[Contribution from the Chemical Laboratory of Brown University]

STUDIES RELATING TO ALKYL TIN COMPOUNDS. IV. PROPERTIES OF THE COMPLEX HYDROXY BROMIDE, $[(CH_3)_3SnOH]_2\cdot(CH_3)_3SnBr$

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As mentioned in a preceding article of this series, Kraus and Harada[1] have prepared compounds of the type $[(CH_3)_3SnOH]_2\cdot(CH_3)_3SnX$ where X is a halogen. These compounds are readily obtained in the form of well-defined crystals and preliminary investigation indicated that they have measurable stability in solution. It appeared of interest to study these compounds in order to gain some knowledge as to the nature of the complex formed. Dissolved in alcohol or acetone, the compounds conduct the electric current with considerable facility much better than corresponding solutions of trimethyl tin halide or trimethyl tin hydroxide. This indicates that a complex cation of some kind is formed which is moderately electropositive. On treating the compound with silver hydroxide in aqueous solution, an hydroxy derivative of the complex cation was obtained which has approximately the same strength as trimethyl tin hydroxide. However, as indicated by conductance measurements, this complex hydroxide, which is isomeric with trimethyl tin hydroxide, gradually breaks down to form the latter compound.

While the precise nature of the complex cation has not, as yet, been determined, it seems fairly clear that it contains three trimethyl tin groups along with two hydroxy groups. The nature of the linkage is uncertain. That trimethyl tin hydroxide is involved, perhaps after the manner of an oxonium compound, seems fairly certain. This is further borne out by the fact that trimethyl tin hydroxide reacts with methyl iodide to yield a compound whose ionization is considerably higher than that of either of its constituents.

Preparation and Properties of $[(CH_3)_3SnOH]_2\cdot(CH_3)_3SnBr$.—The compound may be prepared by a variety of methods. According to Callis[2] it is formed by the action of oxygen on trimethyl tin iodide in the sunlight. As will be shown below, it may also be formed by the oxidation of trimethyl tin in the presence of trimethyl tin bromide and water in benzene solution. It is most conveniently prepared by adding two equivalents of trimethyl tin hydroxide to one of the corresponding bromide (or another halide) in various solvents. We have found chloroform the most convenient solvent for this purpose.

One mole of trimethyl tin bromide is treated with two moles of trimethyl tin hydroxide in chloroform at room temperatures. Reaction takes place immediately with

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[1] Kraus and Harada, This Journal, 47, 2416 (1925).

[2] Callis, Dissertation, Clark University, 1922.

the formation of a supersaturated solution of the compound, which crystallizes out slowly on standing, large, well-formed crystals being produced. On vigorously shaking the solution, the greater proportion of the compound is immediately precipitated in the form of fine crystals, while the remainder of the material crystallizes out as the chloroform evaporates. The crystals so prepared are quite pure and melt sharply at 115° with slow decomposition. They appear to be identical with the compound prepared by Kraus and Harada.[1] Crystals of the compound, prepared and purified by various methods, were analyzed for bromine and tin. The results of the analyses were the same for the various preparations.

Anal. Subs., 0.4503, 0.5277, 0.4819: AgBr, 0.1398, 0.1641, 0.1496. Calcd. for $[(CH_3)_3SnOH]_2(CH_3)SnBr$: Br, 13.17. Found: Br, 13.21, 13.23, 13.21; mean, 13.22. Subs., 0.4229, 0.4120, 0.5124: SnO_2, 0.3159, 0.3076, 0.3736. Calcd.: Sn, 58.83. Found: Sn, 58.84, 58.81, 58.97; mean 58.87.

The results of the analyses indicate that the composition of the compound corresponds to the formula $[(CH_3)_3SnOH]_2{\cdot}(CH_3)_3SnBr$.

