

Thermodynamic Studies of Thallium Halide Formation in Nonaqueous Solvents

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The differences in the order of stability among halide ions for metal halogeno-complexes in nonaqueous solvents and water are examined by means of the thermodynamic constants for the formation of thallium halides of transfer from water to *N,N*-dimethylformamide (DMF) and propylene carbonate (PC). The thermodynamic constants for the formation of thallium halides were calculated from the solubility products of thallium halides. The differences in the order of stability for thallium halides were found to be dependent mainly on the enthalpy changes for the formation of thallium halides of transfer from water to DMF and PC, while the enthalpy changes of transfer for thallium halides are themselves largely influenced by the enthalpy changes for halide ions of transfer from water to DMF and PC.

In previous papers,^{1–4} the formation of metal halogeno-complexes was investigated potentiometrically in dimethyl sulfoxide, *N,N*-dimethylformamide, and propylene carbonate. The order of stability for metal halogeno-complexes (halogeno-cadmium, -lead, -copper and -zinc complexes⁵) among halide ions in nonaqueous solvents was found to be different from that in water. The classification of metals according to their complexation with halide ions is shown in Table 1. The solid line indicates the classification by Ahrlund⁶ in water, while the broken line indicates the classification obtained by our studies in nonaqueous solvents.⁷ The stability of the halogeno-complexes on outside metals of the triangle in Table 1 decreases in the order of $\text{Cl}^- > \text{Br}^- > \text{I}^-$. However, the stability on inside metals is the reversed order; $\text{I}^- > \text{Br}^- > \text{Cl}^-$.

The purpose of the present paper is to elucidate the reason for differences in the stability on metal halogeno-complexes in *N,N*-dimethylformamide, propylene carbonate, and water from the thermodynamic constants for the formation of thallium halides.

Experimental

Materials. The purification of *N,N*-dimethylformamide (DMF) and propylene carbonate (PC), the preparation and purification of tetraethylammonium perchlorate, and the preparation of the saturated thallium amalgam have been described elsewhere.^{8,9} The tetraethylammonium halides and thallium(I)perchlorate (TlClO_4) were obtained commercially and were purified by recrystallization with water-ethanol or ethanol-ethyl acetate mixtures. The electrolytes were dried in a vacuum oven for 2 d in the temperature range of 60–70 °C.

Procedure. The solubilities of thallium(I)halides (TlX) were determined by means of potentiometric titration. A solution of $10^{-3} \text{ mol dm}^{-3}$ of TlClO_4 was titrated with a solution of $5 \times 10^{-2} \text{ mol dm}^{-3}$ of TlX . The indicator electrode was a saturated thallium amalgam electrode, while the reference electrode was an aqueous saturated calomel electrode (SCE) equipped with a nonaqueous salt bridge.⁹ The experimental device is shown in Fig. 1. The potential of the cell was measured on a Hewlett-Packard Model 34703A ohm meter. Each temperature was controlled to an accuracy of 0.1 °C.

Results and Discussion

The titration curves for Tl^+ with Cl^- in PC at 10, 20, and 25 °C are shown in Fig. 2. One well-defined equivalent point at $C_{\text{Cl}^-}/C_{\text{Tl}^+} = 1$ (mol ratio) was found in each titration curve (Fig. 2). The precipitation

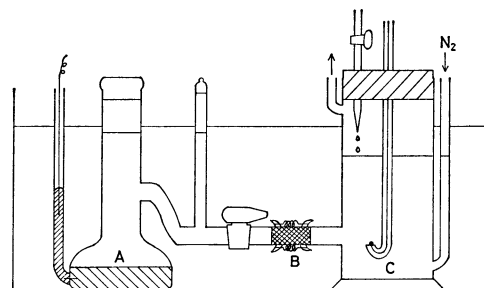


Fig. 1. Experimental device.

A: SCE, B: salt bridge composed of DMF–water mixture containing 0.5 mol dm^{-3} tetraethylammonium perchlorate and aqueous solution containing 1 mol dm^{-3} NaCl ,⁵ C: thallium amalgam electrode.

