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# Thermodynamics of Association of Thallium(III) Ion and Chloride Ion in Aqueous Solution[1]

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Thallium(III) chloride complex ion formation reactions $TlCl_{n-1}^{+4-n} + Cl^- = TlCl_n^{+3-n}$ in aqueous solution have been studied by electromotive force methods (the thallium(III)–thallium(I) electrode in chloride solutions), solubility methods (the solubility of silver(I) chloride in thallium(III) perchlorate solutions), and calorimetric methods. There is no evidence for monomeric species containing more than four chloride ions per thallium(III) ion at $[Cl^-] \leq 1.25$ *M*. At 25° and ionic strength = 3.0 *M*, values of $Q_n = [TlCl_n^{+3-n}]/[TlCl_{n-1}^{+4-n}][Cl^-]$, $\Delta H_n$, and $\Delta S°_n$ are: $n = 1$, $1.46 + 10^7$ l. mole$^{-1}$, $-5.45$ kcal. mole$^{-1}$, $+14.5$ cal. mole$^{-1}$ deg.$^{-1}$; $n = 2$, $2.76 \times 10^5$ l. mole$^{-1}$, $-4.40$ kcal. mole$^{-1}$, $+10.1$ cal. mole$^{-1}$ deg.$^{-1}$; $n = 3$, $3.55 \times 10^3$ l. mole$^{-1}$, $-1.1$ kcal. mole$^{-1}$, $+12.6$ cal. mole$^{-1}$ deg.$^{-1}$; and $n = 4$, 149 l. mole$^{-1}$, $-0.3$ kcal. mole$^{-1}$, $+8.9$ cal. mole$^{-1}$ deg.$^{-1}$. The pattern of these values resembles that for analogous reactions of the isoelectronic mercury(II) chloride complexes.

A comparison of thermodynamic quantities for the thallium(III)–chloride and mercury(II)–chloride complex ion reactions is of interest since these two metal ions are isoelectronic. Values of equilibrium quotients[4] at 25° and enthalpy changes[5] for the four stepwise mercury(II)–chloride reactions are known. The thallium(III)–chloride reactions are less completely characterized by existing studies.[6–10] Although Peschanski and Valladas-Dubois[7] interpreted potential measurements of the silver–silver chloride electrode in thallium(III)–chloride solutions[11] in terms of species containing as many as six chloride ions per thallium(III) ion, this result is not confirmed by the present study or by other workers.[6,8–10] Horrocks and Voigt[8] suggest that pentachlorothallate(III) ion forms to an appreciable extent at concentrations of chloride ion above ∼0.3 *M*. The spectrum of thallium(III) ion in perchloric acid–hydrochloric acid solutions in the wave length range 220–270 mμ suggests that some particular thallium(III)-chloride species is predominant in the concentration range 0.02–0.96 *M* chloride.[12]

The present paper reports the chloride ion concentration dependence of the electromotive force of the thallium(I)–thallium(III) electrode, the solubility of silver chloride in solutions of thallium(III) ion and chloride ion, and the heat of mixing of solutions containing thallium(III) ion with those containing chloride ion. These data, obtained at 25.0° in solutions of ionic strength 0.50 and 3.00 *M*, gave values of the equilibrium quotients

$$Q_n = [TlCl_n^{+3-n}]/[TlCl_{n-1}^{+4-n}][Cl^-]$$

for the reactions $TlCl_{n-1}^{+4-n} + Cl^- = TlCl_n^{+3-n}$ for $n = 1, 2, 3,$ and 4; values of enthalpy and entropy changes for these reactions were obtained at ionic strength 3.0 *M*.

Because of the high acidity of aquothallium(III) ion ($Q = [TlOH^{2+}][H^+]/[Tl^{3+}] = 7.2 \times 10^{-2}$ mole l.$^{-1}$ at an ionic strength of 3.0 *M*),[13] the hydrogen ion concentration was maintained at 3.0 *M* in studies at $I \cong 3.0$ *M;* under these conditions the concentration ratio $[TlOH^{2+}]/[Tl^{3+}]$ has the value ∼$0.02_4$. If this acid dissociation equilibrium quotient depends upon ionic strength in the same way as the equilibrium quotient for formation of chloroiron(III) ion,[14] appropriate allowance being made for the different values of $\Delta Z^2$ (the sum of squares of charges on product species minus the sum of squares of charges on reactant species), the concentration ratio $[TlOH^{2+}]/[Tl^{3+}]$ would be ∼0.09 at $I = 0.50$ *M* with 0.50 *M* hydrogen ion.