The formula of the compound may be written $[(CH_3)_3Sn]_3OBr{\cdot}H_2O$. This would correspond to an oxonium type of compound containing one molecule of water. The attempt was made to prepare an anhydrous compound corresponding to this formula. For this purpose, equivalent amounts of trimethyl tin and trimethyl tin bromide were dissolved in dry benzene under an atmosphere of oxygen. A control experiment was carried out in which moist benzene was employed as solvent. The apparatus was attached to a manometer so that the rate of absorption of oxygen could be measured. Absorption of oxygen took place in both experiments, the rate in moist benzene being about twice that in the dry solvent. In the dry benzene, a white amorphous powder was precipitated, which appeared to be trimethyl tin oxide. In moist benzene, crystals were formed which closely resembled the dihydroxy bromide.[3] Unfortunately, this sample was lost and an analysis of the crystals could not be made. The experiments indicate, however, that, while the dihydroxy bromide is formed in the presence of moisture, it is not formed in the dry solvent.

Some Reactions of $[(CH_3)_3SnOH]_2{\cdot}(CH_3)_3SnBr$

Reduction with Metallic Sodium in Liquid Ammonia.—If the dihydroxy bromide contains one molecule of water as such, we should expect that, on reduction with metallic sodium in liquid ammonia, hydrogen would be evolved and sodium hydroxide precipitated. On the other hand, if hydroxyl groups are present in combination with tin, sodium hydroxide should be formed without evolution of hydrogen, while the trimethyl tin group should be reduced to the corresponding stannide, $NaSn(CH_3)_3$.

A quantity of the dihydroxy bromide (1.526 g.) was dissolved in liquid ammonia, a clear colorless solution being formed. On adding sodium, reaction took place immediately with the precipitation of a white solid which was doubtless trimethyl tin. On further addition of sodium, this solid dissolved, yielding a solution having a faint yellow color. This color is characteristic of sodium trimethyl stannide,[4] which is formed by the action of sodium on trimethyl tin. As the reaction proceeded, a gelatinous precipitate was formed which was doubtless sodium hydroxide. Sufficient sodium was added to impart a permanent blue color to the solution.

In the course of the reaction a small quantity of gas was evolved which was collected

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[3] Since accepted rules for the nomenclature of compounds of this type have not been elaborated, the complex compounds of the type $[(CH_3)_3SnOH]_2{\cdot}(CH_3)_3SnX$ will for convenience be termed "dihydroxy halides."

[4] Kraus and Sessions, THIS JOURNAL, **47**, 2361 (1925).

over water. Assuming the compound to contain one molecule of water, 28 cc. of hydrogen should have been produced. In the experiment 9 cc. of hydrogen was collected. This was given off slowly throughout the course of the reaction. Since the volume of hydrogen found was much below that required for one molecule of water per mole of compound, we must conclude that hydroxyl groups are present in the compound, which, for the most part, are split off on addition of sodium with the formation of sodium hydroxide.

Reaction with Ammonia.—It was suspected that, in a solution of the dihydroxy bromide, there exists an equilibrium between free trimethyl tin hydroxide and trimethyl tin bromide. If such is the case, then on treating the compound with ammonia in a suitable solvent, ammino trimethyl tin bromide, $(CH_3)_3SnBr\cdot NH_3$, should be formed and, if insoluble, precipitated.[5]

A quantity of the dihydroxy bromide was dissolved in chloroform and ammonia gas was passed through the solution. A precipitate was immediately formed. This was thrown on a filter and the excess chloroform evaporated. The resulting solid sublimed on heating and answered to tests for ammino trimethyl tin bromide.

Although ammino trimethyl tin bromide is precipitated under the conditions of the experiment just described, when the dihydroxy bromide is dissolved in liquid ammonia, little change occurs. A quantity of the compound was dissolved in liquid ammonia, the solvent was allowed to evaporate and the melting point of the residue determined. The substance melted at 107°, while the original pure dihydroxy bromide melted at 115°. Apparently, on solution in liquid ammonia, only an inconsiderable amount of the material was transformed. Other properties of the residue, such as the products of thermal decomposition, remained unchanged on treating with liquid ammonia. It seems that in liquid ammonia solution the compound is not extensively dissociated into its constituents.

