Electrometric Titration Studies upon Thallium(III) Salt Solutions

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Data obtained in titrations of gallium(III)[1] and indium(III)[2] salt solutions with alkali suggest the desirability of extending these observations to thallium(III) salt solutions.

Experimental

Thallium(III) sulfate was obtained as a white, crystalline product by dissolving chemically pure thallium(III) oxide in concentrated sulfuric acid and evaporating. It was used in solution in 1 *N* sulfuric acid. Thallium(III) chloride was prepared by room temperature chlorination of chemically pure thallium(I) chloride. It was dissolved in water without addition of acid. Thallium(III) bromide was obtained in aqueous solution by shaking a suspension of pure thallium(I) bromide with bromine until all the solid dissolved and removing excess bromine on the steam-bath. All thallium(III) solutions were standardized by gravimetric determination of the thallium as either oxide or 8-quinolinol chelate.[3] Other chemicals were of analytical reagent quality.

The titration technique employed was the same as that previously described.[1,2]

Results and Discussion

Averaged data for sodium hydroxide titrations are summarized in Table I. Comparison of the precipitation *p*H values with those reported for gallium(III)[1] and indium(III)[2] solutions indicates thallium(III) to be the most acidic species in this series. It is reasonable to assume that the sulfate solutions are less highly complexed than the halide solutions, but a comparison of the average solubility product constant at 25° of 1×10^{-37} as calculated[1,2] for thallium(III) hydroxide from these data with values of 10^{-44} from solubility data in perchloric acid,[4] $10^{-43.6}$ from hydrolysis considerations,[5] and 10^{-46} from potential data on thallium(I) hydroxide–thallium(III) oxide cells,[6] suggests strongly that even here complex formation cannot be neglected. Increased precipitation *p*H with chloride and bromide solutions indicates increased reduction in the concentration of uncomplexed thallium(III) ions. The slightly greater degree of complexing indicated for the bromide solutions is in agreement with the values of stability constants given by Benoit.[5] From Benoit's data, it seems probable that essentially all thallium(III) present in these solutions is present as TlX^{+2} ions, but data essential to absolute evaluations of solubility products on comparative bases are unavailable.

TABLE I

ELECTROMETRIC TITRATION DATA FOR THALLIUM(III) SOLUTIONS

Solution	Temp., °C.	Total thallium(III) concn., mole/l.	Incidence of precipitation *p*H	OH^-/total Tl(III)
$SO_4^=$	10	0.069–0.216	1.01	..[a]
	25	.058– .216	0.99	..[a]
	40	.069– .216	1.14	..[a]
Cl^-	25	.010– .150	3.29	0.67
Br^-	25	.010– .150	3.63	.25

[a] Precipitation occurred before initial free acid present was neutralized.

An observation, that the *p*H of thallium(III) solutions can be raised well above the normal liminal precipitation values without effecting precipitation when acetate is present,[7] suggests extensive complexing by this anion. For *ca.* 0.001 *M* thallium (III) sulfate solutions, precipitation *p*H values at 25° of 1.15, 1.55, 2.00, 5.06 and 5.92 were noted for $C_2H_3O_2^-$ to Tl(III) mole ratios of 0, 5, 10, 50 and 100, respectively. The inhibition of thallium(III) precipitation by acetate suggests the separation of thallium from other cations under these conditions by *p*H control. As a case in point, it was found that solutions containing iron(III) and thallium(III) when brought to *p*H 4.5 with sodium acetate and heated on the steam-bath, precipitate iron(III) oxide quantitatively (as judged by 8-quinolinol precipitation of residual thallium) with a carry of thallium(III) ranging from *ca.* 2 to 8% as the iron to thallium mole ratio changes from 1 to 15.

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The Preparation of Alicyclic Amines. II[1]

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In connection with another problem, some cyclohexylamines were prepared in which the amino group was on a tertiary carbon. These amines were obtained by the reduction of the corresponding nitro compounds as previously described.[2,3]

Three of the nitro compounds were obtained by the addition of 2-nitro-1-butene to cyclopentadiene, and dimethylbutadiene. 2-Nitropropene added to cyclopentadiene but not to the other dienes. Efforts to extend the reaction to nitroölefins of the type $RCH{=}CNO_2R$ have been unsuccessful.

The nitro compounds I, II and III were reduced to the saturated amines with hydrogen and Raney nickel at atmospheric pressure. The aminobicyclo[2.2.1]heptanes from I and II are substituted-norcamphanes. 1,2-Dimethyl-4-nitro-4-ethyl-1-cyclohexene (IV) was selectively reduced to 1,2-dimethyl-4-amino-4-ethyl-1-cyclohexene. The amines were characterized by their benzoyl derivatives.

The thiophene analog of ω-nitrostyrene, ω-nitro-2-vinylthiophene, reacted with butadiene and dimethylbutadiene to form 4-nitro-5-(2-thienyl)-1-cyclohexene (V) and 4-nitro-5-(2-thienyl)-1,2-dimethyl-1-cyclohexene (VI), respectively. The nitro group of the latter was reduced with lithium aluminum hydride to the corresponding cyclohex-

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