The problem of unscrambling medium effects from effects due to formation of new species, so important in studies of weak complexes, *e.g.*, iron(III)–chloride complexes,[14] is relatively unimportant in the thallium(III)–chloride system, in which very stable complexes are formed. In the present studies a more serious problem is determination of the concentration of uncomplexed chloride ion in solutions of very low stoichiometric concentrations of chloride ion; in such solutions

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(4) (a) L. G. Sillén, *Acta Chem. Scand.*, **3**, 539 (1949); (b) Y. Marcus, *ibid.*, **11**, 599 (1957); (c) L. D. Hansen, R. M. Izatt, and J. J. Christensen, *Inorg. Chem.*, **2**, 1243 (1963).

(5) (a) P. K. Gallagher and E. L. King, *J. Am. Chem. Soc.*, **82**, 3510 (1960); (b) G. N. Malcolm, H. N. Parton, and I. D. Watson, *J. Phys. Chem.*, **65**, 1900 (1961); (c) J. J. Christensen, R. M. Izatt, L. D. Hansen, and J. D. Hale, *Inorg. Chem.*, **3**, 130 (1964).

(6) R. Benoit, *Bull. soc. chim. France*, 518 (1949).

(7) D. Peschanski and S. Valladas-Dubois, *ibid.*, 1170 (1956).

(8) D. L. Horrocks and A. F. Voigt, *J. Am. Chem. Soc.*, **79**, 2440 (1957).

(9) B. Baysal, *Actes Intern. Congr. Catalyse, Paris, 1960 I*, 559 [*Chem. Abstr.*, **56**, 1140*c* (1962).

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

(11) Thallium(III) ion is capable of oxidizing silver, and in unreported experiments we have observed this to occur under conditions of electromotive force measurements on the silver–silver chloride electrode. Presumably this is the cause of the erroneous results of Peschanski and Valladas-Dubois[7]; Benoit[6] used silver electrodes with greater success.

(12) G. Harbottle and R. W. Dodson, *J. Am. Chem. Soc.*, **73**, 2442 (1951).

(13) G. Biedermann, *Arkiv Kemi*, **5**, 441 (1953); *Rec. trav. chim.*, **75**, 716 (1956).

(14) Sr. M. J. M. Woods, O. P., P. K. Gallagher, and E. L. King, *Inorg. Chem.*, **1**, 55 (1962).

essentially all of the chloride ion is associated with thallium(III) ion if the concentration of thallium(III) is high enough ($>6 \times 10^{-4}$ $M$) to give steady potentials in the electromotive force studies. This problem was circumvented in studies of the solubility of silver chloride in solutions containing thallium(III) ion, which provided the best data for evaluation of $Q_1$.

## Experimental Details and Results

**Reagents and Solutions.**—Stock solutions of thallium(III) perchlorate in perchloric acid were prepared starting with G. F. Smith thallium(III) perchlorate reagent. Purification involved precipitation of thallium(III) hydroxide using ammonium hydroxide; this was dissolved in aqueous hydrobromic acid, from which thallium(III) was extracted into diethyl ether. The residue resulting from evaporation of ether was dissolved in water, and thallium(III) was taken through several cycles of hydroxide precipitation, washing, and solution in perchloric acid. Washings were free of bromide ion. The thallium content of stock solutions was determined by first reducing thallium(III) ion with excess sodium sulfite in acidic solution, then removing excess sulfur dioxide by boiling, and finally titrating the resulting thallium(I) with standard potassium bromate solution. Omission of treatment with sodium sulfite allowed evaluation of the thallium(I) content.

Thallium(I) perchlorate was prepared starting with thallium(I) formate (Eastman). Formate was destroyed by fuming in perchloric acid, and the thallium(I) perchlorate residue was recrystallized three times from conductivity water.

The total normality of thallium(III) perchlorate–perchloric acid solutions was determined by passing a portion of solution through an ion-exchange resin in the hydrogen ion form, followed by titration of the resulting perchloric acid solutions with standard base.

All solutions were prepared using doubly-distilled water, the second distillation being from an alkaline permanganate solution using a Barnstead still.

All other chemicals were of reagent grade quality and were used without further purification.

**Solubility Measurements.**—Silver chloride, containing silver-110, was precipitated by the method of Gledhill and Malan.[15] The precipitate was washed ten times with conductivity water, then slurried in conductivity water and stored in the dark. Its solubility was measured at 25° in both 3.0 and 0.50 $M$ perchloric acid solutions containing varying amounts of added chloride ion and/or thallium(III) ion. Aliquots were taken after both 4 and 7 days agitation; equilibrium was attained in the shorter time. Particles of solid silver chloride were removed from saturated solution by filtration with an ultrafine Selas bacteriological sintered glass funnel, which was surrounded by thermostated water. The radioactivity of aliquots of saturated solution, determined with a well-type scintillation counter, was compared with the activity of a standard determined at the same time.