Thermal Decomposition.—When the compound is heated under atmospheric pressure, it melts at 115° to form a clear liquid which boils slowly, giving a distillate containing trimethyl tin bromide. This was shown by collecting the distillate, dissolving it in ether, and precipitating the bromide as ammino trimethyl tin bromide by means of ammonia.

A weighed quantity of the compound was introduced into one leg of an inverted U-tube, which was then evacuated. The limb containing the compound was heated. while the other limb was cooled in liquid ammonia. In this experiment, 3.226 g. of compound was subjected to sublimation. Most of the material sublimed to the cooler parts of the tube above the oil-bath. A small quantity of solid residue was left behind, while some liquid was collected in the second limb of the U-tube. Of the total material, 3.0731 g. was found in the sublimate and 0.0428 g. in the residue. By difference, the weight of the distillate was 0.110 g.

The solid residue was analyzed for tin by the modified Krause method.[6]

Using 23.3 mg. of the residue, 29.9 mg. of SnO_2 was obtained, corresponding to 70.68% of tin, as compared with 72.04% required for dimethyl tin oxide. The sublimate for the most part melted at 115°, the same temperature as the original compound. In the distillate, the presence of both water and tetramethyl tin was established.

It is evident that, on heating the original compound, dissociation takes place according to the equation

$$[(CH_3)_3SnOH]_2\cdot(CH_3)_3SnBr = 2(CH_3)_3SnOH + (CH_3)_3SnBr \qquad (I)$$

When the vapors reach the colder portions of the tube, condensation occurs and the reaction is reversed.

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[5] Kraus and Greer, This Journal, **45**, 3078 (1923).

[6] Kraus and Bullard, *ibid.*, **51**, 3606 (1929).

As was shown in a preceding article,[6] when trimethyl tin hydroxide is heated to a temperature from 80 to 100°, it breaks down according to the equation

$$2(CH_3)_3SnOH = (CH_3)_2SnO + (CH_3)_4Sn + H_2O \qquad \text{(II)}$$

In the above experiment, during the process of sublimation, some of the hydroxide decomposed according to this reaction equation, which accounts for the residue of dimethyl tin oxide. The dimethyl tin oxide left behind, weighing 0.0428 g., corresponds to 0.108 g. combined weight of tetramethyl tin and water, according to Equation II. The weight of distillate, as determined by difference, was found to be 0.110 g. The water formed on sublimation of the original compound, therefore, resulted from the decomposition of the trimethyl tin hydroxide and not from the loss of water of hydration.

Molecular Weight.—The preceding experiments indicate that the hydroxyl group retains its linkage to tin in the compounds formed between trimethyl tin hydroxide and the trimethyl tin halides. It was surmised that in solution an equilibrium exists between the compound and its constituents. A determination of the molecular weight of the compound in solution should give clear evidence of dissociation, if such exists.

The compound is not sufficiently soluble in benzene to permit of molecular weight determination in that solvent. Accordingly, its molecular weight was determined in naphthalene by the cryoscopic method. The results are given in Table I.

TABLE I

MOLECULAR WEIGHT OF $[(CH_3)_3SnOH]_2 \cdot (CH_3)_3SnBr$ IN NAPHTHALENE

Naphthalene, g.	Compd., g.	Δt	Mol. wt.
23.38	0.3515	0.408	262
26.16	.2358	.254	252

The formula weight of the dihydroxy bromide is 605.3, while that of the corresponding mixture of trimethyl tin hydroxide and trimethyl tin bromide is 201.6. The value obtained for the mean molecular weight in naphthalene shows that the compound is largely dissociated into its constituents in that solvent.

Conductance of Mixtures of $(CH_3)_3SnBr$ and $(CH_3)_3SnOH$ in Solution.—It was thought that a study of the conductance of the dihydroxy bromide and of various mixtures with trimethyl tin bromide in non-aqueous solvents might yield some information as to the existence of a complex compound and its properties. Accordingly, the conductance of such mixtures was studied in absolute alcohol and in acetone. The conductance was measured in suitable cells by the usual Kohlrausch method and with the usual precautions. No claims are made for exceptional precision, since the object of these experiments was to get the general order of magnitude and the course of the conductance curve as a function of the composition of the solution.

