SOME NEW METALLO-ORGANIC OXONIUM SALTS.⁽¹⁾

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Introduction. Trimethyltin iodide, $(CH_3)_3SnI$, is a colorless liquid becoming brown under the action of sunlight. On withdrawing from the light the solution becomes colorless again. On renewed exposure the color again appears.

After some time small amounts of colorless crystals appear in the solution. This action was first noticed by Callis in 1922.⁽²⁾

He thought that the crystalline compound might be an iodonium salt, $((CH_3)_3Sn)_2I\text{-}I$, formed by molecular rearrangement under the action of sunlight. It was considered worth while to study the crystalline compound formed in this photo-chemical reaction. It was, therefore, decided that a more extensive investigation on this subject should be carried out.

When the compound was analysed for iodine, a value in the neighborhood of 19.5 % was obtained in place of 43.63 % as required for a compound of the iodonium type.

Analysis for tin indicated the presence of three atoms of tin per atom of iodine. It was concluded, therefore, that the formula is inapplicable.

The formula, $((CH_3)_3Sn)_2O\,.\,(CH_3)SnI, H_2O$, for the compound is proposed by the author from the following experimental facts.

Purified trimethyltin iodide did not give the appearance of any crystals. It was, therefore, thought that the crystalline compound must have been formed by the interaction of impurities which accompanied in its preparation.

An experiment, therefore, was made of a mixture of trimethyltin iodide and tetramethyltin and exposed to the sunlight and moist air. A considerable amount of crystals appeared from the solution whose properties and analysis of tin and iodine contents proved to be identical with those of

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(1) This paper incorporates partly a paper published by Kraus and Harada on the *Journal of the American Chemical Society*, 47 (1925), 2416 under the title of "Compounds formed between trimethyltin hydroxide and trimethyltin halides."

(2) Callis, Dissertation, Clark University, 1922.

the compound accidentally obtained from the impure solution by the action of sunlight.

Properties. The compound is readily soluble in water and alcohol and only slightly soluble in such organic solvents as benzene and ether.

Its aqueous solution is slightly acidic. It decomposes slowly at above 143° C. and melts at about 150° C., depending upon the rate of heating into trimethyltin iodide and trimethyltin hydroxide with a little trace of white substance.

When the aqueous solution of the compound was treated with silver hydroxide, silver iodide was precipitated. On evaporation of the clear filtrate on the water bath it did not leave any substance. However, a peculiar odour was noticed during the evaporation. The volatile substance, therefore, was collected by means of a condenser, in the form of colorless crystals.

The examination of the crystalline compound showed that it was trimethyltin hydroxide. With silver nitrate solution it readily precipitates silver iodide, but on standing or heating, the solution and the precipitate becomes dark brown. The quantitative analysis for iodine and tin conforms the following formula :(1)

$$((CH_3)_3Sn)_2O\,.\,(CH_3)_3\,Sn\,I,\,H_2O. \qquad (I)$$

Sometimes lumpy crystals appeared from the solution which, perhaps, may be the same in an impure state. These were, therefore, dissolved in alcohol and heated, the solution then becoming brown and relatively strong acidic. From this solution, on cooling, colorless crystals were obtained as short needles. This compound is somewhat difficultly soluble in water and alcohol, insoluble in ether and benzene, melts and at the same time decomposes at 221° C. (incorrected). Its aqueous solutions show much stronger acidic properties than that of the first type of compound. When treated with silver nitrate, silver iodide is immediately precipitated. With silver hydroxide it precipitates silver iodide, and from the clear filtrate only trimethyltin hydroxide was again obtained in the pure state by distillation, as in the case of the first compound.

It was found that the contents of tin and iodine agrees to the following formula :(2)

$$((CH_3)_3Sn)_2O\,.\,HI\,,\,H_2O \qquad (II)$$

If the proposed formula (I) is correct, it might be expected that the compound, $((CH_3)_3Sn)_3O$, or compounds, $((CH_3)_3Sn)_2O$ and $(CH_3)_3Sn$, in

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(1) Preparation and analytical results, see Kraus and Harada, *J. Am. Chem. Soc.*, 47 (1925), 2416.

