBr^{2+} + TlBr_2^+ \quad (22)$$

k_{12} is calculated from c_{12} in the same way as was followed for k_{01}; its value is given in Table I. The parameter c_{13} can be considered in the same way as c_{02}, that is

$$TlBr^{2+} + TlBr_3 \underset{k_{22}}{\overset{k_{13}}{\rightleftharpoons}} 2TlBr_2^+ \quad (23)$$
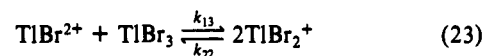
and $k_{13} = c_{13}\pi$. Finally, the parameter c'_{12} belongs to the anation of the $TlBr^{2+}$ complex:

$$TlBr^{2+} + Br^- \underset{k'_{-12}}{\overset{k'_{12}}{\rightleftharpoons}} TlBr_2^+ \quad (24)$$

and $k'_{12} = c'_{12}\pi$. The intercept of the dependence of the line width on $[Tl^{3+}]_{tot}$ is the sum of two terms of eq 19: the nonexchange
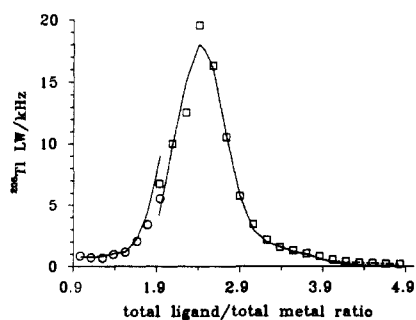
Figure 5. Dependence of line width of $TlBr_n^{3-n}$ complexes (fast-exchange regime, one signal) on total ligand/metal ratio at $[Tl]_{tot} = 0.02$ M (O) and $[Tl]_{tot} = 0.05$ M (□). Full line represents line widths calculated by using rate constants for the complexes $TlBr_n^{3-n}$ ($n = 0$–4); dashed line is calculated by taking into account the species $TlBr_5^{2-}$ also. The values of the rate constants are given in Table I. $T = 25$ °C.

Figure 6. Dependence of pseudo-first-order rate constants on total ligand/metal ratio at $[Tl]_{tot} = 0.05$ M. Full line represents the result of parameter fitting (cf. eq 25). $T = 25$ °C.

line width c_0 and $c'_{12}[Br^-]$. Four intercept values were determined at different R values and were found to be as follows: 37 ± 13 (calcd 37) at $R = 0.42$, 57 ± 7 (44) at $R = 0.78$, 47 ± 15 (65) at $R = 1.27$, and 103 ± 37 (127) at $R = 1.54$. The agreement between the intercepts and the values calculated by use of k'_{12} is acceptable considering the very low concentration of the free bromide ligand and the high standard deviation of the k'_{12} value. The slopes can also be verified by means of eq 19 with the rate constants determined above: $11\,011 \pm 240$ ($10\,720$) at $R = 0.42$, 5530 ± 130 (5650) at $R = 0.78$, $18\,750 \pm 870$ ($17\,700$) at $R = 1.27$, and $32\,830 \pm 1570$ ($31\,540$) at $R = 1.54$.

We did not follow the same way to analyze the experimental results for the signal of $TlBr_2^+$ in the slow-exchange range (i.e., for $R < 1.7$) because the number of experimental points was less than the number of parameters that determined them. Furthermore, at $R > 1.7$ the chemical shift was not constant but increased slightly with increasing R, indicating the contribution of fast exchange between the second and third complexes. The dependence of the line width of $TlBr_2^+$ on the total thallium concentration also showed a deviation from linearity (Figure 4C). Since the application of the above considerations (eqs 12 and 17–19) is justified strictly only for slow exchange, the pseudo-first-order rate constant for $TlBr_2^+$ was determined by model calculations using eq 4–8 and the rate constants determined earlier. At $R > 1.8$ only one signal was observed and the dependence of the line width on R is shown in Figure 5. The values of k_{23}^{obs} obtained from fitting of calculated spectra to the experimental ones were considered in the following way:

