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STUDIES RELATING TO METALLO-ORGANIC COMPOUNDS. III. COMPOUNDS FORMED BETWEEN ALKYL TIN HALIDES AND AMMONIA AND THE AMINES

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It is known that ammonia, as well as certain of the amines, combines with metallo-organic compounds of the type $M^nR_{n-1}X$, where M is a metal of normal valence n, R is a univalent organic group, and X is a strongly electronegative element or group of elements. Compounds of this type have been studied in particular by Werner and Pfeiffer,[1] and the results have been interpreted in terms of Werner's theory. The physical-chemical properties of the different compounds formed by the metallo-organic halides with ammonia and the amines have led us to infer a different constitution. The trimethyl tin group, like other groups of the same type, of the general formula M^nR_{n-1}, closely resembles hydrogen or the methyl group in its properties. These groups exhibit a marked tendency to add to ammonia or the amines to form compounds of the ammonium type, in which the metallo-organic group is directly attached to nitrogen. The analogy between trimethyl tin iodide and methyl iodide, for example, is complete in this respect. Both add to a tertiary amine, such as pyridine, to form compounds of relatively high melting points, which, in the pure state as well as in solution, exhibit marked electrolytic properties. It is to be anticipated that these compounds in the liquid mixture will not be entirely stable; that is, in a mixture of the two components, the melting-point curve will exhibit a rounded maximum. While, however, methyl iodide does not add to ammonia or the primary or secondary amines readily under ordinary conditions, trimethyl tin iodide, as well as the other halides of the same group, adds readily to ammonia, the primary and secondary amines, as well as to the tertiary amines, to form compounds of the ammonium type. The group, therefore, resembles hydrogen perhaps somewhat more closely than it does the methyl group.

This behavior on the part of the metallo-organic compounds of this class is not restricted to compounds of tin but probably holds generally, although thus far only tin and mercury compounds have been investigated. It is true, however, that silicon exhibits a similar behavior, triphenyl silicyl chloride combining with one molecule of ammonia to form a compound. Carbon also exhibits this same property. This is shown in a striking manner by those compounds of carbon in which the central carbon atom has approximately the same affinity for the negative electron as have the corresponding metallo-organic groups. Carbon groups of this type are

[1] Werner and Pfeiffer, *Z. anorg. Chem.*, 17, 82 (1898).

found among the compounds of the triphenylmethyl type. Triphenylmethyl chloride, for example, adds a molecule of ammonia to form a comparatively stable compound.

It appeared of interest to investigate the compounds formed in a number of cases. In particular, it appeared of importance to investigate certain of the tin compounds, inasmuch as Werner and Pfeiffer concluded that two molecules of ammonia or an amine were added in the case of these compounds. Thus they found that triethyl tin iodide takes up two molecules of aniline, while the literature indicates that triethyl tin iodide also takes up two molecules of ammonia.

In determining the number of molecules of amine combined with the metallo-organic halide, in general, a determination of the halogen content of the compound was made. These analyses usually checked closely and sufficed to distinguish between one and two molecules of the amine in the compound. In the case of ammonia, however, direct determination of the ammonia was likewise made. In cases where results seemed doubtful, a rough determination of the melting-point curve of mixtures of the constituents was made.

Experimental Part

Trimethyl Tin Chloride and Ammonia.—Trimethyl tin chloride was prepared by treating tetramethyl tin with chlorine in an ice bath with the exclusion of light. The chloride was purified by distillation and finally by recrystallization from petroleum ether at low temperatures.

Trimethyl tin chloride is readily soluble in all types of solvents. The ammonia complex, however, is soluble only in solvents which are capable of dissolving typical salts. The compound does not melt but sublimes at higher temperatures at ordinary pressures.

Trimethyl tin chloride was introduced into a glass tube provided with suitable stopcocks and arranged so that it could be weighed. Ammonia was passed over the compound at ordinary temperatures and pressures after which the ammonia absorbed was determined by weighing, a correction being made for ammonia in the vapor state.

Subs., 0.7384: NH_3 absorbed, 0.0574. Calc. 1 mol. of NH_3, 7.87. Found: 7.77.

Trimethyl tin chloride was placed in a tube and ammonia condensed in the same at liquid ammonia temperatures, until all the compound was in solution. The excess of ammonia was then evaporated and finally pumped off for a short time.

Subs., 0.1707, 0.2639: AgCl, 0.1100, 0.1751. Calc. for 1 mol. of ammonia: Cl, 16.40; calc. for 2 mols.: 15.20. Found: 15.94, 16.41.

It is probable that under these conditions the compound takes up two molecules of ammonia, one molecule of which, however, is apparently not firmly held.

A sample of the same material was again placed on the pump and exhausted for two hours, and analyses made as before.

