ΔF are accurate to about 25 cal., those of ΔH to about 100 cal. and the value of ΔS to about 0.5 cal. per degree.

We thank D. W. Pearce of this Laboratory for his helpful suggestions concerning the purification and preparation of the cerium compounds.

Summary

A two phase cerium amalgam has been used as an electrode with cerium(III) sulfate solutions. The standard molal potential has been calculated for 15, 25 and 35° from the data. From the measurement of the cell potentials it was determined that a two phase cerium amalgam is obtained at concentrations greater than 0.312% cerium by weight. The mean activity coefficients of cerous sulfate from 0.007 *m* to saturation and the free energy, heat and entropy changes for the cell reaction have been calculated.

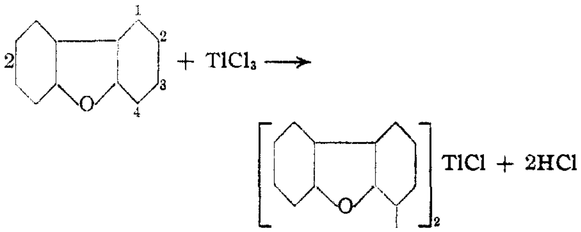
WEST LAFAYETTE, INDIANA RECEIVED NOVEMBER 2, 1942

NOTES

The Direct Thallation of Dibenzofuran[1]

BY HENRY GILMAN AND R. K. ABBOTT, JR.

In view of the known direct replacement of nuclear hydrogen by gold (auration) and by mercury (mercuration), it appeared that a similar substitution should take place with thallium (thallation). We have observed that a reaction of this kind does take place with dibenzofuran and thallium trichloride. The position of thallation was established by treating the R_2TlCl compound with iodine to give the known 4-iododibenzofuran. It is interesting to note that all metalations of dibenzofuran (by metals, inorganic salts or RM compounds) involve the 4-position, which is not the case with some related heterocycles like dibenzothiophene.[2] The metalation reaction which has been shown to take place with gold, mercury and thallium does not appear to take place to any significant extent with related lead compounds.



Although trivalent thallium forms complexes[3] with many compounds, these have not been converted to carbon–thallium types. We had no success in attempts to rearrange the thallium trichloride–pyridine complex[4] to a dipyridylthallium chloride. Goddard,[5] some years ago, tried a related reaction with the thallium trichloride complex of *p*-aminophenylmercury chloride. Numerous complexes have been prepared of thallium trichloride with diazonium salts,[6] but there is no record of their having been converted to organothallium compounds. Various phenols have been treated with thallium trichloride and thallium tribromide.[7] In some of these reactions a complex is formed; in others, the thallium trichloride acts as a chlorinating and oxidizing agent, being reduced to thallous chloride. This latter mode of reaction is common with many amines. For example, Renz[8] showed that α-naphthylamine hydrochloride is oxidized to a deep violet dye, in striking contrast to β-naphthylamine hydrochloride which gives a crystalline complex.

There is no significant tendency for a thallous salt to undergo oxidation–reduction to a trivalent thallic salt and metallic thallium. Exploratory experiments in which thallous acetate was heated with furan, thiophene, dibenzofuran and N-phenylcarbazole gave in every case complete recovery of the thallous acetate.

Experimental

In a three-necked flask equipped with nitrogen inlet, stirrer and short delivery tube were placed 31 g. (0.1 mole) of thallium trichloride, as a saturated aqueous solution,

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[1] Paper XLVIII in the series "Relative Reactivities of Organometallic Compounds."

[2] Gilman, Meals, O'Donnell and Woods, THIS JOURNAL, **65**, in press (1943).

[3] Meyer, *Z. anorg. Chem.*, **24**, 321 (1900); Rabe and Steinmetz, *Ber.*, **35**, 4447 (1902).

[4] Meyer, *Ber.*, **35**, 1319 (1902).

[5] Goddard, *J. Chem. Soc.*, **123**, 1161 (1923).

[6] Nesmeyanov, Kocheshkov and Klimova, *Ber.*, **68**, 1877 (1935); Nametkin and Mel'nikov, *J. Gen. Chem.* (U. S. S. R.), **5**, 373 (1935); Kocheshkov and Nesmeyanov, *ibid.*, **6**, 144 (1936).

[7] Mel'nikov and Gracheva, *ibid.*, **7**, 467 (1937); see also Marino, *Gazz. chim. ital.*, **371**, 55 (1907).