$$k_{23}^{obs} = k_{22}[TlBr_2^+] + k_{23}[TlBr_3] + k'_{23}[Br^-] \qquad (25)$$

The model calculation showed that up to $R = 2.6$ the exchange is not disturbed by the exchange between the third and fourth complexes, and k_{23}^{obs} could be fitted to eq 25, giving $k_{23} = (8.2 \pm 1.6) \times 10^6$ and $k'_{23} = (5.6 \pm 1.4)$ M^{-1} s^{-1} (cf. Figure 6A). No value could be determined for k_{22} in spite of the fact that the opposite reaction (k_{13}) was found to occur (vide supra). This is probably because the contribution of the term $k_{22}[TlBr_2^+]$ in eq 25 is very low, at most 9% (at $R = 1.92$). By use of the rate constants determined for the exchange between the second and third complexes (eq 25), the nonlinear dependence of the line width of $TlBr_2^+$ on the total thallium concentration at $R = 1.33$ and 1.55 was satisfactory as verified by model calculation (cf. Figure 4C).

Exactly the same way was followed in order to obtain the rate constants for the exchange between the third and fourth complexes, and the results are given in Table I and Figure 6B. The exchange occurs between $TlBr_2^+$, $TlBr_3$, and $TlBr_4^-$ by two parallel ways, cf. eqs 1 and 3.

As shown in Figure 5, at $R > 3.8$ the calculated line widths do not fit to the experimentally determined ones. Different types of extra exchange reactions between the second, third, and fourth complexes were considered without success.

Finally, we have found one possibility that is in agreement with the experimental data. It demands extending of the chemical
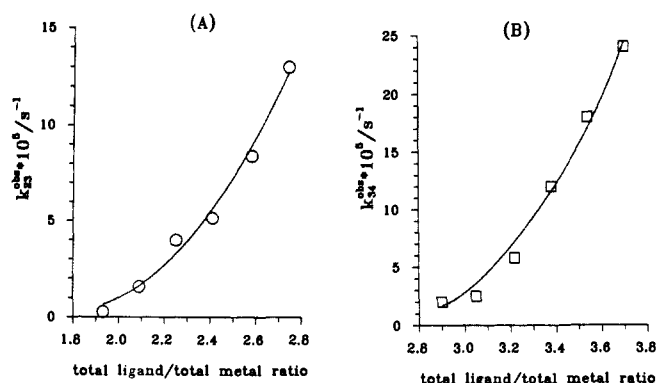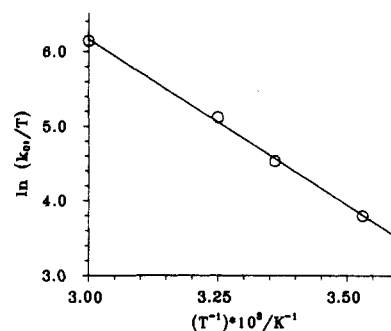
model, so that it includes exchange between the fourth and some higher complex(es).[5a,13b] This exchange might be rather fast but still observable on the actual time scale determined by the difference between the chemical shifts of the species $TlBr_4^-$ and $TlBr_5^{2-}$ (or $TlBr_6^{3-}$). A rough estimation of the rate of bromide exchange between the fourth and the fifth complexes can be obtained as follows. According to the assumption[5a] that for the reaction

$$TlBr_n^{3-n} + Br^- \rightleftharpoons TlBr_{n+1}^{2-n} \qquad (26)$$

the Tl NMR chemical shift change per n is about -600 ppm for complexes with octahedral structure, the individual chemical shift for the species $TlBr_5^{2-}$ would be about -800 ppm. Then an estimation was made for the stability constant of the fifth complex. An upper limit for this constant was found potentiometrically in slightly different ionic medium[4] to be $\log K_5 \leq -0.4$. We are not able to determine K_5 since its value is very low, and consequently, the large excess of the bromide necessary for significant formation of $TlBr_5^{2-}$ will change the quality of the ionic medium, which may influence the values of the chemical shifts. However, our data and the data of ref 5 indicate that $\log K_5$ is much lower than -0.4. The lowest K_5 compatible with our experimentally found line widths was found to be $\log K_5 \sim -1$. Assuming only the complex formation reaction (cf. eq 3), that is $k'_{45}[Br^-]$ term, to occur, we obtain $k'_{45} \sim 6 \times 10^6$ M^{-1} s^{-1} ($\sim 4 \times 10^7$ for $\log K_5 = -0.4$). With these values the dependence of the line widths as a function of R could be described satisfactorily. (For further discussion of this subject, see below.)

