401. *Thallium Tri-iodide and Related Compounds.*

By A. G. Sharpe.

Thallium tri-iodide is conveniently prepared from thallous iodide, iodine, and hydriodic acid. The only intermediate phase in its thermal decomposition to thallous iodide and iodine is Tl_3I_4; dissociation pressures of this substance and some polyiodides are shown to increase along the series Tl_3I_4, CsI_3, RbI_3, TlI_3, KI_3. The standard free energy of $TlI_4{}^-{}_{(aq.)}$, calculated from the data of Maitland and Abegg (*Z. anorg. Chem.*, 1906, **49**, 341), is $-40{,}340$ cal., and the reactions of thallium tri-iodide with iodide and hydroxyl ions are discussed with reference to the thallous–thallic potentials.

Since its first preparation by Nicklès (*Compt. rend.*, 1864, **58**, 537), who digested thallous iodide with an alcoholic solution of iodine and evaporated the mixture over sulphuric acid, the properties of thallium tri-iodide have excited occasional interest. Wells and Penfield (*Z. anorg. Chem.*, 1894, **6**, 312) showed it to be isomorphous with rubidium and cæsium tri-iodides, and accordingly formulated it as thallous tri-iodide. Maitland and Abegg (*ibid.*, 1906, **49**, 341) showed that it yields complex iodides (*e.g.*, $KTlI_4$) with alkali-metal iodides, and described it as an example of inorganic tautomerism. Berry, Lowry, and Goldstein (*J.*, 1928, 1748) found that its solution in methyl alcohol, which does not give the absorption spectrum of the $I_3{}^-$ ion, yields thallic oxide when shaken with sodium carbonate solution. This communication discusses the interpretation of these facts, describes a new preparation for the compound, and gives information about its thermal decomposition.

The preparation from thallous iodide and iodine in methyl alcohol has the disadvantage that, owing to the low solubility of the iodide and of an intermediate iodide Tl_3I_4, the composition of which has been confirmed, very long digestion is necessary for complete conversion into the tri-iodide. A more convenient method is evaporation at room temperature of the solution obtained by dissolving thallous iodide in a solution of iodine in hydriodic acid. The solution yields thallium tri-iodide and not the anhydrous acid $HTlI_4$ on evaporation; the latter substance, like many other hypothetical complex halogeno-acids of formula HMX_4, would involve a co-ordination number of five for the central atom or two for a halogen, or the presence (unlikely on energetic grounds) of a free proton.

The key to the understanding of the solution chemistry of thallium tri-iodide and related compounds is the effect of complex-ion formation or precipitation of an extremely sparingly soluble substance on the redox potential of the thallous–thallic system. The standard potential of the thallous–thallic couple is given as $-1{\cdot}23$ v in nitric acid (Noyes and Garner, *J. Amer. Chem. Soc.*, 1936, **58**, 1268), $-1{\cdot}22$ v in sulphuric acid (Partington and Stonehill, *Trans. Faraday Soc.*, 1935, **31**, 1365), or $-1{\cdot}25$ v at zero ionic strength in perchloric acid (Sherrill and Haas, *J. Amer. Chem. Soc.*, 1936, **58**, 952). In these solutions, therefore, iodine will not oxidise Tl^+ to Tl^{3+}, since the iodide–iodine standard potential is only $-0{\cdot}53$ v; the calculated values for ΔG° and K for the reaction

$$Tl^+ + I_2 \rightleftharpoons Tl^{3+} + 2I^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

are indeed, approximately $+33{,}200$ cal. and 10^{-24}. In the presence of sufficient iodide ions, however, the reaction becomes

$$TlI_{(s)} + I_3{}^-{}_{(aq.)} \rightleftharpoons TlI_4{}^-{}_{(aq.)} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

The standard free energies of TlI and $I_3{}^-{}_{(aq.)}$ are computed by Latimer ("The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, New York, 1938) to be $-29{,}976$ and $-12{,}290$ cal. respectively. The free energy of $TlI_4{}^-{}_{(aq.)}$ is unknown, but may be estimated from the free energies of $Tl^{3+}{}_{(aq.)}$ and $I^-{}_{(aq.)}$ [$+49{,}750$ and $-12{,}330$ cal. (Latimer, *loc. cit.*)] and the value of $1{\cdot}95 \times 10^{30}$ given by Maitland and Abegg (*loc. cit.*) for K for the reaction

$$Tl^{3+}{}_{(aq.)} + 4I^-{}_{(aq.)} \rightleftharpoons TlI_4{}^-{}_{(aq.)} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

as $-40{,}340$ cal. This leads to values of $\Delta G^\circ = +1920$ cal. and $K = 0{\cdot}04$ for reaction (2).