(2) Kraus and Harada, ibid.

liquid ammonia would be obtained by treating with equivalent amount of sodium to the iodine.

Since the compound of type (I) is soluble in liquid ammonia, while the compound of type (II) such as, iodide and bromide are practically insoluble, an experiment was carried out with the iodide, $((CH_3)_3Sn)_2O\text{–}(CH_3)_3Sn\,I, H_2O$, as follows:

To one molecular proportion (4.03 gr.) of the compound in liquid ammonia solution one molecular proportion of metallic sodium (0.15 gr. by weight) was added little by little. A white precipitate was immediately formed. The solvent was evaporated at room temperature giving the reaction mixture which was washed with water, until it was free from sodium iodide and other dissolved impurities. Thus trimethyltin group, $(CH_3)_3\,Sn$, and its oxide, $((CH_3)_3\,Sn)_2\,O$, were obtained in the quantity expected. The following reaction probably has taken place:

$$[((CH_3)_3\,Sn)_3\,O]\,.\,I + Na \rightarrow [((CH_3)_3\,Sn)_3\,O] \rightarrow ((CH_3)_3\,Sn)_2\,O + (CH_3)_3\,Sn$$

Same substances were obtained from the action of the compound on trimethyltin sodium which was prepared according to Kraus and Sessions.⁽¹⁾ The reaction may have taken place as follows:

$$((CH_3)_3\,Sn)_3\,O\,.\,I + (CH_3)_3\,Sn\,Na \rightarrow ((CH_3)_3\,Sn)_2\,O + 2\,(CH_3)_3\,Sn + Na\,I$$

Formations. $((CH_3)_3\,Sn)_2\,O\,.\,(CH_3)_3\,Sn\,X\,,\,H_2O$. It was found that when one molecular proportion of trimethyltin halide was treated with two molecular proportions of trimethyltin hydroxide in hot benzene solution, a crystalline compound was formed whose properties appeared to be identical with those of the compound previously obtained by the action of sunlight on impure trimethyltin halide, and on analysis gave similar results.

From trimethyltin free group: A quantity of trimethyltin group, $(CH_3)_3\,Sn$, which was obtained by either of the following reactions:

$$\text{(I)}\quad (CH_3)_3\,Sn\,OH + Na \rightarrow (CH_3)_3\,Sn + Na\,OH$$

$$\text{(II)}\quad (CH_3)_3\,Sn\,X + Na \rightarrow (CH_3)_3\,Sn + Na\,X$$

in liquid ammonia, was dissolved in moist benzene, along with trimethyltin halide, and this solution was subjected to oxidation in the dark. After some days crystals appeared. However, with dry benzene solution powder-like precipitate was formed, which when treated with alcoholic solution or water, became crystallized. These crystals were similar to those previously obtained.

$((CH_3)_3\,Sn)_2\,O\,.\,HX,\,H_2O$: When one molecular proportion of trimethyltin hydroxide or oxide was treated respectively with one molecular proportion of trimethyltin halide, under relatively hot alcoholic solution, or

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(1) *J. Am. Chem. Soc.*, 47 (1925), 2361.

of halogen acid, these compounds were formed in crystalline form. The chlorine compound such as $((CH_3)_3\,Sn)_2\,O\,.\,HCl\,,\,H_2O$ was prepared when one molecular proportion of trimethyltin hydroxide was treated with one molecular proportion of trimethyltin chloride in hot dry benzene. A heavy liquid, however, settled which readily absorbed water and immediately gave the crystalline compound. It shows, therefore, that water is necessary for the formation of all these crystalline compounds as their water of crystallization. The direct determination of the water of crystallization of these compounds was not carried out, since the compounds are slightly volatile and decomposible over dehydrating agents.