TABLE 1. CLASSIFICATION OF METALS ACCORDING TO THEIR COMPLEXATION WITH HALIDE IONS

Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As
Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb
W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi

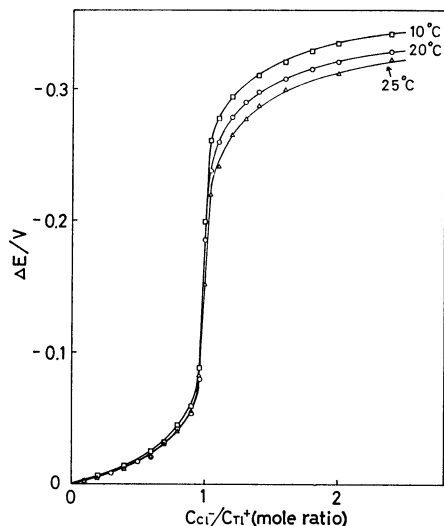


Fig. 2. Potentiometric titration curves for Tl^+ with Cl^- in PC at 10, 20, and 25 °C.

ΔE : potential shift caused by addition of Cl^- , tetraethylammonium perchlorate: 0.1 mol dm^{-3} .

appeared in the range from 10 to 30 °C soon after halide ions were added. This fact shows that the precipitation of TlX occurred as is shown in Eq. 1. In previous papers,¹⁰ it was confirmed that the



Nernst equation was obeyed in DMF and PC containing TlClO_4 in the range from 1×10^{-4} to 2×10^{-3} mol dm^{-3} . The solubility products of TlX , assuming no complex formation of Tl^+ with Cl^- , and using the activity coefficients of TlX in DMF and PC,¹⁰ were calculated from the titration curves on the basis of the Nernst equation. The order of the solubility products of TlX in DMF and PC is; $\text{TlI} > \text{TlBr} > \text{TlCl}$. The enthalpy changes ($\Delta H^\circ_{(\text{TlX})}$) for the formation of TlX were obtained graphically from the slope of the $\log K_{s0}$ vs. $1/T$ plot (Vant Hoff plot, Eq. 2), where the K_{s0}

$$\log K_{s0} = \frac{\Delta H^\circ_{(\text{TlX})}}{2.303R} \frac{1}{T} + \text{const.} \quad (2)$$

are solubility products. Figure 3 shows the plots of $\log K_{s0}$ vs. $1/T$ in DMF, PC, and water. The solubility products in water were obtained by means of the solubilities quoted from the literature.^{11,12} The order of the solubility products in water is the reverse of that DMF and PC, as is shown in Fig. 3. The values of $\log K_{s0}$ for TlX in DMF and PC at 25 °C are given in Table 2. The values of $\log K_{s0}$ in DMF are in fair agreement with those of the literature.^{10,13} However, the $\log K_{s0}$ values in PC are not in agreement with those of Salomon.¹⁴ It is presumed that this disagreement arises from the use of the lithium-lithium halides reference electrode, since lithium metal may react with PC.¹³

The free-energy changes ($\Delta G^\circ_{(\text{TlX})}$) for the formation of TlX can be correlated to $\log K_{s0}$ with the temperature in Eq. 3, and

$$\Delta G^\circ_{(\text{TlX})} = 2.303RT \log K_{s0} \quad (3)$$

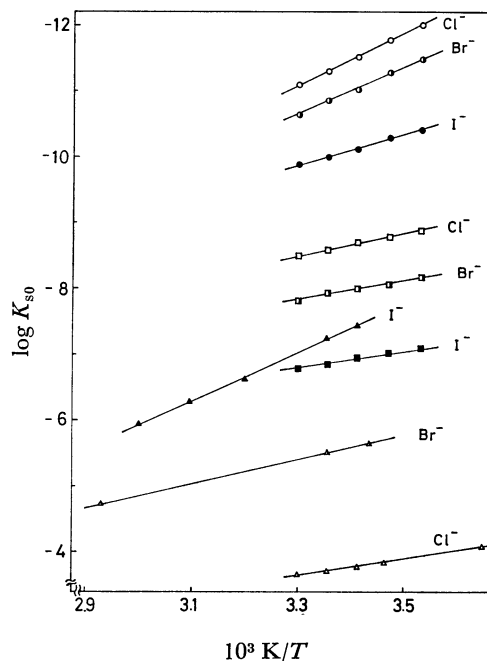


Fig. 3. Plot of $\log K_{s0}$ vs. $1/T$ for thallium halides in DMF, PC, and water.

