a molar frictional constant of 2.48×10^{16} (both at 20°); a comparison with the molar frictional constant calculated for a spherical molecule of the same molecular mass and volume shows that the molecule of Bence-Jones protein is spherical and has a radius of $2.18\mu\mu$.

3. At P_H values lower than 3.5 the molecule breaks up into some non-centrifugible substance, the remaining protein having the normal molecular weight. The acid hydrolysis of the protein is accompanied by a rise in light absorption.

4. At P_H values higher than 7.5 a slight alkaline hydrolysis sets in, producing a non-centrifugible substance, but the main change brought about by the high P_H is a splitting up of the molecule into a centrifugible substance which probably has a molecular weight equal to half that of the normal molecule. In the P_H range 12.2–12.7 the sedimentation constant has a value of 1.69×10^{-13}. The light absorption increases in the P_H range 7.5–12.2 and then becomes constant again.

5. A comparison between Bence-Jones protein and egg albumin with regard to molecular weight, sedimentation constant and molar frictional constant shows that the values are identical within the limits of experimental error. Although these two proteins are entirely different as to chemical composition and isoelectric point, their molecular mass and size are almost identical.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

STUDIES RELATING TO ALKYL TIN COMPOUNDS.
III. SOME PROPERTIES OF TRIMETHYL TIN HYDROXIDE

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Recently Kraus and Harada[1] have described compounds formed between trimethyl tin hydroxide and trimethyl tin halides corresponding to the formula $[(CH_3)_3SnOH]_2(CH_3)_3SnX$. In attempting to establish the constitution of these compounds, it was found necessary to study the properties of trimethyl tin hydroxide, and, particularly, its thermal decomposition. The present paper records the results of the latter investigation.

Preparation of $(CH_3)_3SnOH$.—According to Cahours,[2] trimethyl tin hydroxide is formed on treating trimethyl tin halides with a strong solution of an alkali. The hydroxide is readily soluble in water and sublimes at temperatures above 80°. Considerable difficulty was experienced in the preparation of the pure hydroxide, which was invariably accompanied by a large loss of material. As will be shown later, this loss was probably due

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[1] Kraus and Harada, THIS JOURNAL, **47**, 2416 (1925).

[2] Cahours, *Ann.*, **114**, 377 (1860).

to decomposition of the hydroxide at the higher temperatures. The following method of preparation was found to yield fairly satisfactory results.

Trimethyl tin bromide is introduced into a flask containing a 55% solution of sodium hydroxide (m. p. 40°) at a temperature just above its melting point. The flask is placed in a horizontal position in a sheet metal steam-bath with the neck projecting through an opening in one side. A closely fitting glass tube slipped over the neck of the flask outside the box serves as condenser. Sublimation is continued until droplets of moisture begin to appear on the walls of the condenser. The sublimate consists of practically pure trimethyl tin hydroxide containing a trace of moisture which is removed by means of ordinary drying agents in a desiccator. The yield is in the neighborhood of 75%.

Anal. Subs., 0.4297: SnO_2, 0.3065. Calcd. for $(CH_3)_3SnOH$: Sn, 65.69. Found: Sn, 66.08.

Thermal Decomposition of $(CH_3)_3SnOH$.—According to Cahours,[2] trimethyl tin hydroxide undergoes decomposition at higher temperatures according to the equation

$$2(CH_3)SnOH = [(CH_3)Sn]_2O + H_2O \qquad (1)$$

Our own experiments, to be described below, indicate that decomposition takes place according to the equation

$$2(CH_3)_3SnOH = (CH_3)_2SnO + (CH_3)_4Sn + H_2O \qquad (2)$$

This reaction, in all likelihood, takes place in two stages, as follows

$$2(CH_3)_3SnOH = [(CH_3)_3Sn]_2O + H_2O \qquad (3)$$

$$[(CH_3)_3Sn]_2O = (CH_3)_2SnO + (CH_3)_4Sn \qquad (4)$$

On attempting to sublime a quantity of the hydroxide at 200° in a tube placed in an electric furnace, practically no sublimate appeared, while a white residue was left behind in the tube. On analysis,[3] this residue was found to consist largely of dimethyl tin oxide.

Anal. Subs., 0.3161, 0.3328: SnO_2, 0.2922, 0.3072. Calcd. for $[(CH_3)_3Sn]_2O$: Sn, 69.13; for $(CH_3)_2SnO$: Sn, 72.05. Found: Sn, 72.81, 72.71.

A quantity of trimethyl tin hydroxide was placed in one leg of an inverted U-tube which was then evacuated and sealed. The limb containing the hydroxide was kept in boiling water for three days. The major portion of the hydroxide underwent decomposition. A distillate, consisting of two liquids, collected in the second leg. The less volatile of these proved to be water, while the more volatile was identified as tetramethyl tin, b. p. 77.5°. The residue in the first leg of the U-tube was washed with absolute alcohol to remove traces of undecomposed hydroxide and the resulting product was analyzed for tin.