Solubilities measured in solutions containing no thallium(III) ion were used to evaluate both the solubility product appropriate for each ionic strength and also the concentration of chloride ion in the stock solution of perchloric acid. Data from experiments at three different concentrations of added chloride ion ($0–1 \times 10^{-5}$ $M$) at each ionic strength lead to values: $Q_s = [Ag^+][Cl^-] = 0.89 \times 10^{-10}$ mole$^2$ l.$^{-2}$ (3.00 $M$ $HClO_4$), $= 2.38 \times 10^{-10}$ mole$^2$ l.$^{-2}$ (0.50 $M$ $HClO_4$), and $2.6 \times 10^6$ $M$ chloride ion in the 3.00 $M$ perchloric acid. The average differences between the observed solubility in these six experiments and the values calculated using these parameters were 2% (3.00 $M$ $HClO_4$) and 6% (0.50 $M$ $HClO_4$). The work of Berne and Leden[16] suggests the concentration of neutral silver chloride in these saturated solutions to be ~1–2% of the concentration of silver ion; this species was ignored in these calculations.

Values of the solubility of silver chloride in solutions containing thallium(III) ion allow calculation of $\bar{n}$, the average number of chloride ions bound per thallium(III) ion

$$\bar{n} = \frac{C_{Cl} + S - Q_s/S}{C_{III}}$$

in which $C_{Cl}$ and $C_{III}$ are the stoichiometric concentrations of chloride ion and thallium(III), respectively, and $S$ is the solubility of silver chloride. Eleven solutions of thallium(III) ($C_{III} = 0.0033–0.010$ $M$) in 3.00 $M$ perchloric acid were studied; values of $\bar{n}$ were in the range 0.36–0.76. Four solutions of thallium(III) ($C_{III} = 0.010$ $M$) in 0.50 $M$ perchloric acid were studied; values of $\bar{n}$ were in the range 0.39–0.74.

From these $\bar{n}$ data values of $Q_1$ and $Q_2$ were obtained by high-speed digital computation.[17] The values of $Q_1$ so obtained are $1.46 (\pm 0.034) \times 10^7$ and $5.22 (\pm 0.19) \times 10^6$ l. mole$^{-1}$ for ionic strength 3.0 and 0.5 $M$, respectively. These are considered better values than those derived from the electromotive force measurements. The value of $Q_2$ derived from the solubility measurements, $1.9 \times 10^5$ l. mole$^{-1}$ at both ionic strengths, is much less reliable since the maximum values of $\bar{n}$ were less than unity in the solubility studies. Values of $\bar{n}$ calculated using these parameters generally agree with the observed values to within ~0.01 unit.

**Electromotive Force Measurements.**—The apparatus and procedures used were very similar to those employed in the iron(III)–chloride study.[14] Each half-cell compartment, equipped with a shiny platinum electrode, contained thallium(I) perchlorate, thallium(III) perchlorate, and perchloric acid. Measured volumes of solution containing chloride ion were added to one half-cell. This chloride-containing solution had the same composition as that already present in the cell except that perchloric acid was replaced partially by hydrochloric acid, and, therefore, the stoichiometric concentrations of thallium(I), thallium(III), and hydrogen ion remained constant. The change of ionic strength due to complex ion formation was negligible since the thallium(III) concentration was $\sim 10^{-3}$ $M$ in most experiments.

The reaction occurring with passage of 2 faradays of current is

$$Tl^{3-}(C_{III}) + Tl^{+}(C_{I}\alpha_{10}([Cl^-])) = Tl^{3+}(C_{III}\alpha_{30}([Cl^-])) + Tl^{+}(C_I) \pm \text{ion transfer}$$

in which $C_I$ is the stoichiometric concentration of thallium(I), $\alpha_{10}([Cl^-])$ is equal to $[Tl^+]/C_I$, and $\alpha_{30}([Cl^-]) = [Tl^{3+}]/C_{III}$. The quantity of interest, $\alpha_{30}([Cl^-])$, which is related to equilibrium quotients for thallium(III)–chloride complex ion formation reactions

$$\{\alpha_{30}([Cl^-])\}^{-1} = 1 + Q_1[Cl^-] + Q_1Q_2[Cl^-]^2 + \ldots$$

can be obtained from the electromotive force of the cell by the relationship

$$-\log \alpha_{30}([Cl^-]) = \frac{2E}{0.05916} - \log \alpha_{10}([Cl^-])$$

if it is assumed both that the liquid junction potential is negligible and that the activity coefficients of uncomplexed thallium(I) ion and thallium(III) ion are constant with substitution of perchlorate ion by chloride ion. The correction term $\alpha_{10}([Cl^-])$ is

$$\{\alpha_{10}([Cl^-])\}^{-1} = 1 + Q'_1[Cl^-] + Q'_1Q'_2[Cl^-]^2$$

in which $Q'_i = [TlCl_i{}^{1-i}]/[TlCl_{i-1}{}^{2-i}][Cl^-]$. For correcting electromotive force values obtained at ionic strength of 3.00 $M$, a value $Q'_1 = 1.0$ l. mole$^{-1}$ determined at ionic strength 4.00 $M$ by Nilsson[18] was used. The value of $Q'_1$ for ionic strength 0.50 $M$