(□ □ □): DMF, (○ ● ●): PC, (△ △ △): water.

TABLE 2. LOGARITHMS OF SOLUBILITY PRODUCTS FOR TlX AT 25 °C

Solvent	TlX	$\log K_{s0}$			
DMF	TlCl	-8.58	-8.58 ^{a)}	-9.0 ± 0.5 ^{b)}	
	TlBr	-7.94	-8.13 ^{a)}		
	TlI	-6.86	-7.06 ^{a)}		
PC	TlCl	-11.31	-11.30 ^{a)}	-12.39 ^{c)}	-10.6 ^{d)}
				-12.4 ± 0.5 ^{b)}	
	TlBr	-10.84	-10.96 ^{a)}	-12.66 ^{c)}	-12.0 ^{d)}
	TlI	-9.99	-9.84 ^{a)}	-12.22 ^{c)}	-11.4 ^{d)}

a) Ref. 10. b) Ref. 13. c) Ref. 14. d) F. G. K. Baucke and C. W. Tobias, *J. Electrochem. Soc.*, **116**, 34 (1969). Approximate data obtained by emission spectroscopy.

TABLE 3. THERMODYNAMIC CONSTANTS FOR FORMATION OF THALLIUM HALIDES IN DMF, PC, AND WATER AT 25 °C

Solvent	TlX	$\frac{\Delta G^\circ_{(\text{TlX})}}{\text{kJ mol}^{-1}}$	$\frac{\Delta H^\circ_{(\text{TlX})}}{\text{kJ mol}^{-1}}$	$\frac{T\Delta S^\circ_{(\text{TlX})}}{\text{kJ mol}^{-1}}$
DMF	TlCl	-48.98	-30.51	+18.46
	TlBr	-45.33	-29.38	+15.95
	TlI	-39.14	-26.86	+12.28
PC	TlCl	-64.51	-77.33	-12.82
	TlBr	-61.85	-70.40	-8.55
	TlI	-56.98	-46.62	+10.36
Water	TlCl	-21.34	-26.30	-4.97
	TlBr	-31.43	-34.57	-3.13
	TlI	-41.36	-71.05	-29.69

the entropy changes ($T\Delta S^\circ_{(\text{TlX})}$) were calculated from the $\Delta H^\circ_{(\text{TlX})}$ and $\Delta G^\circ_{(\text{TlX})}$. These thermodynamic

constants in DMF and PC were compared with those in water. The thermodynamic constants in DMF, PC, and water at 25 °C are given in Table 3. The thermodynamic constants in water, in the same manner as with DMF and PC, were obtained graphically. In Table 3, the order of the stability of TIX with $\Delta G^\circ_{\text{tr(TIX)}}$ in DMF and PC is found to be $\text{TlCl} > \text{TlBr} > \text{TlI}$, while it is $\text{TlI} > \text{TlBr} > \text{TlCl}$ in water. Accordingly, the results in DMF and PC do not give support to the classification of the thallium ion obtained by Ahrland.⁶⁾ The reason for difference in stability in nonaqueous solvents and water was investigated by means of the thermodynamic constants for the formation of TIX of the transfer from water to DMF and PC. These constants, $\Delta G^\circ_{\text{tr(TIX)}}$, $\Delta H^\circ_{\text{tr(TIX)}}$ and $T\Delta S^\circ_{\text{tr(TIX)}}$, are listed in Table 4. From the values of $\Delta G^\circ_{\text{tr(TIX)}}$, it is manifest that TlCl becomes the most stable compound among the TIX compounds. The differences in $\Delta H^\circ_{\text{tr(TIX)}}$ and $T\Delta S^\circ_{\text{tr(TIX)}}$ between TlCl and TlI are -48.40 and $-18.54 \text{ kJ mol}^{-1}$ for transfer from water to DMF, and -75.46 and $-47.90 \text{ kJ mol}^{-1}$ for transfer from water to PC, respectively. Therefore, it was found that the enthalpy changes in transfer from water to DMF and PC contribute much to the free-energy changes of the transfer.

