

Short Communications

Kinetics of Ligand Exchange in Aqueous Thallium(III) Halide Solutions. A ^{205}Tl NMR Study

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The formation of Tl(III) halide complexes TlX_n^{3-n} , ($X=\text{Cl}, \text{Br}$) in aqueous solutions has recently been studied by ^{205}Tl NMR both in dilute (0.05 M) and concentrated (1.0 and 2.6 M) solutions.¹ The ^{205}Tl chemical shift was measured at constant concentration of Tl(III) and varying concentrations of the halide. When only one signal was observed due to rapid exchange, the observed chemical shift is given by

$$\delta_i^{\text{obs}} = \sum_n p_n^i \cdot \delta_n \quad (1)$$

At each concentration $p_n^i = [\text{TlX}_n^{3-n}]/[\text{Tl}]_{\text{tot}}$ depends on the stability constants which together with the chemical shifts δ_n for the different species were determined by a least-squares fitting procedure. During this investigation considerable variations in the ^{205}Tl line widths due to exchange processes were observed. Similar variations in line width were also observed many years ago by Figgis² but since the individual ^{205}Tl chemical shifts for the different Tl(III) halide species were not known at that time, it was impossible to extract any kinetic information from the data. In this communication we report lifetimes for some TlX_n^{3-n} complexes which were evaluated from the observed ^{205}Tl line widths and the shifts for the individual species determined in our previous work.¹

For $[\text{Tl}]_{\text{tot}}=0.05$ M separate signals were observed for the species Tl^{3+} , TlCl^{2+} , TlBr^{2+} and TlBr_2^+ showing that the rate of ligand exchange between these complexes is slow on a time scale defined by the difference between their ^{205}Tl chemical shifts. The signals are, however, still broadened due to the exchange, permitting determination of the life times for the different species. When the total thallium concentration is increased, the lines become further broadened and finally coalesce to a single average signal for the exchanging species, see Fig. 1. The large difference between the chemical shifts for the different species gives rise to extremely broad signals (up to 50 kHz) for intermediate exchange rates in some cases. These broad lines could usually not be recorded with a satisfactory signal to noise ratio to make a quantitative line shape analysis meaningful. For some solutions containing two dominating species, A and B, we have evaluated the lifetimes τ_A and τ_B from the line widths using the approximate equations³

$$\Delta\nu_A^{\text{ex}} = 1/\pi\tau_A \quad (2a)$$

$$\Delta\nu_B^{\text{ex}} = 1/\pi\tau_B \quad (2b)$$

for the exchange contribution to the line widths in the slow exchange regime where two separate lines are observed and

$$\Delta\nu_{1/2}^{\text{ex}} = 4\pi p_A^2 p_B^2 (\delta_A - \delta_B)^2 (\tau_A + \tau_B) \quad (3)$$

Table 1. Lifetimes of Tl(III) at 27 °C in the different species evaluated from experimental ^{205}Tl line widths. $p_n = [\text{TlX}_n^{3-n}]/[\text{Tl}]_{\text{tot}}$. The chemical shifts for the different species are taken from reference 1 where the preparation of the solutions also is described.

$[\text{Tl}]_{\text{tot}}$ (M)	$\text{Tl}^{3+} + \text{Cl}^- \rightleftharpoons \text{TlCl}^{2+}$	$\text{Tl}^{3+} + \text{Br}^- \rightleftharpoons \text{TlBr}^{2+}$	$\text{TlBr}^{2+} + \text{Br}^- \rightleftharpoons \text{TlBr}_2^+$	$\text{TlBr}_2^+ + \text{Br}^- \rightleftharpoons \text{TlBr}_3$	$\text{TlBr}_3 + \text{Br}^- \rightleftharpoons \text{TlBr}_4^-$
	$p_0 = p_1 = 0.5$ $\tau_A = \tau_B$ (s)	$p_0 = p_1 = 0.5$ $\tau_A = \tau_B$ (s)	$p_1 = p_2 = 0.5$ $\tau_A = \tau_B$ (s)	$p_2 = p_3 = 0.5$ $\tau_A = \tau_B$ (s)	$p_3 = p_4 = 0.5$ $\tau_A = \tau_B$ (s)
~ 2.6	$1.5 \cdot 10^{-6a}$	$2 \cdot 10^{-6b}$	$3 \cdot 10^{-6c}$	$2 \cdot 10^{-7d}$	$1 \cdot 10^{-6e}$
1.7^f	$5 \cdot 10^{-6}$	$4 \cdot 10^{-6}$	$4 \cdot 10^{-6}$		
1.0^f	$8 \cdot 10^{-6}$			$4 \cdot 10^{-7}$	$1 \cdot 10^{-6}$
0.8^f	$1 \cdot 10^{-5}$	$1 \cdot 10^{-5}$			
0.5^f	$2 \cdot 10^{-5}$				
0.31^f	$7 \cdot 10^{-5}$				
0.05^g	$3 \cdot 10^{-4}$	$5 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$1 \cdot 10^{-6}$	$5 \cdot 10^{-6}$

^a $[\text{Tl}]_{\text{tot}} = 2.20$ M, $[\text{HClO}_4] = 2.12$ M. ^b $[\text{Tl}]_{\text{tot}} = 2.31$ M, $[\text{HClO}_4] = 2.23$ M. ^c $[\text{Tl}]_{\text{tot}} = 2.70$ M, $[\text{HClO}_4] = 0.95$ M. ^d $[\text{Tl}]_{\text{tot}} = 2.76$ M. No acid or ionic medium. ^e $[\text{Tl}]_{\text{tot}} = 2.71$ M. No acid. $[\text{Li}^+] = 0.5$ M. ^f $[\text{HClO}_4] + [\text{Li}^+] = 3$ M. ^g $[\text{HClO}_4] = 3$ M, $[\text{NaClO}_4] = 1$ M.

in the rapid exchange regime where only one signal is observed. $(\delta_A - \delta_B)$ is the chemical shift difference in Hz. The evaluated lifetimes are presented in Table 1.