If the proposed formula (I) and (II) are correct, the compounds might be expected to dissociate according to the equations:

$$\text{I.}\quad ((CH_3)_3\,Sn)_3\,O\,.\,X \rightleftarrows ((CH_3)_3\,Sn)_2\,O + (CH_3)_3\,Sn\,X$$
$$\text{or}\quad \rightleftarrows ((CH_3)_3\,Sn)_3\,O + X$$
$$\text{II.}\quad ((CH_3)_3\,Sn)_2\,O\,.\,HX \rightleftarrows ((CH_3)_3\,Sn\,OH + (CH_3)_3\,Sn\,X$$
$$\text{or}\quad \rightleftarrows ((CH_3)_3\,Sn\,OH + (CH_3)_3\,Sn\,X$$

Trimethyltin halides possess a high degree of hydrolysis in aqueous solutions, and trimethyltin oxide with water decomposes into the hydroxide which is a weak base.

The aqueous solution of the first type of halide is weakly acidic, because with silver hydroxide, as already described, on standing or heating becomes alkalline, owing to the formation of the base and which decomposes into trimethyltin hydroxide according to the following equation:

$$((CH_3)_3\,Sn)_2\,O\,.\,(CH_3)_3\,Sn\,I + Ag\,OH \rightarrow ((CH_3)_3\,Sn)_2\,O\,.\,(CH_3)_3\,Sn\,OH + H_2O \rightarrow 3\,(CH_3)_3\,Sn\,OH.$$

Concerning the second type of compound it may be regarded that the compound formed between one molecule of a weak base and one molecule of a strong acid is more stable than that of the first type of compound.

They conduct electric current in alcohol, water, acetone and liquid ammonia solutions while trimethyltin halide and hydroxide are poor conductors in the same solutions. Further discussion of this subject will be presented in a subsequent paper.

It, therefore, appears that the compounds in question are salts of an oxonium type.

Accordingly, the following conclusion is reached: That the formation of the compound between trimethyltin iodide and tetramethyltin taking place under sunlight may be represented by the following equation scheme:

$$1.\quad 2\,(CH_3)_3\,Sn\,I \underset{\text{dark}}{\overset{\text{light}}{\rightleftarrows}} ((CH_3)_3\,Sn)_2 + I_2$$
$$2.\quad ((CH_3)_3\,Sn)_2 + 1/2\,O_2 \rightarrow ((CH_3)_3\,Sn)_2\,O$$

On the other hand the free iodine reacts slowly with tetramethyltin as follows:

$$3.\quad I_2 + CH_3\,Sn\,(CH_3)_3 \rightarrow (CH_3)_3\,Sn\,I + CH_3\,I$$

and $(CH_3)_3\,Sn\,I$ undoubtedly reacts with trimethyltin oxide to form the salt.

$$4.\quad ((CH_3)_3\,Sn)_2\,O + (CH_3)_3\,Sn\,I \rightarrow ((CH_3)_3\,Sn)_2\,O\,.\,(CH_3)_3\,Sn\,I$$

Summary

The formation of the compound, $((CH_3)_3\,Sn)_2\,O.\,(CH_3)_3\,Sn\,X, H_2O$, from trimethyltin halide by the action of sunlight in the presence of air have been studied and the mechanisms of the formation were interpreted. Identical products have been prepared by the following methods: (A) By oxidizing of trimethyltin group along with trimethyltin halide in benzene solution in the dark, and (B) by treating two molecular proportions of trimethyltin hydroxide with one molecular proportion of trimethyltin halide in hot benzene solution.

2. Compounds exhibit salt-like properties, being readily soluble in water, alcohol, acetone and liquid ammonia, and insoluble in benzene and ether. They conduct electric current appreciably in their solutions.

3. When the liquid ammonia solution is treated with an equivalent amount of metallic sodium in respect to the iodine trimethyltin oxide, $((CH_3)_3\,Sn)_2\,O$, and trimethyltin group, $(CH_3)_3\,Sn$, are produced.

4. Compounds of the type, $((CH_3)_3\,Sn)_2\,O\,.\,HX, H_2O$, have been prepared by treating of one molecular proportion of trimethyltin hydroxide with one molecular proportion trimethyltin halide or one molecular proportion of trimethyltin oxide with one molecular proportion of halogen acid under suitable conditions.

5. They are salt-like properties, being soluble in water and alcohol, and insoluble in nonionizing solvents such as benzene and ether.

6. Their melting points and stabilities are higher than those of the type, $((CH_3)_3\,Sn)_2\,O\,.\,(CH_3)_3\,Sn\,X, H_2O$.

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