Absolute Alcohol.—The conductance of a solution of the dihydroxy bromide was compared with that of an equivalent mixture of its constituents in absolute alcohol. The specific conductance of the alcohol was 0.5 × 10^{-6}. All measurements were carried out at 25°. The results are given in Table II, concentrations being expressed in moles per liter and the specific conductance L in reciprocal ohms.

TABLE II

CONDUCTANCE OF $[(CH_3)_3SnOH]_2\cdot(CH_3)_3SnBr$ AND OF MIXTURES OF $(CH_3)_3SnOH$ AND $(CH_3)_3SnBr$ IN ABSOLUTE ALCOHOL AT 25°

$(CH_3)_3SnOH$	$(CH_3)_3SnBr$	$[(CH_3)_3SnOH]_2$ $(CH_3)_3SnBr$	$L \times 10^4$
0.03314	0.0	0.0	0.03
.02601	.01657	.0	.87
.03314	.01657	.0	.96
.0	.01657	.0	.54
.0	.0	.01657	.95

As may be seen from the table, a solution of the compound at a concentration of 0.0166 mole per liter has a specific conductance of 0.95 × 10^{-4}, which is substantially identical with that of an equivalent mixture of its constituents. It follows that, when solutions of trimethyl tin hydroxide and bromide are mixed, reaction takes place immediately with the formation of a complex compound. It will be noted that the conductance of the pure hydroxide, at a concentration equivalent to that of hydroxide in a solution of the compound, was only 0.03 × 10^{-4}, while that of a corresponding solution of trimethyl tin bromide was 0.54 × 10^{-4}. In other words, in ethyl alcohol solution, the conductance of the compound is nearly twice as great as the sum of that of its constituents taken separately in the same solvent. The molecular conductance of the compound at a concentration of 0.0166 molar is approximately 5.8.

Acetone.—As Kraus and Callis[7] have shown, the alcohols, or other hydroxy compounds, react with trimethyl tin bromide to form a complex cation which is fairly electropositive and the solutions of which are therefore markedly ionized. It was to be expected, therefore, that, in other types of solvents, the relative conductance of the dihydroxy bromide and of trimethyl tin bromide would differ greatly from that found in alcohol.

The conductance of the dihydroxy bromide was compared with that of various mixtures of the hydroxide and the bromide in acetone at 25°. The specific conductance of the acetone used was 1.2 × 10^{-6}. A solution containing 0.01657 mole of dihydroxy bromide per liter had a specific conductance of 101 × 10^{-6}, while a solution of trimethyl tin bromide at the same concentration had a conductance of only 2.06 × 10^{-6}. The conductance of a solution of the hydroxide of equivalent concentration (0.033 N) was not determined but a 0.1 N solution of the hydroxide was found to have a specific conductance of 5.02 × 10^{-6}. It is evident that

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[7] Kraus and Callis, THIS JOURNAL, **45**, 2624 (1923).

the dihydroxy bromide is a much better conductor than either of the constituents at corresponding concentrations. It is noteworthy that, in acetone, trimethyl tin hydroxide is a slightly better conductor than is the corresponding bromide.

A 0.1 N solution of trimethyl tin bromide in acetone was made up and varying amounts of hydroxide were added. The specific conductance of these solutions was measured in the usual way. The values are tabulated below.

