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.

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.

TABLE I

ELECTROMETRIC TITRATION DATA FOR THALLIUM(III) SOLUTIONS

Solution	Temp., °C.	Total thallium(III) concn., mole/l.	Incidence of precipitation *p*H	Incidence of precipitation 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.

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(2) T. Moeller, THIS JOURNAL, **63**, 2625 (1941).

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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═CNO₂R 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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(1) Abstracted from the Ph.D. dissertation of M. Maienthal, 1949, and the Master's dissertation of J. A. Gallagher, 1951.

(2) C. F. H. Allen, A. Bell and J. W. Gates, Jr., *J. Org. Chem.*, **8**, 373 (1943).

(3) D. V. Nightingale and V. Tweedie, THIS JOURNAL, **66**, 1968 (1944).

enylamine which was characterized by its benzoyl derivative. Lack of time prevented efforts to improve the yields of the amines in this series.

Experimental[4]

2-Nitro-2-ethylbicyclo[2.2.1]heptene-5 (I).—A solution of 37 g. (0.37 mole) of freshly distilled 2-nitro-1-butene[5] and 32 g. (0.55 mole) of cyclopentadiene containing 0.1 g. of hydroquinone was heated in an autoclave at 103–115° for three hours, then allowed to cool overnight. The dark brown reaction product was first distilled from a Claisen flask at reduced pressure. After removal of the forerun containing unreacted starting materials and the dimer of cyclopentadiene, the adduct distilled at 75–78° (5 mm.) as a light yellow liquid; yield 38 g. (61%). Fractionation of this product through a small column yielded a colorless liquid with a camphor-like odor. The physical constants of a center cut were b.p. 79° (5 mm.), $n^{20}\mathrm{D}$ 1.4888.

Anal. Calcd. for $C_9H_{13}NO_2$: C, 64.63; H, 7.83. Found: C, 64.46; H, 7.58.

Reduction of I.—A solution of 19.5 g. (0.12 mole) of I in 50 ml. of methanol was reduced with Raney nickel (3 g.) and hydrogen at slightly more than atmospheric pressure and room temperature. The solvent was removed by distillation and the 2-amino-2-ethylbicyclo[2.2.1]heptane was isolated in the usual manner. The amine distilled as a colorless liquid, b.p. 59–60°, $n^{20}\mathrm{D}$ 1.4825, yield 7 g. (44%).

Anal. Calcd. for $C_9H_{17}NO$: C, 77.62; H, 12.31. Found: C, 77.74; H, 12.56.

The benzoyl derivative of the amine melted at 193–194°.

Anal. Calcd. for $C_{16}H_{21}NO$: C, 78.97; H, 8.70. Found: C, 79.20; H, 8.70.

2-Nitro-2-methylbicyclo[2.2.1]heptene-5 (II).—A solution of 40 g. (0.46 mole) of 2-nitropropene[6] and 65 g. (1 mole) of cyclopentadiene was heated in an autoclave for 90 minutes and allowed to cool overnight. The dark brown liquid yielded a main fraction (24 g., 34%), b.p. 70° (10 mm.), which solidified on cooling. The crude product was purified by vacuum sublimation to yield a waxy, colorless solid m.p. 84–86°. The compound sublimed near the melting point.

Anal. Calcd. for $C_8H_{11}NO_2$: C, 62.72; H, 7.24. Found: C, 62.90; H, 7.40.

Reduction of II.—A solution of 14 g. (0.09 mole) of II in 50 ml. of methanol was reduced as described above. The 2-amino-2-methylbicyclo[2.2.1]heptane distilled as a colorless liquid, b.p. 60° (20 mm.), $n^{20}\mathrm{D}$ 1.4809, yield 5 g. (45%).

Anal. Calcd. for $C_8H_{15}N$: C, 76.73; H, 12.08. Found: C, 76.50; H, 12.25.

The benzoyl derivative of the amine melted at 134–135°.

Anal. Calcd. for $C_{15}H_{19}NO$: C, 78.56; H, 8.35. Found: C, 78.26; H, 8.46.

4-Nitro-4-ethyl-1-cyclohexene (III).—A solution of 15 g. (0.5 mole) of 2-nitro-1-butene, 18 ml. (0.21 mole) of butadiene and 0.1 g. of hydroquinone was heated in a Carius tube at 120–130° for four hours. The adduct distilled at 82–84° (5 mm.), $n^{21}\mathrm{D}$ 1.4810, yield 8.5 g. (37%).

Anal. Calcd. for $C_8H_{13}NO_2$: C, 61.91; H, 8.44. Found: C, 62.24; H, 8.64.

Reduction of III.—A solution of 13 g. of III in 50 ml. of methanol was reduced as described above. The 1-amino-1-ethylcyclohexane distilled at 63.65° (17 mm.), $n^{20}\mathrm{D}$ 1.4603, yield 6.6 g. (62%).