As can be seen, the rate of exchange in the 50 mM solutions is of the same order of magnitude for the three reactions



All these reactions involve Tl(III)-complexes with octahedral structure.⁴ In all three cases the lifetimes become considerably shorter with increasing thallium concentration indicating that the reaction order might be higher than one with respect to Tl(III) but it should be kept in mind that the ionic strength and consequently also the activity factors vary with the total thallium concentration (see Fig. 3 in Ref. 1) which also affects the observed lifetimes.

The exchange reaction

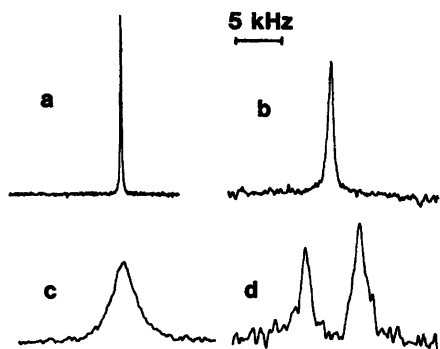


Fig. 1. ^{205}Tl spectra recorded at 51.9 MHz and 27 °C from aqueous solutions with the composition $\text{TlCl}_{0.5}$ for a, $[\text{Tl}]_{\text{tot}} = 2.2$ M; b, $[\text{Tl}]_{\text{tot}} = 1.0$ M; c, $[\text{Tl}]_{\text{tot}} = 0.31$ M; d, $[\text{Tl}]_{\text{tot}} = 0.050$ M. The preparation of the solutions and the NMR conditions are described in Ref. 1.

involves a change from octahedral to trigonal bipyramidal coordination with the thallium atom approximately in the plane of the three bromides and the two water molecules in the apex positions.⁴ The reaction



also involves a change of coordination *viz.* from trigonal bipyramidal to tetrahedral.⁴ In the 50 mM solutions the rate of exchange for reactions (7) and (8) are two orders of magnitude faster than the exchange between the octahedral complexes. Furthermore, for these two reactions the effect of increasing the thallium concentration is considerably smaller than for the reactions (4)–(6). Unfortunately, it has not been possible to investigate if these observations also hold for the corresponding chloride complexes since it is not possible to prepare solutions containing just TlCl_2^+ and TlCl_3 or TlCl_3 and TlCl_4^- complexes.

The lifetimes determined from NMR lineshapes are the inverse of pseudo first order rate constant and in order to verify a reaction mechanism the dependence of the lifetimes on the concentrations of the different reacting species must be investigated.⁵ The data presented in this communication are not complete enough to permit any conclusions about the detailed reaction mechanisms. However, the results indicate differences in the mechanisms for the ligand exchange between octahedral complexes and for the exchange reactions that involve tetrahedral or trigonal bipyramidal coordination of the thallium ion.

Only a few studies of ligand exchange kinetics of Tl(III) complexes have been reported in the literature. Funada *et al.*⁶ and Abraham *et al.*⁷ have studied the exchange of some organic ligands and Quadder⁸ has studied sulfate complexes by ultrasonic absorption. The only study of halide complexes is the work by Lincoln *et al.*⁹ who have used ³⁵Cl relaxation measurements in dilute Tl(III) solutions with a very high excess of chloride. In these solutions TlCl_4^- is the dominating species¹ and from the observed ³⁵Cl relaxation times it was possible to give an upper limit for the lifetime of the chloride ion in the complex ($\tau < 4 \cdot 10^{-6}$ s). When comparing this figure with the lifetimes reported in Table 1 it should be noted that the concentration of free halide ions is very low (10^{-9} – 10^{-4} M) in the solutions studied in this work.

1. Glaser, J. and Henriksson, U. *J. Am. Chem. Soc.* 103 (1981) 6642.
2. Figgis, B.N. *Trans. Faraday Soc.* 55 (1959) 1075.
3. Pople, J.A., Schneider, W.G. and Bernstein, H.J. *High-Resolution Nuclear Magnetic Resonance*, McGraw Hill, New York 1959, p. 219.
4. Glaser, J. and Johansson, G. *Acta Chem. Scand. A* 36 (1982) 125.
5. Chan, S.O. and Reeves, L.W. *J. Am. Chem. Soc.* 95 (1973) 670.
6. Funada, R., Imamura, T. and Fujimoto, M. *Bull. Chem. Soc. Jpn.* 52 (1979) 1535.
7. Abraham, R.J., Hawkes, G.E. and Smith, K.M. *Tetrahedron Lett.* 24 (1975) 1999.
8. Quadder, A. *Z. Phys. Chem. (Frankfurt am Main)* 88 (1974) 160.
9. Lincoln, S.F., Sandercock, A.C. and Stranks, D.R. *Aust. J. Chem.* 28 (1975) 1901.

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