[8] Renz, *Ber.*, **35**, 1110, 2768 (1902).

and 33.5 g. (0.2 mole) of carefully purified dibenzofuran. A slow stream of nitrogen maintained throughout the experiment was found to reduce materially the amount of darkening. The mixture was heated with constant stirring; in the neighborhood of 80° the whole mass became liquid and two layers were formed, the organic layer being on top. The temperature was held at 110° for one hour, during which time most of the water was driven off and a small amount of dibenzofuran steam distilled. The temperature was then raised to 165° and held there for four hours. During this time the rest of the water was driven off and there was a gradual evolution of hydrogen chloride. The reaction mixture darkened appreciably during this time, the two layers became one and a bright yellow solid deposited on the bottom of the flask. The reaction was allowed to cool under nitrogen and then was extracted with 100 ml. of 95% ethyl alcohol to remove all the unreacted dibenzofuran. The residue was then repeatedly extracted with absolute ethyl alcohol until a solution on cooling deposited no crystals. In this manner 5.1 g. of material was extracted which represented a 9% yield of di-4-dibenzofurylthallium chloride.

Anal. Calcd. for $C_{24}H_{14}O_2ClTl$: Tl, 35.5. Found: Tl, 35.3.

The yellow solid which remained after the alcoholic extractions was recrystallized from a large quantity of boiling water and shown to contain only thallium and chlorine.

Anal. Calcd. for Tl_2Cl_3: Tl, 79.5. Found: Tl, 79.9.

No unreacted thallium trichloride was present, as was demonstrated by the failure to obtain the characteristic dark brown precipitate with potassium iodide solution.

To demonstrate the point of entrance into the dibenzofuran nucleus, 2.9 g. (0.005 mole) of the R_2TlCl compound was suspended in 50 ml. of chloroform and 2.5 g. (0.01 mole) of iodine was added. The mixture was stirred and refluxed for five hours, filtered from thallous iodide, and the solvent removed under reduced pressure. The residue was recrystallized twice from methanol to give 1.1 g. or 38% of 4-iododibenzofuran which melted at 69–72° and which gave no depression in a mixed melting point with an authentic sample.

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Thallous Salts as Derivatives of Sulfonic Acids

BY HENRY GILMAN AND R. K. ABBOTT, JR.

Incidental to an examination of organothallium compounds we have observed that thallous salts appear to be reagents of choice for characterizing or derivatizing some sulfonic acids. Hitherto, the best general types for this purpose have been the amines, and the *p*-toluidine[1] and phenylhydrazine[2] salts.

Some advantages of the thallous salts are as follows: (1) They are readily prepared in practically quantitative yields from the sulfonic acid or its sodium salt. (2) They crystallize readily, and preferably from water, to give generally high-melting solids. (3) One of the methods of preparation (from the free sulfonic acid and thallous hydroxide) can be used titrimetrically to get a neutralization equivalent incidental to the preparation of the derivative. (4) The ease of formation of large, well-defined crystals suggests their application in micro-procedures.

Experimental

Procedure: from Free Sulfonic Acid.—The free sulfonic acid (about 0.01 mole) dissolved in a little warm water is titrated with about 0.1 *N* thallous hydroxide solution, using phenolphthalein as an indicator. Thallous hydroxide was prepared from equivalent quantities of thallous sulfate and barium hydroxide, each dissolved in a minimum volume of boiling water. The precipitate of barium sulfate was allowed to digest for three hours on the steam-plate to improve the filtering qualities of the precipitate. The clear solution was then concentrated under reduced pressure, and the normality determined by titration with standard acid.

From the Sodium Sulfonate.—To the sodium sulfonate, dissolved in a small volume of water, is added the calculated quantity of thallous formate[3] dissolved in a few drops of water. In a few cases a precipitate forms immediately in hot solution, but more often crystals are deposited only as the solution cools.

The thallous formate procedure depends on the greater insolubility in water of the thallous sulfonate as compared with the sodium sulfonate. From our present limited studies only two sodium sulfonates could not be used as such. In both these cases, sodium benzenesulfonate and sodium 1,2,3,4-tetramethylbenzene-5-sulfonate, the thallous salt was about as soluble as the sodium salt, and both deposited as the aqueous solution was cooled.

The thallous salts of other acids (including sulfinic, phosphonic, and arsonic types) are being examined.

It might be mentioned that the thallous salts may be particularly suitable for the separation and isolation of isomers. For example, the three tetramethylbenzenesulfonates differ significantly in solubility: thallous 1,2,4,5-tetramethylbenzene-3-sulfonate is very insoluble in water; thallous 1,2,3,4-tetramethylbenzene-5-sulfonate is extremely soluble; and thallous 1,2,3,5-tetramethylbenzene-4-sulfonate is of intermediate solubility in water. Several of the thallous sulfonates described in Table I were prepared from 0.1 g. of the sulfonic acid with customary, non-micro technique. The different crystal forms of the thallous sulfonates should be helpful in any development of micro-analytical procedures.

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[1] Fieser, THIS JOURNAL, 51, 2460, 2471 (1929).

[2] Latimer and Bost, *ibid.*, 59, 2500 (1937).

[3] The thallous formate used was purchased from the Eastman Kodak Company.