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(15) J. A. Gledhill and G. McP. Malan, *Trans. Faraday Soc.*, **48**, 258 (1952).

(16) E. Berne and I. Leden, *Svensk Kem. Tidskr.*, **65**, 88 (1953).

(17) Z Z. Hugus, Jr., "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, pp. 379–390.

(18) R. Nilsson, *Arkiv Kemi*, **10**, 363 (1956).

was obtained by correcting the value $K^0_1 = 4.0$, obtained by Hu and Scott,[19] to $Q'_1 = 1.8$ l. mole$^{-1}$ by using the mean stoichiometric activity coefficient of sodium chloride at this ionic strength. Hu and Scott obtained a value $K^0_2 = 0.37$, and since the value of $\Delta Z^2$ is zero for the reaction $TlCl + Cl^- = TlCl_2^-$, this value was used for $Q'_2$ at both ionic strength 0.50 and 3.00 *M*.

Data relevant to evaluation of the maximum number of chloride ions bound by thallium(III) were obtained at both ionic strength 0.50 and 3.00 *M*. At chloride ion concentrations for which the predominant thallium(III) species is tetrachlorothallate(III) ion, the value of $\log^{-1}(2E/0.05916)/([Cl^-]^4\alpha_{10}([Cl^-]))$ is equal to $Q_1Q_2Q_3Q_4$. This function was calculated using data obtained in one experiment at ionic strength 3.00 *M* and in three experiments at ionic strength 0.50 *M*. At 3.00 *M* ionic strength, fifteen readings of electromotive force at concentrations of chloride ion between 1.24 and 0.03 *M* lead to values of $\log^{-1}(2E/0.05916)/([Cl^-]^4\alpha_{10}([Cl^-]))$ all within 5% of $2.93 \times 10^{18}$ l.$^4$ mole$^{-4}$. The average deviation of individual values from this average value was $0.08 \times 10^{18}$ l.$^4$ mole$^{-4}$. The three experiments at ionic strength 0.50 *M* were made at thallium(III) concentrations of $6.12 \times 10^{-4}$, $1.02 \times 10^{-3}$, and $2.04 \times 10^{-3}$ *M*. The average values of $\log^{-1}(2E/0.05916)/([Cl^-]^4\alpha_{10}([Cl^-]))$ obtained in each experiment, with the number of points, the chloride ion concentration range, and the average deviation given in parentheses are $2.02 \times 10^{16}$ l.$^4$ mole$^{-4}$ (14 points, 0.15–0.46 *M* chloride ion, average deviation $\pm 0.02 \times 10^{16}$ l.$^4$ mole$^{-4}$), $2.24 \times 10^{16}$ l.$^4$ mole$^{-4}$ (22 points, 0.097–0.46 *M* chloride ion, average deviation $\pm 0.02 \times 10^{16}$ l.$^4$ mole$^{-4}$), and $2.08 \times 10^{16}$ l.$^4$ mole$^{-4}$ (17 points, 0.097–0.41 *M* chloride ion, average deviation $\pm 0.04 \times 10^{16}$ l.$^4$ mole$^{-4}$), respectively.

The approximate constancy of this function over a wide range of chloride ion concentration proves that species with five and/or six chloride ions per thallium(III) *are not predominant* in these solutions. (Using equilibrium quotients presented by Peschanski and Valladas-Dubois,[7] one calculates for 0.20 *M* chloride ion 0.3% tetrachlorothallate(III) ion, 7.3% pentachlorothallate(III) ion, and 92.4% hexachlorothallate(III) ion as the distribution of thallium(III) species.)