Anal. Calcd. for $C_8H_{17}N$: C, 75.52; H, 13.47. Found: C, 75.39; H, 13.65.

The benzoyl derivative of the amine melted at 101.5–102°.

Anal. Calcd. for $C_{15}H_{21}NO$: C, 77.88; H, 9.15. Found: C, 77.69; H, 9.34.

1,2-Dimethyl-4-nitro-4-ethyl-1-cyclohexene (IV).—A solution of 36 g. (0.35 mole) of 2-nitro-1-butene and 56 g. (0.68 mole) of dimethylbutadiene was heated in an autoclave at 125–130° for two hours. The adduct distilled at 94–94.5° (8 mm.), $n^{20}\mathrm{D}$ 1.4837, yield 17 g. (40%).

Anal. Calcd. for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35. Found: C, 65.40; H, 9.26.

Reduction of IV.—A solution of 20 g. of IV in 50 ml. of methanol was reduced as outlined above. The unsaturated amine, 1,2-dimethyl-4-amino-4-ethyl-1-cyclohexene, distilled at 107–110° (30 mm.), $n^{20}\mathrm{D}$ 1.4811, yield 6 g. (28%).

Anal. Calcd. for $C_{10}H_{19}O$: C, 78.36; H, 12.50. Found: C, 78.19; H, 12.45.

The benzoyl derivative of the amine melted at 103–104°.

Anal. Calcd. for $C_{17}H_{23}NO$: C, 79.33; H, 9.01. Found: C, 97.31; H, 9.20.

4-Nitro-5-(2-thienyl)-1-cyclohexene (V).—ω-Nitro-2-vinylthiophene[7] (5.4 g. 0.35 mole) and 15 ml. of butadiene were heated in a Carius tube at 140° for six hours. The crude adduct was recrystallized from petroleum ether (60–70°) and decolorized with activated charcoal. The white crystals so obtained melted at 69–70°, yield 4.5 g. (61%).

Anal. Calcd. for $C_{10}H_{11}NO_2S$: C, 57.39; H, 5.30. Found: C, 57.42; H, 5.49.

4-Nitro-5-(2-thienyl)-1,2-dimethyl-1-cyclohexene (VI).—Dimethylbutadiene (8.2 g., 0.1 mole) and 7.7 g. (0.05 mole) of ω-nitro-2-vinylthiophene were heated in a Carius tube for six hours at 140°. The adduct was recrystallized from alcohol and melted at 80.5–81°, yield 10 g. (84%).

Anal. Calcd. for $C_{12}H_{15}NO_2S$: C, 60.73; H, 6.37. Found: C, 60.88; H, 6.62.

Reduction of VI.—A solution of 2.3 g. of VI in absolute ether was reduced with lithium aluminum hydride by the procedure of Gilsdorf and Nord,[8] but not enough of the amine was obtained for purification by distillation. The crude amine was converted to its benzoyl derivative, m.p. 191.5–192°.

Anal. Calcd. for $C_{19}H_{21}NOS$: C, 73.28; H, 6.79. Found: C, 73.54; H, 6.57.

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(4) The carbon and hydrogen analyses were done by K. T. Zilch and J. A. Gallagher.

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Condensations with Halogenated Aldehydes. IX.[1] β,β,β-Trichloro-α,α-bis-(halogenotolyl)-ethanes, β,β,β-Trichloro-α,α-bis-(hydroxy-(or methoxy)-dichlorophenyl)-ethanes and Related Compounds

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In connection with stereochemical and toxicological[3,4] studies we have prepared several of the highly substituted ethanes named in the title. Table I summarizes the data for the DDT analogs prepared by Baeyer condensation from chloral and the twelve monohalogenotoluenes, 2,4-dichlorophenol or 2,4-dichloroanisole. Their behavior toward alcoholic potassium hydroxide was studied quantitatively (see Table I, last column) and on a preparative scale (Table II). The position of the substituents in the aromatic nuclei was deduced from the mode of formation of the compounds and from their behavior toward alkali, and toward chromic anhydride in acetic acid.

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(1) Paper VI, *Monatsh.*, **83**, 828 (1952); paper V, *Z. Naturforsch.*, **7b**, 277 (1952). Earlier papers cited there. See also 2nd supplement to the 1st supplementary volume of *Pharmasie*, **99**, 177 (1947), and *Z. Naturforsch.*, **6b**, 179 (1951); **7b**, 251 (1952).

(2) Berlin-Charlottenburg 9, Bolivarallee 8, Germany.

(3) R. Riemschneider, *Z. angew. Entomol.*, **35**, 2/4 (1953).

(4) *Cf.* paper presented on April 1, 1953, at the Chemists' Meeting in Innsbruck, Austria. *Cf. Angew, Chem.* **65**, 267 (1953).