Since no correction has been made for finite ionic strengths or the addition of an excess of iodine in hydriodic acid, the calculated data are in satisfactory agreement with the observation that reaction (2) takes place.

For the precipitation of thallic oxide from the tri-iodide and sodium carbonate solution detailed calculation is impossible because of the absence of data for the tri-iodide. The isomorphism of TlI_3 and RbI_3 appears to establish the structure of the solid as thallous tri-iodide, but the absorption spectrum in methyl alcohol (which has been confirmed) shows that different ionic species are present in solution. We may, however, represent the overall change

$$2TlI_3 + 6OH^- \rightleftharpoons Tl_2O_3 + 6I^- + 3H_2O \quad . \quad . \quad . \quad . \quad (4)$$

as taking place in stages (5)—(8):

$$TlI_3 \rightleftharpoons Tl^+ + I_3^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$I_3^- + 2OH^- \rightleftharpoons OI^- + 2I^- + H_2O \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$Tl^+ + OH^- + OI^- + H_2O \rightleftharpoons Tl(OH)_3 + I^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$2Tl(OH)_3 \rightleftharpoons Tl_2O_{3(s)} + 3H_2O \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Reaction (6) is known to take place spontaneously since potassium tri-iodide is decolorised by alkali. Thallic oxide forms no hydrate (Hüttig and Mytyzek, *Z. anorg. Chem.*, 1930, **192**, 187) and is very sparingly soluble ($2{\cdot}5 \times 10^{-10}$ g. per l. at 25°). From the free-energy data assembled by Latimer (*loc. cit.*) $\Delta G°$ for reaction (7) is found to be approximately $-58{,}000$ cal.; the great difference between this result and that for reaction (1) arises partly from the very low solubility of thallic oxide and partly from the increase in oxidising power when iodine is converted into hypoiodite. As is to be expected, it has been found that thallic oxide is quantitatively precipitated when iodine and alkali are added to a solution of a thallous salt. More familiar but similar examples of the effect of pH in oxidation-reduction processes are the reduction of oxygen by ferrous hydroxide and the oxidation of plumbous ions to the dioxide by alkaline hypochlorite but not by chlorine in acid solution.

The formation of the sparingly soluble intermediate iodide Tl_3I_4 may now be reconsidered. In reaction (1) the amount of iodide formed would not be enough to convert all of the thallium into the complex ion TlI_4^-, but the formation of an insoluble substance containing some of the thallium in a complex ion corresponding to a higher oxidation state might well be thermodynamically possible. Measurement of the magnetic susceptibility of the iodide Tl_3I_4 by Dr. R. S. Nyholm shows the compound to be diamagnetic, thus eliminating the possibility of Tl^{2+} or TlI_4^{2-} ions in the structure. It is tentatively suggested that the intermediate iodide be formulated as $Tl_2^{I}Tl^{III}I_4$, analogous to triplumbic tetroxide $Pb_2^{II}\,Pb^{IV}O_4$, the structure of which has been elucidated by Gross (*J. Amer. Chem. Soc.*, 1941, **65**, 1107), Straumanis (*Z. physikal. Chem.*, 1942, **52**, *B*, 127), and Byström and Westgren (*Arkiv Kemi, Min., Geol.*, 1943, **16**, *B*, No. 14). It is noteworthy that bromine water oxidises thallous bromide to the insoluble yellow dibromide Tl_2Br_3 in which the mean oxidation state of the thallium is higher than that in the intermediate iodide; this substance has long been formulated as $Tl_3(TlBr_6)$, but up to the present no structural investigation of any of the intermediate halides of thallium has been reported.