Since the three experiments at ionic strength 0.50 *M* were run at different concentrations of thallium(III), the absence of a monotonic trend in the values $2.02 \times 10^{16}$, $2.24 \times 10^{16}$, and $2.08 \times 10^{16}$ l.$^4$ mole$^{-4}$ for the function being considered indicates that the predominant thallium(III) species in these solutions are monomeric. This thallium(III) concentration range ($6 \times 10^{-4}$ to $2 \times 10^{-3}$ *M*) is much lower than that for which it was concluded that dimeric species exist.[20]

The electromotive force data at each ionic strength were treated by high-speed digital computation in which both the concentration of uncomplexed chloride ion and the equilibrium quotients $Q_n$ ($n = 1$ to 4) were obtained by iteration.[17] One calculation was carried out with $Q_1$ fixed at the value obtained from solubility measurements. From 96 data points at $I = 3.0$ *M*, the values of $Q_2$, $Q_3$, and $Q_4$ so derived are $2.76\ (\pm 0.5) \times 10^5$, $3.55\ (\pm 0.9) \times 10^3$, and $1.49\ (\pm 0.3) \times 10^2$ l. mole$^{-1}$, respectively. From 106 data points at $I = 0.50$ *M*, the values of $Q_2$, $Q_3$, and $Q_4$ are $1.25\ (\pm 0.1) \times 10^5$, $4.82\ (\pm 0.6) \times 10^2$, and $65.3\ (\pm 7)$ l. mole$^{-1}$, respectively. In another calculation, all parameters were determined by electromotive force data alone. The values obtained from this calculation at $I = 3.0$ *M* are $Q_1 = 5.13\ (\pm 0.6) \times 10^7$, $Q_2 = 1.96\ (\pm 0.3) \times 10^5$, $Q_3 = 1.17\ (\pm 0.2) \times 10^3$, and $Q_4 = 1.86\ (\pm 0.2) \times 10^2$ l. mole$^{-1}$, and at $I = 0.5$ *M* are $Q_1 = 1.06\ (\pm 0.03) \times 10^6$, $Q_2 = 9.03\ (\pm 0.4) \times 10^4$, $Q_3 = 3.09\ (\pm 0.1) \times 10^2$, and $Q_4 = 69.6\ (\pm 3)$ l. mole$^{-1}$.

The concentration of uncomplexed chloride ion, the important variable, is relatively uncertain in electromotive force experiments at low chloride ion concentration; at the beginning of an experiment when $C_{III} \gg C_{Cl}$, over 99.9% of the chloride ion is tied up as complex. On the other hand, the concentration of uncomplexed chloride is obtained directly in the solubility measurements. Therefore, the equilibrium quotients $Q_2$, $Q_3$, and $Q_4$ obtained from electromotive force data by fixing $Q_1$ at the value obtained from solubility measurements are considered more reliable.

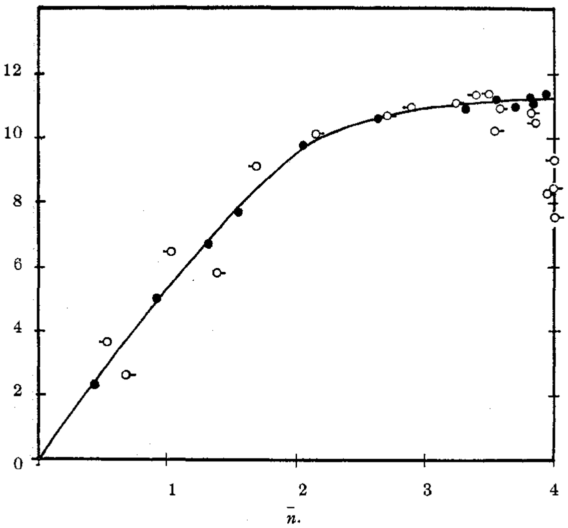

Fig. 1.—Net heat evolved in mixing thallium(III) perchlorate solution and hydrochloric acid solution. Ordinate: net heat in kcal./mole; abscissa: $\bar{n}$, calculated using best values of $Q_n$ ($n$ = 1–4); symbols: ●, series with 3.20 *M* HCl in bulb (the solid line was calculated using parameters given in the text; these were obtained by fitting the theoretical curve to these points); ⊸, series with 0.427 *M* $Tl(ClO_4)_3$ + 5.41 *M* $HClO_4$ in bulb; ⊸, series with 0.351 *M* $Tl(ClO_4)_3$ + 4.45 *M* $HClO_4$ in bulb.

The values of $\beta_4 = (Q_1Q_2Q_3Q_4)$ obtained as the product of these "best" values of equilibrium quotients for the stepwise reactions ($2.12\ (\pm 0.15) \times 10^{18}$ l.$^4$ mole$^{-4}$ at $I = 3.0$ *M* and $2.05\ (\pm 0.07) \times 10^{16}$ l.$^4$ mole$^{-4}$ at $I = 0.50$ *M*) are more reliable than values obtained in the correlations, already discussed, which demonstrated that species containing more than four chloride ions per thallium(III) ion do not form to an appreciable extent. In the latter correlations, no account was taken of appreciable trichlorothallium(III) in the solutions being considered.