TABLE III

CONDUCTANCE OF 0.1 N $(CH_3)_3SnBr$ IN ACETONE IN THE PRESENCE OF $(CH_3)_3SnOH$

Concn. $(CH_3)_3SnOH$	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	0.15	0.20
Ratio of hydroxide to bromide	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.5	2.0
Sp. cond. $\times 10^4$	0.0345	1.13	2.06	2.93	3.73	4.45	5.19	5.85	6.37	6.88	7.37	9.36	10.73

As may be seen from the table, on adding trimethyl tin hydroxide to a solution of trimethyl tin bromide in acetone, the conductance is greatly increased. For an addition of one-tenth mole of the hydroxide per mole of bromide, the conductance is increased approximately 30 times, while for an addition of 2 moles it is increased 300 times. It may be pointed out that the final solution, containing 2 moles of hydroxide per mole of bromide, had a molecular conductance of 10.7. This value approaches that of some salts.

A second series of measurements was carried out with solutions containing 0.0166 mole of trimethyl tin bromide and varying amounts of trimethyl tin hydroxide from 0.0 to 0.0833 N. In other words, the ratio of hydroxide to bromide varied from 0.0 to 5.0. The specific conductance of the solutions was corrected for the conductance of the solvent and was approximately corrected for the conductance of excess trimethyl tin bromide, it being assumed that two molecules of hydroxide combine with one molecule of bromide. The results, including the corrections, are given in Table IV.

TABLE IV

CONDUCTANCE OF 0.0166 $N(CH_3)_3SnBr$ IN ACETONE AT 25° IN THE PRESENCE OF $(CH_3)_3SnOH$

Ratio of hydroxide to bromide	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.5	2.0	3.0	5.0
Corr. applied $L \times 10^6$	2.07	2.03	1.98	1.94	1.90	1.85	1.81	1.76	1.72	1.67	1.63	1.41	1.2	1.2	1.2
Corr. sp. cond. $\times 10^6$	0.0	9.5	18.5	25.8	33.9	39.6	46.2	50.1	56.8	60.6	66.8	88.1	105	131.0	174.0

The original solution of trimethyl tin bromide had a conductance of 2.07×10^{-6}. On adding only 0.1 mole of hydroxide per mole of bromide, the conductance was raised to 11.8×10^{-6}. The correction due to the conductance of the solvent and to excess bromide was 2.03×10^{-6}, leaving a conductance of 9.5×10^{-6} due to the compound formed between the hydroxide and the bromide. On further addition of the hydroxide, the specific conductance increased, although the rate of increase fell off with increase of total hydroxide added. It may be noted, however, that, on increasing the trimethyl tin hydroxide from two to five moles per mole of bromide, the specific conductance increased from 105×10^{-6} to 174×10^{-6}, or approximately 70%. This indicates that, while a complex electrolyte is formed between the hydroxide and the bromide, it is considerably dissociated in solution. The extent of this dissociation, however, is probably much lower in acetone or in alcohol than it is in naphthalene, as is indicated by the molecular weight in the latter solvent.

The constitution of the complex cation of the dihydroxy bromide cannot be inferred with any degree of certainty from available data. Considering the behavior of trimethyl tin bromide in hydroxy and amino solvents, one might be inclined to ascribe a formula of the oxonium type to the complex cation. Since two molecules of hydroxide are present in the compound, it would then be necessary to consider, either that two oxygen atoms are linked together or that a much more complex structure is involved. For the present, the precise structure of this complex cation must be left open.

The Ditrimethyl Tin Hydroxy Hydroxide, $[(CH_3)_3SnOH]_2 \cdot (CH_3)_3SnOH$.—The experiments described above indicate the existence of a complex cation corresponding to the formula $\{[(CH_3)_3SnOH]_2 \cdot (CH_3)_3Sn\}^+$. If such a complex cation exists, we should expect that, on treating the corresponding bromide with silver oxide in aqueous solution, the hydroxide of this ion would be formed. This hydroxide would be isomeric with trimethyl tin hydroxide. In order to determine whether a complex hydroxide is formed under these conditions, the conductance of equivalent solutions of the two hydroxides was compared.