At $R = 0.3$, where only reaction 13 occurs, the temperature dependence was investigated between 10 and 60 °C. The Arrhenius plot of the temperature dependence of the rate constants is shown in Figure 7. The activation parameters are $\Delta H^* = 38$ (± 4) kJ mol^{-1} and $\Delta S^* = -32$ (± 2) J mol^{-1}, where the values in parentheses represent the computed standard deviations, ($\pm 2\sigma$). Another estimate of the uncertainties can be obtained by considering the random errors of measurements ($\pm 10\%$ in k values and ± 0.5 °C in T): $\Delta H^* = 38 \pm 8$ kJ mol^{-1} and $\Delta S^* = -32 \pm 12$ J mol^{-1}.

Figure 7. Arrhenius plot of the rate constant dependence on the temperature for k_{01}.

Discussion

Stability Constants. For calculation of the rate constants, knowledge of the correct equilibrium constants for the thallium-(III) bromide complexes is of critical importance. For the present ionic medium, 3 M $HClO_4$, no equilibrium data are available. However, it can be proved by means of the specific interaction method that replacement of Li^+ for H^+ does not cause significant change in the equilibrium constants.[21,22] Specifically, for the thallium(III) chloride system, where experimental data are available for both 3 M $LiClO_4$[23] and 3 M $HClO_4$,[24] the stability constants have practically the same values for both ionic media (within 0.15 logarithmic unit). Furthermore, the specific interaction calculation based on the experimental data of Woods[24] yields stability constants for $TlCl_n^{3-n}$ complexes in different ionic media in good agreement with the experimental ones.[20]
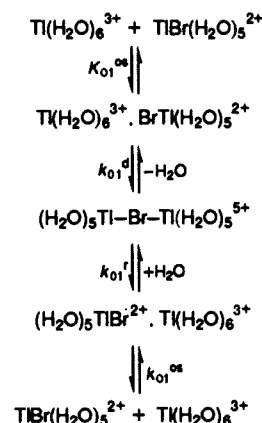
Accordingly, for the determination of the kinetic parameters for $TlBr_n^{3-n}$ complexes we decided to use the stability constants determined potentiometrically in 3 M $LiClO_4$ by Yakovlev et al.[19] We have controlled that in the R range $2.3 < R < 4.8$, where fast exchange on the actual Tl NMR time scale takes place, the stability constants β_3 and β_4 determined by using our experimental chemical shift data are in concordance with the values of ref 19. In addition, by use of the specific interaction calculation based on the data of refs 4 and 6, the stability constants $\beta_1-\beta_4$ for the thallium(III) bromide complexes in 3 M $HClO_4$ could be calculated (Table III) and were found to be in reasonable agreement with the constants from ref 19.

There are assumptions in the literature about the stability of the higher complexes, $TlBr_5^{2-}$ and $TlBr_6^{3-}$, in aqueous solution,[6,7] but their existence is debated.[4,5a] The high value of log $K_5 \simeq 2^{6,7}$ determined with a (silver/silver bromide) electrode is contradicted by the results of Ahrland et al.[4] The latter authors pointed out that the use of silver/silver halide electrode in the strongly oxidizing Tl(III) solutions is of doubtful validity. As stated above, no change was found in the experimental chemical shifts in the range $4.2 < R < 4.8$ at $[Tl^{3+}]_{tot} = 0.05$ M, indicating that complexes higher than $TlBr_4^-$ do not form in appreciable concentration. However, at $[Tl_{3+}]_{tot} = 0.25$ M a slight decrease of the measured chemical shift was found for R increasing between 4.2 and 7, which may indicate that higher complexes are present. Although the equilibrium concentration of these complexes could not be high at $[Tl^{3+}]_{tot} = 0.05$ M (cf. Figure 1), they can have a kinetic effect. Concluding, we found that the stability constants $\beta_1-\beta_4$ of Yakovlev et al.[19] are correct and valid in the present ionic medium. The stability constant for the complex $TlBr_5^{2-}$, log $K_5 \sim -1$ M, determined from our kinetic data as described above, should be considered only as a rough estimation.