Subs., 0.3426, 0.3823: AgCl, 0.2280, 0.2557. Found: Cl, 16.46, 16.55.

These results show clearly that while trimethyl tin chloride probably takes up two molecules of ammonia, only one molecule is firmly held.

Trimethyl Tin Chloride and Aniline.—Trimethyl tin chloride was dissolved in petroleum ether and aniline added. A solid precipitate was formed which was thrown on the filter, washed with ether and then dried.

Subs., 0.5254, 0.6144: AgCl, 0.2559, 0.3028. Calc. for 1 mol. of aniline: Cl, 12.13. Found: 12.04, 12.19.

The melting-point curve of mixtures of trimethyl tin chloride and aniline was examined. An equimolar mixture solidified homogeneously at 84.5°. With 1.5 mols. of aniline per mol. of chloride initial precipitation took place at 72°. With two mols. of aniline per mol. of chloride the mixture remained liquid at room temperatures.

It is evident that trimethyl tin chloride combines with one molecule of aniline.

Trimethyl Tin Chloride and Pyridine.—Trimethyl tin chloride was treated with pyridine in petroleum ether solution. A white product precipitated at 0° which was washed with petroleum ether and dried; m. p., 37°.

Subs., 0.2522, 0.2668: AgCl, 0.1303, 0.1383. Calc. for 1 mol. of pyridine: Cl, 12.74. Found: 12.78, 12.82.

Trimethyl tin chloride and pyridine combine in equimolar proportions.

Trimethyl Tin Iodide and Ammonia.—A sample of trimethyl tin iodide was dissolved in ammonia, the excess of solvent was evaporated, and the residual vapor removed by connecting to a vacuum pump for a few minutes. The compound was then analyzed for iodine.

Subs., 0.1784, 0.2542: AgI, 0.1326, 0.1910. Calc. for 1 mol. NH_3: I, 41.24; calc. for 2 mols. NH_3: 39.08. Found: 40.18, 40.62.

A sample of the same material was then placed on the pump for a period of one hour, after which it was analyzed.

Subs., 0.3565, 0.5784: AgI, 0.2716, 0.4442. Found: I, 41.18, 41.51.

A sample of the iodide was dissolved in ether and a stream of ammonia gas passed through the solution. The compound precipitated from solution and was washed with ether and dried.

Subs., 0.1867, 0.2076: AgI, 0.1374, 0.1518. Found: I, 39.78, 39.53.

Trimethyl tin iodide evidently combines with two molecules of ammonia, one of which is lost readily, as is indicated by the fact that the sample which was subjected to the action of the pump for only a short period still yielded iodine values intermediate between those for compounds containing one and two molecules of ammonia, respectively. On the other hand, the iodine content of the compound which was precipitated from ether solution and not subjected to the action of the pump corresponds fairly closely to that of a compound containing two molecules of ammonia.

Trimethyl Tin Iodide and Aniline.—The freezing-point curves of various mixtures of trimethyl tin iodide and aniline were determined. In Table I are given the temperatures at which initial precipitation occurred.

TABLE I

FREEZING-POINT DATA FOR MIXTURES OF TRIMETHYL TIN IODIDE AND ANILINE

Mol.-per cent. aniline	Initial temperature of precipitation °C.	Mol.-per cent. aniline	Initial temperature of precipitation °C.
6.88	52	66.65	95.2
20.11	77	72.22	94.5
34.21	88	76.2	93
50.77	93.5	78.96	92
60.84	95	81.83	90.7

It is evident that trimethyl tin iodide and aniline form a compound containing two molecules of aniline which melts homogeneously at 95.2°. The melting-point curve is extremely flat, which indicates that the compound is comparatively unstable.

Trimethyl Tin Iodide and Pyridine.—An equimolar mixture of trimethyl tin iodide and pyridine was found to melt at 60.5°, the temperature remaining constant until complete solidification had taken place. The further addition of one-half molecular equivalent of pyridine lowered the initial point appreciably, while with the addition of two molecular equivalents of pyridine the initial point of precipitation was lowered to 55°. The mixture was still mushy at room temperatures. Trimethyl tin iodide and pyridine combine in equimolar proportions.

Triethyl Tin Iodide and Pyridine.—Werner and Pfeiffer were unable to obtain a solid precipitate from mixtures of triethyl tin iodide and pyridine. Accordingly, mixtures of these two constituents were subjected to lower temperatures and the course of the melting-point curve approximated. With 40 mol.-per cent. of pyridine the mixture was still soft at —30°. With 50 mol.-per cent. of pyridine the mixture solidified homogeneously at —17°. On further addition of pyridine the melting point was lowered. The mixture containing 66 mol.-per cent. of pyridine still contained liquid at —30°. Trimethyl tin iodide remains liquid at —36°. Trimethyl tin iodide and pyridine thus form a compound in equimolar proportions which solidifies homogeneously at —17°. This accounts for the failure of Werner and Pfeiffer to establish the formation of a compound.