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[3] The analyses were carried out according to a modification of the method of Krause, *Ber.*, **55**, 896 (1922). Krause oxidized the compounds by means of a mixture of sulfuric and nitric acids in a crucible. We have found it more advantageous to carry out the oxidation in pyrex tubes having a diameter of approximately 15 mm. and a length of from 15 to 20 cm. Under these conditions the chances of loss are very greatly reduced over the crucible method. In the case of certain compounds which are oxidized with extreme difficulty, fuming sulfuric and nitric acids are employed. In general, fuming acids are not required in the case of tin compounds, but they often are necessary in the case of germanium and silicon. With the use of a counterpoise, reproducible results were obtained with pyrex tubes. If extreme accuracy is required, silica tubes are preferable.

Anal. Subs., 0.1530, 0.1533: SnO_2, 0.1417, 0.1419. Calcd. for $(CH_3)_2SnO$: Sn, 72.05. Found: Sn, 72.95, 72.91.

The residue was dissolved in dilute hydrochloric acid and on evaporating there were recovered crystals melting at 107°; this identifies them as dimethyl tin dichloride, m. p. 108°. As is apparent from the above analysis, the tin content of the residual product was in all cases slightly higher than is required for dimethyl tin oxide. This discrepancy was probably due to partial decomposition of dimethyl tin oxide, as will be shown below. Trimethyl tin hydroxide evidently decomposes according to Equation 2. It is remarkable that, volatile as the hydroxide is, it is so largely decomposed at a moderate temperature. It is of interest to note that according to Chambers and Scherer,[4] triphenyl tin hydroxide decomposes at higher temperatures with the formation of diphenyl tin oxide and tetraphenyl tin.

Thermal Decomposition of Trimethyl Tin Oxide.—A quantity of trimethyl tin oxide, prepared by the oxidation of trimethyl tin,[5] was placed in one limb of an evacuated, inverted U-tube and heated to 120° in a paraffin-bath. A small quantity of liquid collected in the second limb of the tube which failed to freeze at liquid ammonia temperatures. The temperature of the paraffin-bath was then raised to 190° and maintained for some time. On opening the tube, the presence of a permanent gas was noted. The liquid formed in this reaction was identified as tetramethyl tin, b. p. 77.7°. The white residue in the first limb of the tube was analyzed for tin.

Anal. Subs., 0.2272, 0.2839: SnO_2, 0.2068, 0.2587. Calcd. for $(CH_3)_2SnO$: Sn, 72.05. Found: Sn, 71.69, 71.77.

The low value found for tin may have been due to a side reaction, as was indicated by the presence of a permanent gas. For the most part reaction proceeds according to Equation 4. When trimethyl tin hydroxide is heated, therefore, reaction, in all likelihood, first proceeds according to Equation 3, in which trimethyl tin oxide is formed; the latter compound, in turn, decomposes according to Equation 4.

Thermal Decomposition of Dimethyl Tin Oxide.—The high values obtained for tin in the residue left on decomposing trimethyl tin hydroxide suggested that dimethyl tin oxide is not completely stable under the conditions of these experiments. Accordingly, a quantity of dimethyl tin oxide was sealed in one leg of an evacuated U-tube, which was then heated with a free flame, while the other leg was cooled in ice water. A small quantity of liquid appeared in the second leg of the tube and was identified as tetramethyl tin. The residue in the first leg turned black while at the same time a gaseous pressure was built up in the tube. A quantity of this gas was collected and its density determined. The density corresponded to a mean molecular weight of 43.7. It was thought that this high value was due to the presence of tetramethyl tin. Therefore, in a second preparation, the gas was passed through a condenser cooled in liquid ammonia. The density of the resulting gas was found to correspond to a mean molecular weight of 26.5. This seemed to indicate that, while the methyl groups, in part, combined to form ethane, some of them interacted to form methane and ethylene. On passing the gas through a solution of potassium permanganate, the solution was immediately decolorized, indicating the presence of unsaturated hydrocarbons.

The tube used in the first preparation was evacuated and the material heated for some time to a temperature of about 400°. The black residue left behind was analyzed for tin.

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[4] Chambers and Scherer, THIS JOURNAL, **48**, 1054 (1926).

[5] Kraus and Sessions, *ibid.*, **47**, 2363 (1925).

Anal. Subs., 0.3714, 0.1291: SnO_2, 0.4022, 0.1396. Calcd. for SnO_2: Sn, 78.76; for SnO, Sn, 88.12. Found: Sn, 85.29, 85.23.