Reaction Mechanisms. We propose, for the bromide exchange between the $TlBr_n^{3-n}$ complexes, the same reaction paths as previously suggested for the chloride system.[12] The path without net chemical change (represented by eq 1) was identified for all the complexes. The comparison of the rate constants for the both ligands (cf. Table I) lends additional support for the originally proposed (for the chloride complexes) dissociatively activated interchange mechanism.[12] Scheme I shows this reaction path for the example of the aqua and first complexes.

This scheme differs from the classical picture of the I_d-type ligand substitution processes[25,26] because the "coming ligand" is a complex as well. It means that either the dissociation of a water molecule (k_{01}^d) or the rearrangement of the chemical bonds (k_{01}^r)

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Scheme I

in the outer-sphere complex, can be the rate-determining step. Although the negative activation entropy does not indicate a dissociative rate-determining step, one can imagine that the negative formation entropy of the outer-sphere complex is larger than the positive activation entropy of the rate-determining step.[27] On the other hand, the relatively high activation enthalpy characterizes the dissociatively activated process rather than the associatively activated one.[28] Using the Bjerrum–Fouss equation, we can estimate the outer-sphere association constant,[29] $K_{01}^{os} = 7.5 \times 10^{-5}$ M and according to Scheme I, $k_{01} = k_{01}^{rds}K_{01}^{os}$. The rate constant of the rate-determining step can now be calculated to be $k_{01}^{rds} \sim 4 \times 10^8$ s^{-1}. In the same way, if we consider another exchange reaction where the aqua complex is also a reactant, (cf. eq 15), $K_{02}^{os} = 4.7 \times 10^{-3}$ M and $k_{02}^{rds} \sim 2 \times 10^8$ s^{-1}. The rate constants for the corresponding reaction paths in the Tl(III)–Cl$^-$ system were found to be $k_{01}^{rds} \sim 6 \times 10^8$ s^{-1} and $k_{02}^{rds} \sim 1 \times 10^8$ s^{-1}.[12] Thus, all four reactions in which the aqua complex takes part have rate constants for the rate-determining step (k^{rds}) of the same order of magnitude. For the I_d mechanism, k_{mn}^{ra} should be the rate constant for the process, in which the water molecule leaves the ion pair (k^d), probably the aqua complex part of the latter. This would mean that all four calculated k^{rds} values would belong to this reaction step and, hence, that these values should be very close to each other. In fact, this is also the case. Concluding, the independence of the k^{rds} values on the quality of the ligand supports our earlier proposition that the mechanism is dissociative interchange, with the rate-determining step being water leaving the aquated Tl^{3+} ion. Sutin estimated theoretically the water-exchange rate constant for the Tl^{3+} aqua complex to be 3 × 10^9 s^{-1}.[30] Although our values are lower by almost 1 order of magnitude, the agreement is acceptable because we used the simplest estimation of K^{os} values without considering, for example, the effect of the ionic strength.[31] (Recalculation of K^{os} to the high ionic strength requires use of equations of questionable validity.) In a way similar to that for the reactions corresponding to k_{01} and k_{02}, consideration of the exchange reactions between the higher complexes gives the following rate constants for the rate-determining step: $k_{12}^{rds} \simeq 6 \times 10^6$ s^{-1} ($K_{12}^{os} = 1.2 \times 10^{-2}$ M), $k_{23}^{rds} \simeq 3 \times 10^7$ s^{-1} ($K_{23}^{os} = 0.3$ M), $k_{34}^{rds} \simeq 8 \times 10^7$ s^{-1} ($K_{34}^{os} = 0.3$ M) and $k_{13}^{rds} \simeq 8 \times 10^6$ ($K_{13}^{os} = 0.3$ M). Good agreement can be found if these k^{rds} values are compared to the corresponding values obtained for the chloride system, cf. Table I. Furthermore, the calculated rate constant for the reaction corresponding to k_{13} is also in agreement with the reactions corresponding to k_{12} (for both the bromide and the chloride systems), probably because the rate-determining step is the same. In our previous paper, for the higher complexes the rearrangement

