From the known pressures and rates as plotted in Fig. 2, it is possible to calculate an average atomic absorption coefficient form ercury at various pressures when subjected to a pressure of 10 cm. of hydrogen. This calculation has been made and the results are plotted in Fig. 5. The absorption coefficient shows the same type of variation that was noted by Hughes and Thomas[1] for pure mercury under its own vapor pressure.

Conclusion

The vapor pressures of mercury over thallium amalgams at 26° have been determined. From these the activities have been calculated and shown to agree reasonably well with those calculated from the electromotive force measurements of Richards and Daniels. The broadening of the absorption line of mercury by hydrogen for its own resonance light has been studied, and the change in the atomic absorption coefficient of mercury in the presence of hydrogen for its resonance line has been determined.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

STUDIES RELATING TO METHYL TIN DERIVATIVES. I. INTRODUCTION. II. ACTION OF ZINC ON TRIMETHYL TIN BROMIDE. III. TRIMETHYL TIN PHENOLATE. IV. DECAMETHYLSTANNOBUTANE

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I. Introduction

The heavier elements of the fourth group are, in many respects, analogous to carbon. Various hydrides of these elements have been prepared and their properties have been found to correspond fairly closely with those of corresponding carbon compounds. The stability of the hydrides decreases with increasing atomic number, so that their study is not generally practicable. We have but few radicals of these elements corresponding to methyl, ethyl, phenyl, etc.

However, if the hydrogen atoms attached to an element, such as tin, are substituted by alkyl or aryl groups, radicals are obtained whose properties correspond closely to those of similar carbon radicals. Thus the group $(C_6H_5)_3Sn$, or triphenylstannyl, bears a close physical and chemical resemblance to triphenylmethyl, $(C_6H_5)_3C$. In the case of most carbon compounds, the tendency of two unsaturated carbon atoms to combine with each other is so great that stable coupling occurs and the group becomes inactive. On the other hand, in the case of the corresponding tin compounds, the coupling is relatively weak and the groups exhibit marked reactivity.

While such compounds as sodium methyl, sodium ethyl, etc., have been obtained, their reactivity is so great that they are not generally usable for synthetic purposes. This difficulty, in the case of carbon compounds, has been largely overcome through the use of the Grignard reagent, in which an alkyl or aryl group is coupled to magnesium. In the case of tin, compounds of the type $NaSnR_3$ or Na_2SnR_2 are readily obtained and they are convenient reagents for introducing the organic tin groups into various compounds. The alkali metal salts mentioned serve very much the same purpose in the chemistry of tin that the Grignard reagent does in the chemistry of carbon.

Compounds such as sodium trimethyl tin, $NaSnR_3$, are readily soluble in liquid ammonia and in this solvent they react conveniently with many other substances, particularly halogenated compounds. Kraus and Greer[1] have described a number of syntheses in which sodium trimethyl tin was used. In the present investigation the use of the same reagent has been extended to the preparation of various compounds. A considerable number of incidental problems developed which it was found necessary to study and an account of these will be given in the sequel.

II. Action of Zinc on Trimethyl Tin Bromide

Frankland[2] reported that triethyl tin is formed by the action of zinc on triethyl tin chloride in aqueous solution. With a view to utilizing a similar reaction in the preparation of trimethyl tin, the action of zinc on trimethyl tin bromide was investigated. It was found that while reaction takes place between trimethyl tin bromide and zinc, no trimethyl tin is formed. Instead, there are produced tetramethyl tin, trimethyl tin hydroxide and metallic tin.

Procedure.—Trimethyl tin bromide was prepared by adding an equivalent quantity of bromine to tetramethyl tin in the cold,[3] the product being purified by fractional distillation. About 40 grams of this bromide, dissolved in 100 cc. of water, was sealed in a tube with freshly polished strips of zinc. The tube was fitted with a stopcock through which it was evacuated. It was then placed in a bath of boiling water for several days. Initially a red solid was precipitated on the surface of the zinc, but on continued

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[1] Kraus and Greer, THIS JOURNAL, **47**, 2568 (1925).

[2] Frankland, *Ann. Chem. Pharm.*, **85**, 329 (1853).

[3] This method of preparing the various halogenated derivatives of tetramethyl tin has since been abandoned in this Laboratory. Mr. Stafford has shown that by heating mixtures of tetramethyl tin with stannic chloride in appropriate proportions, the monochloride, dichloride or trichloride may be obtained at will in practically pure condition. The two liquids are mixed in the cold and the mixture is later heated in a sealed tube until the reaction is complete. The same method has been employed by Mr. Eatough in preparing halogenated derivatives of tetraphenyl tin. This method of preparation is advantageous since there is no loss of organic groups and substantially pure products are obtained. Since writing the above, the same method has been described by K. A. Kozeschkow, *Ber.*, **62**, 996 (1929).

heating this disappeared and a volatile yellow oil appeared and settled in the bottom of the tube.