The analyses indicate that the mixture consisted of 30.5% of stannic oxide and 69.5% of stannous oxide. On heating dimethyl tin oxide, reaction for the most part takes place according to the equations

$$\begin{tikzcd} & (CH_3)_4Sn + SnO_2 \\ 2(CH_3)_2SnO \arrow[ur] \arrow[dr] & \\ & 2(C_2H_6) + 2SnO \end{tikzcd}$$

The above experiments show that if trimethyl tin oxide is formed in the thermal decomposition from trimethyl tin hydroxide, it is immediately decomposed to dimethyl tin oxide and tetramethyl tin. At still higher temperatures dimethyl tin oxide is decomposed, a mixture of stannous and stannic oxides being left behind, while tetramethyl tin and hydrocarbons are evolved.

Molecular Weight of Trimethyl Tin Hydroxide in Benzene.—The molecular weight of the hydroxide was determined in benzene solution by the cryoscopic method. The results are given in Table I.

TABLE I

MOLECULAR WEIGHT OF $(CH_3)_3SnOH$ IN BENZENE

Benzene, g.	$(CH_3)_3SnOH$, g.	Δt	Mol. wt.
46.23	0.1460	0.072°	219
41.39	.1343	.073°	222

The formula weight of trimethyl tin hydroxide is 180.8. Apparently, the hydroxide is appreciably associated in benzene solution. This result is in agreement with observations of Smith and Kipping.[6] They determined the molecular weight of tribenzyl tin hydroxide in benzene at its freezing point and in chloroform at its boiling point. For the molecular weight they obtained the values 660 and 727–821 in these two solvents, respectively. The formula weight of tribenzyl tin hydroxide is 409. It seems, then, that the tertiary alkyl tin hydroxides have a marked tendency to polymerize when dissolved in solvents of this type.

Summary

A method is described for the preparation of trimethyl tin hydroxide. The apparent molecular weight of the hydroxide in benzene indicates that it is slightly polymerized.

At slightly elevated temperatures trimethyl tin hydroxide decomposes, dimethyl tin oxide, tetramethyl tin and water being formed.

Trimethyl tin oxide undergoes thermal decomposition with the formation of dimethyl tin oxide and tetramethyl tin. At elevated temperatures dimethyl tin oxide decomposes, in part, with the formation of ethane and stannous oxide and, in part, with the formation of stannic oxide and tetra-

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[6] Smith and Kipping, *J. Chem. Soc.*, **103**, 2042 (1913).

methyl tin. Small quantities of methane and unsaturated hydrocarbons are also formed.

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[CONTRIBUTION FROM THE UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD, UNIVERSITY OF ST. ANDREWS]

THE COUPLING OF GLUCOSE AND GAMMA-FRUCTOSE. CONVERSION OF SUCROSE INTO ISO-SUCROSE

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From the theoretical standpoint the primary condition necessary for the synthesis of sucrose is to have in hand an equimolecular mixture of tetra-acetylglucose and tetra-acetyl-γ-fructose which can be subjected to the action of a dehydrating agent. In a previous paper[1] we have described the results obtained when the required γ-form of tetra-acetylfructose was prepared both from fructose and from inulin but when the compound was condensed with tetra-acetylglucose the only crystalline product isolated by us was not the octa-acetate of sucrose but the corresponding derivative of a new disaccharide which we termed "*iso*-sucrose." This failure to synthesize sucrose octa-acetate cannot be attributed to faulty manipulation in the sense that traces of acids had decomposed any sucrose derivatives which had been formed. Nor can it be ascribed to the use of a fructose acetate containing an oxygen ring in a different position from that present in the fructose component of sucrose. In our former work we established, and have since confirmed, the fact that *iso*-sucrose is much more readily hydrolyzed by acids than sucrose itself, and the ready isolation of the *less stable* disaccharide is a guarantee that the more stable isomeride had not been decomposed. Lest it be maintained that the tetra-acetylfructose used by us was not the same γ-form as is present in sucrose, we have now varied the procedure so as to ensure that this objection cannot apply.

When sucrose octa-acetate is acted on by acetyl bromide dissolved in glacial acetic acid, the disaccharide is ruptured into its components and the product consists of an equimolecular mixture of tetra-acetylglucose and tetra-acetyl-γ-fructose. It might reasonably have been expected that such a mixture would represent the ideal starting material for the synthesis of sucrose, but all attempts to re-condense the constituents by the action of phosphoric anhydride have again resulted in the formation of crystalline *iso*-sucrose octa-acetate. As before, the reaction yielded syrupy acetates of disaccharides other than *iso*-sucrose and, on occasions, *iso*-trehalose octa-acetate was isolated, but despite numerous variations in procedure no evidence has been obtained of the formation of sucrose

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[1] Irvine, Oldham and Skinner, THIS JOURNAL, **51**, 1279 (1929).