The thermodynamic constants, $\Delta G^\circ_{\text{tr(TIX)}}$, $\Delta H^\circ_{\text{tr(TIX)}}$ and $T\Delta S^\circ_{\text{tr(TIX)}}$, were compared with those of halide ions (X^-) for transfer from water to DMF and PC. These constants, $\Delta G^\circ_{\text{tr}}$, $\Delta H^\circ_{\text{tr}}$, and $T\Delta S^\circ_{\text{tr}}$, with crystal ionic radii of X^- , are given in Table 5. The $\Delta G^\circ_{\text{tr}}$ were calculated by the use of the medium effects^{10,15)} in Eq. 4.

$$\Delta G^\circ_{\text{tr}} = 2.303RT \log_{m71} \quad (4)$$

TABLE 4. THERMODYNAMIC CONSTANTS FOR FORMATION OF THALLIUM HALIDES OF TRANSFER FROM WATER TO DMF AND PC AT 25 °C

Transfer	TIX	$\Delta G^\circ_{\text{tr(TIX)}}$ kJ mol ⁻¹	$\Delta H^\circ_{\text{tr(TIX)}}$ kJ mol ⁻¹	$T\Delta S^\circ_{\text{tr(TIX)}}$ kJ mol ⁻¹
From water to DMF	TlCl	-27.64	-4.21	+23.43
	TlBr	-13.89	+5.19	+19.08
	TlI	+2.22	+44.19	+41.97
From water to PC	TlCl	-43.18	-51.03	-7.85
	TlBr	-30.41	-35.83	-5.42
	TlI	-15.62	+24.43	+40.05

TABLE 5. THERMODYNAMIC CONSTANTS FOR HALIDE IONS OF TRANSFER FROM WATER TO DMF AND PC AT 25 °C

Transfer	X ⁻	$r(\text{\AA})^a$	$\log m71$	$\Delta G^\circ_{\text{tr}}$ kJ mol ⁻¹	$\Delta H^\circ_{\text{tr}}$ kJ mol ⁻¹	$T\Delta S^\circ_{\text{tr}}$ kJ mol ⁻¹
From water of DMF	Cl ⁻	1.81	+6.51	+37.15	+21.17	-15.98
	Br ⁻	1.96	+4.35	+24.81	+4.10	-20.71
	I ⁻	2.20	+1.56	+8.91	-12.30	-21.21
From water of PC	Cl ⁻	1.81	+5.36	+30.58	+26.40	-4.18
	Br ⁻	1.96	+3.31	+18.87	+13.56	-5.31
	I ⁻	2.20	+0.47	+2.68	-3.26	-5.94

a) Crystal ionic radii.

The $\Delta H^\circ_{\text{tr}}$ are available in the literature.^{16,17)} The $\Delta G^\circ_{\text{tr}}$ shown in Table 5 is the greatest positive value for Cl⁻, which has the smallest ionic radius and the most strongly solvated anion in water, DMF and PC^{18,19)} among the X⁻ compounds. The fact shows that Cl⁻ is the most unstable anion for transfer from water to DMF and PC. Therefore, it is considered that the free-energy changes for the formation of TIX, $\Delta G^\circ_{\text{tr(TIX)}}$, are greatly influenced by the free-energy changes of X⁻, $\Delta G^\circ_{\text{tr}}$, for transfer from water to DMF and PC. From a comparison of $\Delta H^\circ_{\text{tr}}$ with $T\Delta S^\circ_{\text{tr}}$ among the X⁻, it can be seen that the values of $\Delta H^\circ_{\text{tr}}$ contribute much to those of $\Delta G^\circ_{\text{tr}}$. Accordingly, it may be concluded that the differences shown in Table 1 in the order of stability for metal halogeno-complexes in DMF, PC, and water depend mainly on the enthalpy changes ($\Delta H^\circ_{\text{tr(TIX)}}$) for the formation of TIX, and that the $\Delta H^\circ_{\text{tr(TIX)}}$ are greatly influenced by the enthalpy changes ($\Delta H^\circ_{\text{tr}}$) of halide ions.

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