**Calorimetric Experiments.**—Calorimetric experiments, run at $I = 3.0$ *M* and ~25°, involved equipment and procedures already described.[5a,14] Twenty-four experiments were performed in which a bulb containing thallium(III) perchlorate and perchloric acid was broken into a solution of perchloric acid and hydrochloric acid, and twelve experiments were performed in which a bulb containing hydrochloric acid was broken into a solution of thallium(III) perchlorate and perchloric acid. Corresponding to each type of experiment, appropriate runs were performed to determine the heat of dilution of thallium(III) perchlorate–perchloric acid or of hydrochloric acid with 3.00 *M* perchloric acid. The same heat of dilution was assumed in experiments involving both thallium(III) ion and chloride ion. The net heat attributable to the formation of thallium(III)–chloride complexes was comparable to the correction for the heat of dilution in experiments involving thallium(III) perchlorate–perchloric acid in the bulb; the correction was much smaller in experiments in which hydrochloric acid was in the bulb; for this reason these experiments are considered more reliable.

Figure 1 shows the net heat evolved per mole of thallium(III) as a function of $\bar{n}$. The value of $\bar{n}$ for each experimental solution was calculated using $Q_1 = 1.46 \times 10^7$, $Q_2 = 2.76 \times 10^5$, $Q_3 = 3.55 \times 10^3$, and $Q_4 = 149$ l. mole$^{-1}$. Stepwise enthalpy changes were calculated using a high-speed digital computer. The experiments in which hydrochloric acid was in the bulb give the values: $\Delta H_1 = -5.45 \pm 0.14$, $\Delta H_2 = -4.40 \pm 0.26$, $\Delta H_3 = -1.1 \pm 0.3$, and $\Delta H_4 = -0.3 \pm 0.3$ kcal. mole$^{-1}$. The experimental

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[19] K. Hu and A. B. Scott, *J. Am. Chem. Soc.*, **77**, 1380 (1955).

[20] B. N. Figgis, *Trans. Faraday Soc.*, **55**, 1075 (1959); this study of the effect of chloride ion on chemical shifts of $Tl^{205}$ nuclear magnetic resonance was interpreted in terms of the existence of a very stable species, $Tl_2Cl_9^{3-}$. Since these studies were carried out at thallium(III) concentrations in excess of 0.28 *M*, the interpretation is not inconsistent with our study.

Table I

Thermodynamic Quantities[a] Associated with the Reactions

$TlCl_{n-1}^{4-n} + Cl^- = TlCl_n^{3-n}$ ($n$ = 1, 2, 3, and 4), 25°

| | $n$ = 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| | | $I = 0.50\ M$ | | |
| $Q_n \times$ mole l.$^{-1}$ | $5.22 \times 10^6$ | $1.25 \times 10^5$ | 482 | 65.3 |
| | | $I = 3.0\ M$ | | |
| $Q_n \times$ mole l.$^{-1}$ | $1.46 \times 10^7$ | $2.76 \times 10^5$ | $3.55 \times 10^3$ | 149 |
| $-\Delta H_n \times$ mole kcal.$^{-1}$ | 5.45 | 4.40 | 1.1 | 0.3 |
| $\Delta S^\circ_n \times$ mole deg. cal.$^{-1}$ | 14.5 | 10.1 | 12.6 | 8.9 |
| | | $I = 0$ | | |
| $K^\circ_n$ (est.) | $5.3 \times 10^7$ | $5.8 \times 10^5$ | $1.0 \times 10^3$ | 65.3 |

[a] Equilibrium quotients are based on the molar concentration scale, and the "standard" entropy changes correspond to a standard state with solute species at a hypothetical ideal 1 $M$ concentration in aqueous solution of ionic strength = 3.0 $M$. For uncertainties in values of $Q_n$ and $\Delta H_n$, see the text; the uncertainties in $\Delta S^\circ_n$ are ±0.5, ±0.9, ±1.0, and ±1.0 cal. mole$^{-1}$ deg.$^{-1}$, respectively.

heats of the other series deviate from values calculated using these values of $\Delta H_n$ by a disappointingly large amount. (Taking data from these other series into account in the calculation of values of $\Delta H_n$ raises their uncertainties greatly and makes reaction 4 endothermic. The values based on all the data are $\Delta H_1 = -5.5 \pm 0.6$, $\Delta H_2 = -4.1 \pm 1.0$, $\Delta H_3 = -2.6 \pm 1.0$, and $\Delta H_4 = +2.4 \pm 0.8$ kcal. mole$^{-1}$.)

## Discussion

A summary of thermodynamic quantities associated with the stepwise association reactions is given in Table I. Included are estimates of the equilibrium constants $K^0_n$ for zero ionic strength, obtained by multiplication of values of $Q_n$ for $I = 0.50\ M$ by $(0.68)^{-\Delta Z^2}$, in which 0.68 is the mean activity coefficient of sodium chloride at $I = 0.50\ M$.