A 0.1 *N* solution of the complex hydroxide was prepared by treating the corresponding bromide with freshly precipitated silver oxide until the solution gave no test for bromine. The solution was kept in the neighborhood of 0° throughout its preparation. After allowing the precipitated silver bromide to settle, the supernatant solution was siphoned into a cell in which its conductance was measured. If trimethyl tin hydroxide is formed in the above preparation, it would have a concentration of 0.3 *N*. The specific conductance of a 0.3 *N* solution of trimethyl tin hydroxide in water at 0 and 25° was found to be 0.890×10^{-4} and 2.03×10^{-4}, respectively. The specific conductance $L \times 10^4$, of the solution of the complex hydroxide, as measured at different times and temperatures, is given in Table V.

TABLE V

CONDUCTANCE OF 0.1 *N* $(CH_3)_3SnOH_2(CH_3)_3SnOH$ IN WATER

Temp., °C.....	0	0	25	25	29	26	25	25	25.05
Time, hours...	0	12	0	12	24	48	60	72	120
$L \times 10^4$......	0.256	0.453	0.565	0.923	1.710	2.048	1.978	1.984	2.040

As may be seen from the table, the conductance of the freshly prepared solution of the complex hydroxide is approximately one-fourth that of trimethyl tin hydroxide at the same temperature. Thus, the specific conductance of the freshly prepared solution at 25° was 0.56×10^{-4}, while that of the trimethyl tin hydroxide was 2.03×10^{-4}. The complex hydroxide is not stable. It gradually goes over to trimethyl tin hydroxide, the reaction rate being greatly influenced by the temperature; but even at 0°, the specific conductance increased from 0.26×10^{-4} to 0.45×10^{-4} in a period of twelve hours. Nevertheless, even at 25°, the conversion of the complex hydroxide is not complete until at the end of nearly one hundred hours. At the end of 120 hours, the specific conductance was found to be 2.04×10^{-4} at 25°, while that of a 0.3 *N* solution of trimethyl tin hydroxide was found to be 2.03×10^{-4}.

The above results show that two moles of trimethyl tin hydroxide combine with one mole of trimethyl tin bromide to form a complex electrolyte in which the bromine is largely ionized. The bromide ion may be replaced by hydroxyl, by treating with silver oxide. The resulting base is a comparatively weak electrolyte, its ionization being about the same as that of trimethyl tin hydroxide at the same molal concentration. It is gradually converted to the normal hydroxide on standing.

Reaction between Trimethyl Tin Hydroxide and Methyl Iodide.—Harada has found evidence that a compound is formed when trimethyl tin hydroxide is treated with methyl iodide in acetone solution.[8]

In order to test this point further, a solution was made up containing 0.1 mole of trimethyl tin hydroxide per liter, and to this was added 0.05 mole of methyl iodide. The conductance of this solution was measured at 25°. The specific conductance of the pure acetone was 1.2×10^{-6} while that of a 0.1 *N* solution of methyl iodide was 1.4×10^{-6} and of the hydroxide, at the same concentration, 5.2×10^{-6}.

Immediately on adding methyl iodide to the solution of trimethyl tin hydroxide, the conductance began to increase and this continued over a considerable period of time. The results are given in Table VI.

The initial values of the conductance rose very rapidly with time. The addition of a large excess of methyl iodide at the end of sixteen hours

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[8] Harada, Thesis, Clark University, 1923.

TABLE VI

CONDUCTANCE OF MIXTURES OF $(CH_3)_3SnOH$ AND CH_3I IN ACETONE

Time, hours	0	0.43	1.0	4.5	13.0	16.0	16.6[a]	18.0	20.0	25.8	42.7	49.0	67.0	85.7
$L \times 10^4$	0.184	0.402	0.513	0.987	1.77	2.05	1.86	2.51	3.43	4.59	5.42	5.76	6.10	63.1

[a] At this point a large excess of CH_3I was added.