Dimethyl Tin Dichloride and Pyridine.—The dichloride was dissolved in alcohol and pyridine added, a white precipitate being formed. This product after washing and drying was found to sublime at a temperature of 145°.

Subs., 0.1321, 0.1578: AgCl, 0.0999, 0.1197. Calc. for 2 mols. of pyridine: Cl, 18.77. Found: 18.71, 18.76.

Evidently one molecule of pyridine is added for each equivalent of chlorine present in the molecule of dimethyl tin dichloride.

Ethyl Mercuric Chloride and Ammonia.—A sample of ethyl mercuric chloride was treated with liquid ammonia in a weighing tube. The excess ammonia was evaporated and the last traces removed by means of a pump.

Subs., 1.4408: NH_3 absorbed, 0.0940. Calc. for 1 mol. of NH_3: NH_3, 6.04. Found: 6.12.

Ethyl mercuric chloride and ammonia combine in equimolar proportions.

Amyl Mercuric Iodide and Ammonia.—A sample of amyl mercuric iodide was treated with liquid ammonia in a weighing tube and the amount of ammonia absorbed determined by weight after pumping off the excess.

Subs., 0.7282: NH_3 absorbed, 0.0288. Calc. for 1 mol. of NH_3: NH_3, 4.10. Found: 3.8.

Amyl mercuric iodide and ammonia combine in equimolar proportions.

When ethyl mercuric chloride and amyl mercuric iodide were treated with triethylamine and with pyridine, compounds were precipitated at 0°. These, however, melted or dissolved when room temperatures were reached and were not investigated further.

Discussion

Werner and Pfeiffer attempted to account for the compounds of the trimethyl tin halides with ammonia and the amines on the basis of Werner's theory. They expected to find these compounds combining with two molecules of ammonia or the amines, and indeed they found that in the case of triethyl tin iodide and aniline two molecules of aniline combined with a molecule of the iodide. The results above presented, however, indicate that it is the exception that a trimethyl tin halide combines with two molecules of an amine. Furthermore, in the case of a compound with ammonia, in which instance two molecules are combined with trimethyl tin iodide, one molecule of ammonia is held very loosely while the second molecule is held extremely tenaciously. It is interesting, too, to note that the alkyl mercury halides combine only with a single molecule of ammonia or the amines.

To account for the combination of ammonia and the amines with the alkyl tin halides it appears more rational to assume that the alkyl tin group migrates to the nitrogen atom, yielding pentavalent nitrogen and consequently a compound of the ammonium type. In this case the compound should have the properties of a salt, in view of the known properties of pentavalent nitrogen in the ammonium group. The reaction is entirely similar to that taking place between methyl iodide, for example, and pyridine, in which case reaction takes place according to the following equation: $CH_3I + C_6H_5N = C_6H_5NCH_3I$. In the case of trimethyl tin iodide, reaction takes place according to the equation: $(CH_3)_3SnI + C_6H_5N = C_6H_5NSn(CH_3)_3I$.

This view of the constitution of the compounds formed between the alkyl metal halides and ammonia and its derivatives is in agreement with the properties of the resulting compounds; more particularly, it serves to account for the fact that solutions of the alkyl metal halides in the amines conduct the current with considerable facility, while solutions of the same substances in solvents of the non-basic type are virtually non-conductors.

The alkyl metal groups, such as the trimethyl tin group, have a very marked affinity both for nitrogen and for oxygen. As will be shown in a later paper, these groups are not only able to combine with nitrogen to form compounds of the ammonium type, but under suitable conditions they also combine with oxygen to form stable compounds of the oxonium type.

Summary

The compounds of the alkyl tin and the alkyl mercury halides with ammonia and the amines have been investigated. It has been shown that trimethyl tin chloride and iodide combine with two molecules of ammonia, only one of which is firmly held. Trimethyl tin chloride combines with one molecule of aniline and pyridine, respectively. Trimethyl tin iodide combines with one molecule of pyridine. In the case of aniline, trimethyl tin iodide forms a compound containing two molecules of the former. Dimethyl tin chloride combines with two molecules of ammonia. Ethyl mercuric chloride and amyl mercuric iodide combine each with one molecule of ammonia.

It is pointed out that the results do not agree well with Werner's theory, as outlined by Werner and Pfeiffer. It is suggested that the properties of the resulting compounds are more rationally accounted for on the assumption that the alkyl metal group is transferred from the halogen atom to the nitrogen atom of the amine, thus forming a compound of the ammonium type.

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