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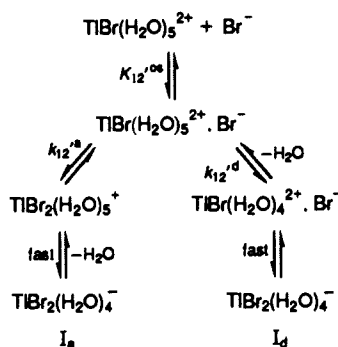
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Scheme II

$$TlBr(H_2O)_5{}^{2+} + Br^-$$

$$K_{12}'^{os} \updownarrow$$

$$TlBr(H_2O)_5{}^{2+} \cdot Br^-$$

$$k_{12}'^a \swarrow \qquad \qquad k_{12}'^d \searrow {-H_2O}$$

$$TlBr_2(H_2O)_5{}^+ \qquad TlBr(H_2O)_4{}^{2+} \cdot Br^-$$

$$fast \updownarrow {-H_2O} \qquad \qquad fast \updownarrow$$

$$TlBr_2(H_2O)_4{}^- \qquad TlBr_2(H_2O)_4{}^-$$

$$I_a \qquad \qquad I_d$$

of the outer-sphere complex was suspected to be the rate-determining step.[12] However, in the light of the present results, we should revise our speculation because the independence of k^{rds} from the nature of the ligand rather indicates a mechanism with the rate-determining step being water dissociation (k^d in Scheme I). We are not able to explain why the water ligand in Tl^{3+}(aq) should be more labile than in the $TlBr^{2+}$ complex. The $Tl-OH_2$ distance is increasing with increasing number of halide ligands in the coordination sphere. It is reported to be 0.2235 pm in the aqua complex and $\sim$0.235 pm in the $TlBr^{2+}$ complex.[8c] Possible explanations for the lability of the aquated thallium(3+) ion can be that the formation of an outer-sphere complex labilizes the water ligands more in the aqua complex than in the first complex. However, in order to explain this fact more experimental data are needed. The trend of the rate constants for higher complexes is $k_{12}{}^{rds} < k_{23}{}^{rds} < k_{34}{}^{rds}$, which is in accordance with the structural data [Tl-OH$_2$ distance is $\sim$0.235 pm in TlBr^{2+}(aq), $\sim$0.245 pm in TlBr$_2{}^+$(aq) and $\sim$0.255 pm in TlBr$_3$(aq)].[8c] Comparison of the chloride and bromide systems (Table I) shows that there are no significant changes of k^{rds} depending on the ligand.

Similarly to the Tl(III)-Cl$^-$ system, anation reactions appear also for the bromide complexes (eq 3) and become dominating with increasing number of the coordinated halides. The dissociative and associative paths of the anation are shown in Scheme II. The second-order rate constants for the anation reactions show the same trend for the bromide and the chloride systems but the rate constants for the former system are larger by an order of magnitude (being close to the diffusion controlled limit) than those of latter (see Table I). Since the values depend on the nature of the ligand, our earlier suggestion that the mechanism is an associatively activated interchange process remains unchanged. One can also calculate the outer-sphere stability constants and the rate constants of the rate-determining step for each complex. The values are $k_{12}'^{rds} \simeq 1 \times 10^9$ ($K_{12}'^{os} \sim 5$ M), $k_{23}'^{rds} \simeq 6 \times 10^{10}$ (1.3 M), and $k_{34}'^{rds} \simeq 5 \times 10^9$ (0.3 M) s^{-1} for the bromide complexes. These values can be compared to the corresponding values for the chloride complexes (Table I). Generally, the influence of the quality of the ligand is expected to be more pronounced for the I_a than for the I_d pathway. However, in the present case the available information does not allow a choice between the two mechanisms. Still, the estimated rate constants are much higher than those suggested for the water exchange for the different TlBr$_n{}^{3-n}$ complexes (vide supra) and are affected more by the quality of the ligand in the coordination sphere. Moreover, if we would have the I_d mechanism, the rate of the water dissociation, $k'mn^d$, would probably increase in the direction Tl-(H$_2$O)$_5$Br^{2+} < Tl(H$_2$O)$_4$Br$_2{}^+$ < Tl(H$_2$O)$_2$Br$_3$ because of the weakening of the thallium-water bonds.[8c,13b] Therefore, these rate constants can be attributed to the ligand penetration rate constants, $k'mn^a$, and the suggested mechanism corresponds to the associative interchange in Scheme II rather than to the dissociative one.