resulted in a marked increase in the rate of reaction, as may be seen from the table. The sum of the conductance due to the components was approximately 0.078×10^{-4}, as against 0.184×10^{-4} for the mixture as initially measured. As time went on, however, the conductance rose. At the end of sixteen hours the specific conductance of the solution had a value approximately twenty-six times that calculated for a mixture of the constituents. At that point, a large excess of methyl iodide was added in order to accelerate the reaction. At the end of eighty-six hours, the solution had reached practically a constant value of 6.31×10^{-4}. Assuming a compound to be formed of the type $[(CH_3)_3SnOH]_2 \cdot CH_3I$, the equivalent conductance of the final solution had a value of 12.6. This value is greater than that of many salts, for example, lithium chloride,[9] lithium nitrate or silver nitrate.[10]

Summary

A convenient method is described for the preparation of the complex dihydroxy bromide, $[(CH_3)_3SnOH]_2 \cdot (CH_3)_3SnBr$. The molecular weight of this compound in naphthalene indicates that it is largely dissociated into its constituents in that solvent.

When the dihydroxy bromide is reduced with sodium in liquid ammonia, some hydrogen is evolved but not enough to correspond to one mole of water in the compound.

Ammino trimethyl tin bromide is precipitated from solutions of the compound in organic solvents. However, the compound is not greatly altered on solution in liquid ammonia.

At higher temperatures the compound is dissociated into its constituents which sublime and recombine. A small proportion of trimethyl tin hydroxide breaks down to dimethyl tin oxide, tetramethyl tin and water under these conditions.

The electrical conductance of the compound in alcohol is approximately twice that of its constituents in the same solvent taken separately.

The conductance of the compound in acetone is much greater than that of its constituents in the same solvent. The conductance of trimethyl tin bromide, on addition of 0.1 mole of hydroxide per mole of

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[9] Sêrkov, *J. Russ. Phys.-Chem. Soc.*, **41**, 9 (1909).

[10] Roshdestwensky and Lewis, *J. Chem. Soc.*, **80**, 2140 (1911).

bromide, is increased thirty times and on addition of two moles, 300 times. On further addition of hydroxide the conductance is further increased, indicating appreciable dissociation of the complex compound in acetone.

On treating the dihydroxy bromide with silver oxide in an aqueous solution, the corresponding hydroxy derivative is obtained. The conductance of the solution clearly indicates that this complex hydroxide has considerable stability. It goes over gradually to trimethyl tin hydroxide, with which it is isomeric.

Trimethyl tin hydroxide forms a complex compound with methyl iodide in acetone. This compound is formed gradually and its solutions are relatively highly ionized. At a concentration of 0.1 N, the equivalent conductance has a value of the order of that of such salts as lithium nitrate and silver nitrate.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE MECHANISM OF CARBOHYDRATE OXIDATION. XIII. THE ACTION OF POTASSIUM HYDROXIDE ON CALCIUM HEXOSEDIPHOSPHATE. A COMPARISON WITH THAT OF GLUCOSE AND FRUCTOSE[1]

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The rates of fermentation of glucose, mannose and fructose are almost the same and the products of these reactions are identical.[3] These facts suggested a fermentation mechanism involving the formation of common intermediates—a condition which seemed easily satisfied on the assumption that these substances were the enediols of the hexoses, especially since no other hexose can yield the same enediols as these, and no other is fermented at a comparable rate. This point of view seemed strengthened through Young's discovery that the same hexosediphosphoric acid[4] ($C_6H_{10}O_4(PO_2(OH)_2)_2$) is formed from each of these three sugars as an intermediate in fermentation as evidenced by the identity, regardless of its source, of all its properties, including optical rotation. Furthermore, this acid has little reducing power except on hydrolysis, and it does not form an osazone without hydrolysis of a phosphate group.

Schlubach and Rauchenberger[5] have recently methylated this common hexosediphosphoric acid and found that only seven methyl groups were

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[1] Read at the Columbus Meeting of the American Chemical Society May, 1929.

[2] E. I. du Pont de Nemours and Co. Fellow, 1928–1929.

[3] Harden, "Alcoholic Fermentation," Longmans, Green and Co., London, **1923**, pp. 32, 48.

[4] Young, *Proc. Roy. Soc.* (London), **81**, 528 (1909).

[5] Schlubach and Rauchenberger, *Ber.*, **60B**, 1178 (1927).