For each value of $n$, the value of $\Delta Z^2$ for a reaction of the thallium(III)–chloride series is different from that for a reaction of the mercury(II)–chloride series. To make a rational comparison of corresponding reactions of these two metal ions, values of $K^0$ should be compared. Equilibrium quotients obtained at ionic strength 0.5 $M$ for mercury(II)–chloride reactions[4] were corrected to zero ionic strength by the same procedure. Comparison of the thallium(III)–chloride and mercury(II)–chloride systems is made by comparison of $\beta_n$ values ($\beta_n = Q_1Q_2 \cdots Q_n$). Values of $\beta_n(\text{Tl}^{\text{III}})/\beta_n(\text{Hg}^{\text{II}})$ for zero ionic strength are $2.0$, 0.18, 21, and 26 for $n$ = 1, 2, 3, and 4, respectively. The expected greater affinity of the more highly charged metal ion for chloride ion is observed, *except for the dichloro species*. Neutral mercury(II) chloride is, of course, exceptionally stable relative to species containing one more and one less chloride ions per mercury(II); the reaction

$$2HgCl_2 = HgCl^+ + HgCl_3^-$$

has an equilibrium constant of $1.4 \times 10^{-6}$, ~$10^6$-fold smaller than the statistically expected value.[21] Although not as striking a value, the equilibrium constant for the analogous reaction of dichlorothallium(III) ion is very small, $K = [TlCl^{2+}][TlCl_3]/[TlCl_2^+]^2 = 1.7 \times 10^{-3}$, which indicates special stability for dichlorothallium(III) ion also. Presumably dichlorothallium(III) ion has the linear configuration Cl–Tl–Cl[10] analogous to that of dichloromercury(II),[22] including strong interaction with solvent water.[5a]

Rational correlation of entropy changes in the successive thallium(III)–chloride reactions should involve values corrected for the change in symmetry number of the thallium(III) reactant and product species, $\Delta S^\circ_{\text{cor}} = \Delta S^\circ + R \ln \sigma_P/\sigma_R$,[23] in which $\sigma_P$ and $\sigma_R$ are the symmetry numbers of product and reactant, respectively. If one assumes distorted octahedral configurations[24] for species containing zero, one, two, and three chlorides, with symmetry numbers 8, 4, 8, and 2, respectively, and a tetrahedral configuration with symmetry number 12 for the species containing four chlorides, the corrected values of $\Delta S^\circ_n$ become 13.1, 10.7, 9.8, and 12.5, cal. mole$^{-1}$ deg.$^{-1}$ for $n$ = 1, 2, 3, and 4, respectively. This trend is qualitatively similar to that observed for the mercury(II) chloride reactions; in particular, the value for $n = 4$ is abnormally high relative to values expected from a simple correlation of $\Delta S^\circ$ with $\Delta Z^2$.[25] An abnormally positive value of $\Delta S^\circ$ for reaction 4 is consistent with the change of coordination number assumed to occur in this reaction.

$$trans\text{-}Tl(OH_2)_3Cl_3 + Cl^- = TlCl_4^- + 3H_2O$$

Since the abnormally positive value for $\Delta S^\circ_{4,\text{cor}}$ is due partially to the high symmetry assumed for tetrachlorothallium(III) ion, this correlation suggests mildly, but does not prove, that a decrease in coordination number, with its concomitant liberation of water molecules, occurs in this reaction.

The pattern of enthalpy changes for stepwise reaction of thallium(III) ion and chloride ion, like the entropy changes, resembles that for the analogous reactions of mercury(II) ion (−5.9, −6.9, −2.2, and +0.1 kcal./mole for reactions with $n$ = 1, 2, 3, and 4,

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[21] Since mercury(II)-chloride complexes are not a series of species in which a particular number of equivalent "sites" are occupied by water or chloride, a straightforward statistical prediction of this equilibrium constant cannot be made.

[22] C. L. van Panthaleon van Eck, H. B. M. Wolters, and W. J. M. Jaspers, *Rec. trav. chim.*, **75**, 802 (1956); C. L. van Panthaleon van Eck, Thesis, Leiden, 1958.

[23] S. W. Benson, *J. Am. Chem. Soc.*, **80**, 5151 (1958).

[24] L. E. Orgel, *J. Chem. Soc.*, 4186 (1958).