Our conclusions for the thallium(III) halide systems, compared to the solvent-exchange reactions studied for Al^{3+}, Ga^{3+}, and In^{3+} ions, confirm the statement that the mechanism turns from a dissociative interchange to an associative one down the periodic system for all studied cases.[27] Since Tl^{3+} is the member of this column with the largest size, the associative mechanism for the
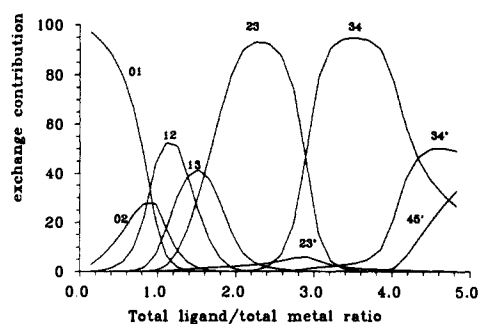

Figure 8. Percentage contribution of different parallel exchange paths (w_{mn}, numbered by the indexes of rate constants) to the total exchange rate $w_{mn} = \sum_{m,n}(k_{mn}[\text{TlBr}_m][\text{TlBr}_n] + k'_{mn}[\text{TlBr}_m][\text{Br}^-])$. $T = 25$ °C. The contribution of the path corresponding to k'_{12} is negligible on this scale.

anation reactions could be expected.

Conclusions

Due to the fortunate distribution of the different complexes in the thallium(III) bromide system in aqueous solution and to the power of the Tl NMR technique for studying fast kinetic processes in solution, we were able to determine 10 dominating ligand exchange pathways for the TlBr$_n{}^{3-n}$ ($n = 1-5$) species (cf. Figure 8). We have found two main types of (second-order) exchange reactions, similar to the ones found for the thallium(III) chloride system.[12] The first type represents a direct exchange of the ligand between two complex species, e.g.

$$Tl^{3+} + {}^*TlBr^{2+} \underset{}{\overset{k_{01}}{\rightleftharpoons}} {}^*Tl^{3+} + TlBr^{2+}$$
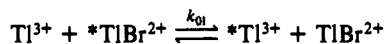
(also for mn pairs: 12, 23, 34, 02, and 13). This reaction is a very unusual type of ligand exchange. It plays a more important role in this chemical system than for the corresponding chloride complexes. This is probably due to the higher stability of the TlBr$_n{}^{3-n}$ complexes and, accordingly, to a very low free bromide concentration, which makes the more common anation reaction less pronounced, especially at low bromide/thallium ratios. The present results confirm the dissociatively activated interchange process proposed previously for the corresponding reaction type in the thallium(III) chloride system. However, the results make us propose now that the rate-determining step for this reaction type is dissociation of a water molecule from the outer-sphere complex, rather than the rearrangement of the chemical bonds in the latter (cf. Scheme I). An important result of the present study is an estimation of the rate constant of water exchange for the aquated thallium(III) ion, $k \sim 3 \times 10^8$ s^{-1}, since this value has not been possible to obtain before and is missing in all published books and articles on hydrated metal ions in solution (e.g., ref 32). The second type of ligand exchange represents the more common complex formation (anation) reactions, e.g.

$$TlBr^{2+} + Br^- \underset{}{\overset{k'_{12}}{\rightleftharpoons}} TlBr_2{}^+$$
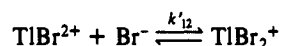
(also for mn pairs: 01, 23, 34, and 45). This type of exchange also has a second-order rate law and dominates at higher R values. The present results are in agreement with are suggestion made for the chloride system, that the mechanism for this reaction is associatively activated interchange.

More detailed discussion of reaction mechanisms in the two studied systems is prevented by (a) scarcity of kinetic and particularily mechanistic information for solutions containing Tl(III) complexes and for other post-transition-metal ions, and (b) uncertainties concerning the structures and the hydration of some of the investigated species (e.g., TlX$_3$·nH$_2$O). Therefore, it seems worthwhile to continue the studies of the dynamic properties of other complexes of thallium(III) as well as to determine the

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structures of the hydrated TlX_n^{3-n} species in solution by means of neutron diffraction. Recently, such measurements have been started. It is our hope that, if successful, they will widen our knowledge of the dynamic behavior of thallium(III) complexes in solution and, in the best case, provide a contribution for better understanding of dynamic processes involving complexed metal ions in general.