After separating the oil from the supernatant liquid by means of a separatory funnel, it was fractionally distilled. Toward the end of this process needle-like crystals appeared and similar crystals also appeared in the original tube on standing. These crystals volatilized readily, when gently heated, indicating that they were trimethyl tin hydroxide.

The Products of Reaction.—The vapor density of the purified oil was determined and its molecular weight calculated. Using a bulb having a volume of 256 cc., the following data were obtained: 0.1945, 0.1575, 0.2031 g. of subs. at 78.5, 64.2, 81.2-mm. pressure and 26.9, 29.0, 27.2° correspond to the mean molecular weights 181.0, 180.4, 182.6; mol. wt. of $(CH_3)_4Sn$, 178.8.

The boiling point of the liquid was found to be 77.5° (uncorr.); the boiling point of tetramethyl tin is 78.0°. The vapor pressure of the liquid corresponded closely with that of tetramethyl tin. Thus at 0 and 27.7°, the vapor pressure of the liquid was found to be 3.5 and 12.0 mm., respectively, as against 3.6 and 11.6 for tetramethyl tin at the same temperatures.

The strips of zinc were removed from the reaction tube and carefully washed. They were found to be covered with a metallic coating, which was scraped off, dissolved in hydrochloric acid and tested with hydrogen sulfide. A yellow precipitate was formed, indicating the presence of tin.

The action of zinc on trimethyl tin bromide differs from that on triethyl tin bromide. While in the latter case triethyl tin is formed, in the former a complex reaction occurs, the chief product being tetramethyl tin. At the same time, trimethyl tin hydroxide and metallic tin are formed in appreciable quantity.

III. Trimethyl Stannyl Phenolate, $C_6H_5OSn(CH_3)_3$

Preparation.—The phenolate of trimethyl tin is readily prepared by the action of trimethyl tin bromide on sodium phenolate in liquid ammonia. Reaction occurs according to the equation

$$C_6H_5ONa + (CH_3)_3SnBr = C_6H_5OSn(CH_3)_3 + NaBr$$

Sodium phenolate is best prepared by adding phenol, in small portions, to a solution of sodium in liquid ammonia. On adding trimethyl tin bromide to the resulting solution of sodium phenolate, trimethyl tin phenolate is immediately precipitated. The product of the reaction was extracted with ether and, after distilling off the excess solvent, the phenolate was distilled under a pressure of 8 mm. at 109°. Under normal pressure, the liquid boils at 223–224° with some decomposition. It is stable in air in the pure condition but becomes colored on exposure to sunlight. It remains liquid at the temperature of boiling ammonia.

Analysis.—The tin content of the compound was determined by the Carius method. Subs., 0.4015, 0.5213: SnO_2, 0.2381, 0.3111. Calcd. for $C_6H_5OSn(CH_3)_3$: Sn, 46.2. Found: Sn, 46.68, 47.00.

Molecular Weight.—The molecular weight was determined by the freezing point method in benzene in the usual manner. Solvent, 37.03, 37.03 g.; solute, 1.389, 1.927; Δt, 0.718, 1.476°; mol. wt. found, 261.1, 267.7; mol. wt. calcd. for $C_6H_5OSn(CH_3)_3$, 257.

Characterization.—When trimethyl tin phenolate is treated with two equivalents of sodium in liquid ammonia, the following reaction occurs

$$(CH_3)_3SnOC_6H_5 + 2Na = NaSn(CH_3)_3 + C_6H_5ONa$$

The resulting solution is colored slightly yellow due to the sodium trimethyl tin. On adding ethyl bromide to the solution, phenetole and ethyl trimethyl tin are formed. The odor characteristic of phenetole was noticeable but it was not found possible to separate it from the associated tin compound. Accordingly, a solution of trimethyl tin phenolate was treated with one atom of sodium, in which case reaction proceeds as follows

$$2(CH_3)_3SnOC_6H_5 + 2Na = [(CH_3)_3Sn]_2 + 2NaOC_6H_5$$

The precipitated trimethyl tin was allowed to settle, the supernatant liquid was siphoned off and the trimethyl tin was repeatedly washed with fresh ammonia. The insoluble product left behind in the reaction tube melted at 23–25°, which agrees with the melting point of trimethyl tin. On brominating this material, trimethyl tin bromide was identified.

The washings containing sodium phenolate were neutralized with acid and treated with bromine water. A heavy white precipitate was formed, which is characteristic of phenol. On extracting an aqueous solution of the hydrolyzed product with ether and removing excess solvent, an oily liquid was obtained having the odor of phenol.