[25] E. L. King, *J. Phys. Chem.*, **63**, 1070 (1959); E. L. King and P. K. Gallagher, *ibid.*, **63**, 1073 (1959).

respectively).[5] The first two reactions have relatively negative enthalpy changes which are close to one another, and the last two reactions are considerably less exothermic. That reaction 2 is more exothermic and reaction 3 less exothermic than might be expected on the basis of a smooth trend with less heat evolution in each successive step[26] is consistent with the special stability of the dichloro species, which is produced in reaction 2 and consumed in reaction 3.

The complexes of thallium(III) ion and chloride ion are very much more stable than are complexes of chloride ion and transition metal ions of charge 3+, *e.g.*, chromium(III) ion[27] and iron(III) ion.[14] At $I = 3\ M$, values of $Q_1$ for reactions of these two metal ions are ~0.2 and 6.6 l. mole$^{-1}$, respectively, ~$10^7$-fold smaller than the value of $Q_1$ for reaction of thallium(III) ion and chloride ion. This enormous difference, arising presumably because of differences in the type of bonding, is due to the difference in enthalpy changes; the entropy changes are similar, +17.2, +16.1, and +14.5 cal. mole$^{-1}$ deg.$^{-1}$ for the reaction $M^{3+} + Cl^- = MCl^{2+}$ for $M^{3+} = Cr^{3+}$, $Fe^{3+}$, and $Tl^{3+}$, respectively. The values of $\Delta S°$ for reactions of different metal ions with a particular anion seem, therefore, to depend largely upon the value of $\Delta Z^2$. The small variation of these values may reflect an expected less positive partial molal entropy for a complex with a stronger metal-ligand bond.

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[26] W. M. Latimer and W. L. Jolly, *J. Am. Chem. Soc.*, **75**, 1548 (1953).
[27] H. S. Gates and E. L. King, *ibid.*, **80**, 5011 (1958).

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# The Thermal Decomposition of Zinc Acetylacetonate Hydrate

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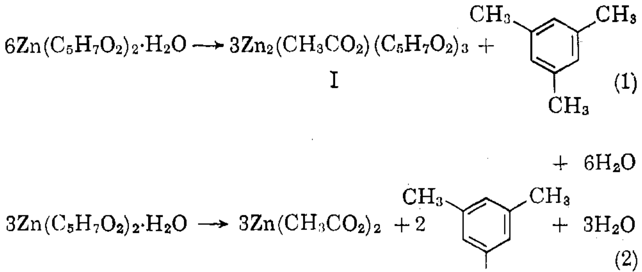
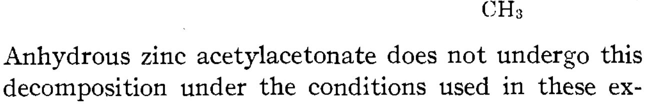
Zinc acetylacetonate hydrate undergoes on heating a decomposition to form mesitylene and acetate ions, the latter being found in the novel compound $Zn_2(CH_3CO_2)(C_5H_7O_2)_3$. Anhydrous zinc acetylacetonate does not undergo this decomposition under analogous experimental conditions. The acetate compound and an analogous benzoate may also be obtained by an independent route.

Although zinc acetylacetonate is known to have low thermal stability,[2] little attention has been paid to its decomposition products. Some volatile decomposition products from a series of other metal acetylacetonates were shown by von Hoene[3] to include acetone, carbon dioxide, acetylacetone, and methane.

We have found that zinc acetylacetonate hydrate at elevated temperatures, preferably at 130° in an inert solvent, undergoes a remarkable decomposition reaction according to the equations



(1)



(2)

Anhydrous zinc acetylacetonate does not undergo this decomposition under the conditions used in these experiments. When the reaction is carried out in open systems such as refluxing xylene, only part of the starting material decomposes according to (1) to yield the acetate-containing compound I, while its major part is found as anhydrous zinc acetylacetonate. When the escape of water is prevented by the use of a sealed tube, the reaction proceeds further to form zinc acetate (eq. 2).

The volatile products of the reaction were collected, separated, and analyzed using vapor phase chromatographic and infrared techniques. Mesitylene (1,3,5-trimethylbenzene) was shown to be the main product along with acetone and traces of acetylacetone. In one reaction, in which xylene was used as a solvent, a mixture of mesitylene and its isomer pseudocumene (1,2,4-trimethylbenzene) was noted.

Some ambiguity is connected with the acetate-containing compound I. While its empirical formula is well confirmed (see Experimental part), its structure remains an open question. Molecular weight determinations in chloroform, dioxane, and camphor gave ambiguous results. Conductivity measurements carried out in chloroform and nitrobenzene indicated little or no ionic dissociation taking place in these solvents. The compound may be recovered unchanged from solutions

[1] National Academy of Sciences Research Fellow.
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[3] J. von Hoene, R. G. Charles, and W. M. Hickam, *ibid.*, **62**, 1098 (1958).