Maximally Diagonal Force Constants in Dependent Angle-Bending Coordinates. 2. Implications for the Design of Empirical Force Fields

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Abstract: The vast amount of information compiled in experimentally determined and quantum-mechanically calculated force fields for small molecules could be used to assist in the further development of empirical potentials used in molecular-mechanics and molecular-dynamics simulations of organic and biological systems. Unfortunately, most such force fields are defined in well-determined sets of internal coordinates, whereas empirical potentials use larger sets of dependent coordinates. This paper illustrates a unique "localized" representation of the angle-deformation potential in dependent coordinates which is exactly diagonal for in-plane bending at trigonal-planar centers and is nearly diagonal for angle bending at tetracoordinate centers. The transformation to this representation is accomplished by introducing "virtual force constants" which couple to the vanishing null-coordinate displacement. Four applications show how this transformation can be used to aid the development of improved empirical potentials. The first extracts localized force constants for angle bending at carbonyl groups in aldehydes, ketones, amides, acids, and esters from published force fields, and then demonstrates that these values are reasonably transferable and are well described by the empirical relationship

$$k_\theta = 1.75 Z_a C_b Z_c (R_{ab} + R_{bc})^{-1} \theta_{abc}^{-2} \exp(-2D)$$

where Z and C are atomic parameters and $D = (R_{ab} - R_{bc})^2/(R_{ab} + R_{bc})^2$ and shows that the corresponding force constants used in MM2, AMBER, VFF, and CHARMM do not exhibit the systematic trends found in the experimental data. The second compares "canonical" and localized force constants for angle bending at methylene groups in alkanes for three published force fields. The third application extends the approach to stretch–bend and bend–bend' interactions and transforms a calculated in-plane force field for ethylene to dependent coordinates to show how one can test model assumptions concerning the importance of and functional form required for specific interactions. The fourth application shows how the transformation to localized force constants can be carried out at a variety of geometries to probe the anharmonicity of the molecular energy surface.

Computational simulations of bioactive macromolecules, and of the substrates, inhibitors, agonists, and antagonists which interact with them, are coming to play an ever larger role in the study of biochemical processes and in the design of pharmaceutical agents.[1] For reasons of computational efficiency, these simulations have generally employed molecular-mechanics or molecular-dynamics calculations based on empirical potentials (force fields). Most simulations have been qualitative in nature and have focussed on the prediction of geometries rather than energies or of gas-phase energies rather than energies in solution. Encouragingly, recent reports have shown that results approaching quantitative accuracy can be achieved for relative free energies of enzyme-inhibitor binding in systems of real chemical interest.[2] Nevertheless, it seems clear that current models for empirical force fields are too simple in form, in that they fail to account for important physical effects which affect the phenomena being modeled. Electrostatic effects in particular are poorly understood, but even "valence interactions" which depend on deformations in bond lengths, bond angles, and dihedral angles are not always modeled accurately. More realistic functional forms need to be developed, and soundly-based parameters need to be determined for a much wider range of chemical functionality. Fortunately, these needs are well understood, and considerable effort to develop improved empirical potentials is being carried out to address them.[3]

This development effort potentially could make use of the many experimental spectroscopic and quantum-mechanical force fields which have been determined for small molecules, but several factors have made it difficult to do so. One potential difficulty arises from the fact that spectroscopic and quantum-mechanical force fields (for the sake of brevity, we shall call these *spectroscopic* force fields) locally expand the potential energy in internal-coordinate displacements about the equilibrium geometry. Such force fields mathematically "fold" all the physical interactions—including those arising from electrostatic and nonbonded interactions—onto the manifold of internal-coordinate displacements. In contrast, *empirical* force fields need to provide ex-

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(3) (a) For one current effort see. for example: Palca. J. *Nature* **1986.** 322. 586. (a) A second effort is reflected in the following: Dasgupta. S.; Goddard. W. A. III *J. Chem. Phys.* **1989.** 90. 7207–7215.