IV. Decamethylstannobutane

Kraus and Greer have prepared methylated tin derivatives containing chains of three and five tin atoms, corresponding to the general formula $(CH_3)_{n+2}Sn_n$. In order to complete this series, the corresponding butane was synthesized.

Preparation.—The method of Kraus and Greer was employed, disodium tetramethylstanno-ethane being first prepared by treating two moles of dimethyl tin dibromide with six moles of sodium. Reaction takes place according to the equation

$$2(CH_3)_2SnBr_2 + 6Na = 4NaBr + Na(CH_3)_2Sn{-}Sn(CH_3)_2Na$$

The butane was then prepared by treating the ammonia solution of the above stannide with two moles of trimethyl tin bromide. Reaction proceeds according to the equation

$$Na(CH_3)_2Sn{-}Sn(CH_3)_2Na + 2(CH_3)_3SnBr = (CH_3)_3Sn{-}Sn(CH_3)_2{-}Sn(CH_3)_2{-}Sn(CH_3)_3 + 2NaBr$$

Reaction takes place readily with separation of the stannobutane in liquid form. After evaporation of the ammonia, the liquid was dissolved in ether, the resulting solution was filtered and the ether removed with a pump.

Analysis.—The final product of reaction was analyzed for tin by the Carius method. Subs., 0.2443, 0.1110: SnO_2, 0.2357, 0.1066. Calcd. for $(CH_3)_{10}Sn_4$: Sn, 75.96. Found: Sn, 76.00, 75.65.

Molecular Weight.—The molecular weight of the compound was determined in benzene by the freezing point method. Solvent, 21.90, 21.90 g.; solute, 0.7371, 0.1098 g.; Δt, 0.276, 0.040°; mol. wt. found, 610, 627; mol. wt. calcd. for $(CH_3)_{10}Sn_4$, 625.

Properties.—The pure compound is a colorless liquid which is somewhat viscous. It oxidizes readily with the formation of a white solid.

With this compound, the complete series of derivatives up to and including the pentane have been synthesized. The synthesis of the butane further confirms the mechanism of the reduction reactions of the dimethyl tin halides suggested by Kraus and Greer.[4]

Summary

1. The action of zinc on trimethyl tin bromide in aqueous solution has been studied. The chief product of reduction is tetramethyl tin. Some trimethyl tin hydroxide and metallic tin are also formed.

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[4] Kraus and Greer, This Journal, **47**, 2570 (1925).

2. Trimethylstannyl phenolate, $C_6H_5OSn(CH_3)_3$, has been prepared by the action of trimethyl tin bromide on sodium phenolate.

3. Decamethylstannobutane, $(CH_3)_{10}Sn_4$, has been prepared.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE MEASUREMENT OF THE CONDUCTANCE OF ELECTROLYTES.

II. IMPROVEMENTS IN THE OSCILLATOR AND DETECTOR

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The new form of alternating current bridge described in the first paper of this series[1] has been used in the study of the principles of design of cells for the measurement of the conductance of solutions. Although in most respects this bridge has met our most exacting requirements, a few improvements in the accessories of the bridge have been made which it seems desirable to describe without waiting until the results on cell design can be published.

Modification of the Oscillator to Give Low Voltages.—During the work on cells it became evident that it would be advantageous to reduce the voltage used considerably below the values (2 to 5 volts) which had been used in the study of the bridge itself and in the study of resistance boxes, in order to reduce the heating effect of the current on the cells and to study polarization and the variation of resistance with voltage which has been reported by others.[2]

The vacuum tube oscillator as originally built and described in the first paper of this series contained an output coil having 140 turns and when this coil was as close as possible to the oscillating coil, gave a maximum voltage of 5.2 volts at 2280 cycles, 4.2 volts at 1090 cycles and 2.3 volts at 500 cycles, when used to measure 10,000 ohms in the bridge. When measuring lower resistances, the voltage was somewhat less. The voltage could be diminished continuously down to about 0.2 volt by moving the output coil along its axis away from the oscillating coil to a distance of six inches, thus diminishing the inductive coupling. To reduce the voltage still more by moving the coil still farther away from the controlling coil did not seem to be wise because this would reduce the influence of the controlling coil without at the same time reducing the influence of outside disturbing factors such as electric light circuits and nearby electric motors. An attempt to reduce the voltage by the use of

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[1] Grinnell Jones and R. C. Josephs, THIS JOURNAL, **50**, 1049 (1928).

[2] W. A. Taylor and S. F. Acree, *ibid.*, **38**, 2416 (1916); C. A. Kraus and H. C. Parker, *ibid.*, **44**, 2438 (1922).