X-Ray powder photography shows that in the thermal decomposition of the tri-iodide to thallous iodide and iodine the only intermediate phase produced is Tl_3I_4; there is no evidence to suggest that the composition of either TlI_3 or Tl_3I_4 is widely variable. The dissociation pressures of these substances and of the tri-iodides of potassium, rubidium, and cæsium have been compared by a competition method in which, for example, thallous iodide and cæsium iodide were allowed to compete for a quantity of iodine sufficient to convert only one of the monoiodides into a tri-iodide; the order of the dissociation pressures is: $Tl_3I_4 < CsI_3 < RbI_3 < TlI_3 < KI_3$. This property of solid thallium tri-iodide is approximately what would be expected from the similarity in unit-cell size of many rubidium and thallous compounds.

EXPERIMENTAL

Preparation of Thallium Tri-iodide.—Thallous iodide (6 g.) was dissolved in a solution of iodine (8 g.) in concentrated hydriodic acid, and the solution was evaporated to constant weight at room temperature *in vacuo* over silica gel. For analysis, a solution of the product in methyl alcohol was shaken with aqueous sodium carbonate: the precipitated thallic oxide was dissolved in sulphuric acid, and after reduction by sulphur dioxide thallium was determined as chromate; iodide in the filtrate was determined as silver iodide (Found: Tl, 34·5; I, 65·3. Calc. for TlI_3: Tl, 35·0; I, 65·1%).

Thermal Decomposition of Thallium Tri-iodide.—Decomposition at 60° *in vacuo* in a flask attached to a vacuum line was followed by weighing at intervals. Preparations of composition $TlI_{2\cdot74}$, $TlI_{2\cdot21}$, $TlI_{1\cdot73}$, and $TlI_{1\cdot40}$ were thus obtained; their TlI contents were checked by heating the materials to constant weight at 150°. The products were examined by *X*-ray powder photography, using CuK_α radiation: $TlI_{2\cdot74}$ gave a strong pattern of TlI_3 and a weak one of Tl_3I_4; $TlI_{2\cdot21}$ gave moderately strong patterns of both TlI_3 and Tl_3I_4; $TlI_{1\cdot73}$ and $TlI_{1\cdot40}$ gave only the pattern of Tl_3I_4; neither form of TlI was found in any of the products. Failure to detect the tri-iodide in two of these products arises from the poorly crystalline nature of this substance; good photographs of even the alkali-metal tri-iodides are not obtained at room temperature. From the detection of the lower iodide at composition $TlI_{2\cdot74}$ and the fact that no change in the spacings of the patterns of TlI_3 and Tl_3I_4 was detected, it is inferred that the compositions of these phases are not variable to any considerable extent.

Properties of the Thallium Iodides.—Lowry and Gilbert (*Nature*, 1929, **123**, 85) found the tri-iodide to be diamagnetic; the susceptibilities of TlI_3 and Tl_3I_4, measured by Dr. R. S. Nyholm, are respectively $-0{\cdot}56$ and $-0{\cdot}28 \times 10^{-6}$ c.g.s. units at 20°. The absorption spectrum of the tri-iodide in methanol was measured with a Beckman photo-electric absorptiometer: Max. at 392—394 and 251—252 mμ; $\varepsilon = 6480$ and 15,250 respectively. The relative dissociation pressures of TlI_3 and CsI_3 were investigated as follows. Thallium tri-iodide (0·227 g.) and cæsium iodide (0·252 g.) were weighed into flasks fitted one with a cone and one with a socket. The flasks were joined, heated to 200°, and allowed to cool extremely slowly during several days. The gain in weight of the cæsium iodide (0·094 g.) was equal to the loss in weight of the thallium compound, and repetition of the heating and cooling procedure produced no change. From these results the calculated composition of the residue from thallium tri-iodide is $TlI_{1\cdot32}$; the dissociation pressures are thus: $Tl_3I_4 < CsI_3 < TlI_3$. The attainment of a true equilibrium in this experiment was confirmed by starting with thallous iodide and cæsium tri-iodide: the thallous iodide was converted into $TlI_{1\cdot33}$, *i.e.*, Tl_3I_4. Similar competitions between all of the possible pairs of iodides established the order of dissociation pressures as that quoted above.

The Tl_3I_4 used was obtained by Maitland and Abegg's method (*loc. cit.*). Thallous iodide was determined by thermal decomposition at 100° and thallium as chromate (Found: TlI, 88·6; Tl, 54·5. Calc. for Tl_3I_4: TlI, 88·9; Tl, 54·7%).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[*Received, February 28th,* 1952.]