According to Johnson and Bates[18] the products of hydrolysis of Structure I would be carbon dioxide, ammonia and R—NH—CHR′—COOH.

Summary

1. The amino nitrogen, carbon dioxide and ammonia liberated from casein by sulfuric acid hydrolysis during intervals of from five to 30 hours have been determined.

2. Amino nitrogen from the acid hydrolysis of casein was found to become constant after about 20 hours.

3. The total ammonia liberated by acid hydrolysis is in excess of the carbon dioxide at the beginning, but after five hours these substances appear to be evolved at approximately the same rates.

4. Structures are presented representing the possible sources of the carbon dioxide and of part of the ammonia obtained by the acid hydrolysis of casein.

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THE DIMETHYLTIN GROUP AND SOME OF ITS REACTIONS

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Many of the less electropositive elements exhibit marked amphoteric properties.[1] With the exception of hydrogen, these elements have valences greater than unity, and in case part of these valences are satisfied by hydrocarbon groups, the number of amphoteric valences is less than the maximum. An element of valence n yields a univalent group $R_{n-1}M^n$. Such a group may appear either as positive or as negative ion, or as neutral group.[2] Common examples of groups of this type are triphenylmethyl, trimethyltin, triethyl-lead, etc.

We should also expect to obtain divalent groups of the type $R_{n-2}M^n$, which should act as divalent positive or negative ions and should be capable of existing in the neutral state. The diphenyltin group, $(C_6H_5)_2Sn$,[3] has been obtained in the neutral condition, as has also the diethyltin group, $(C_2H_5)_2Sn$.[4] Compounds of the type R_2SnX_2, in which X is a halogen, are well known and their behavior in solution gives indication of the existence of a divalent cation, R_2Sn^{++}.[5] Nothing is known thus far of compounds of the type N_2SnR_2, where N is a strongly positive element and SnR_2 acts as a divalent anion. It is the purpose of the present investiga-

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[18] Johnson and Bates, This Journal, **38,** 1087 (1916).

[1] Kraus, *ibid.*, **44,** 1216 (1922); *Trans. Am. Electrochem. Soc.*, **45,** 175 (1924).

[2] Kraus, This Journal, **46,** 2196 (1924).

[3] Krause, *Ber.*, **53,** 173 (1920).

[4] Frankland, *Ann.*, **85,** 338 (1853).

[5] Zelinsky and Krapiwin, *Z. physik. Chem.*, **21,** 46 (1896).

tion to supply further data regarding the properties of divalent groups, particularly the dimethyltin group, $(CH_3)_2Sn$.

The method adopted in this investigation is similar to that employed by Kraus and Sessions[6] in the study of the trimethyltin group. On reducing dihalides, $(CH_3)_2SnX_2$, with sodium in liquid ammonia, we should expect to obtain the free group R_2Sn or, on further reduction, the disodium salt of this group, $Na_2Sn(CH_3)_2$. However, the process of reduction, as well as other reactions in which this group is concerned, is much more complex than might be expected because of the pronounced tendency of tin atoms to form chains. These chains, it appears, are comparatively stable and play an important role in the process of reduction as well as in subsequent reactions in which these reduction products are concerned.

Reduction of Dimethyltin Halides

Preparation of Materials.—For many purposes, dimethyltin dibromide is most conveniently used in the preparation of the dimethyltin group.

The dibromide is readily prepared by further brominating trimethyltin bromide. This is done by slowly dropping an equivalent quantity of bromine into trimethyltin bromide while the temperature is gradually raised from 50° to 80°. Sunlight is preferably excluded. The crude product of bromination is freed from monobromide by washing with petroleum ether. Dimethyltin dibromide melts at 76°.

Dimethyltin dichloride may be prepared by chlorinating the monochloride, but care must here be exercised to exclude sunlight, as otherwise reaction may proceed explosively. The chloride melts at 107°.

Anal. Subs., 0.8080, 0.8571: AgCl, 1.0472, 1.1107. Calcd. for $(CH_3)_2SnCl_2$: Cl, 32.29. Found: 32.06, 32.06.

Reduction of Dimethyltin Dihalides with Sodium.—When metallic sodium is added to a solution of dimethyltin dibromide in liquid ammonia, immediate reaction occurs. The product obtained depends upon the amount of sodium added and, to some extent, on the conditions under which addition is made. On small additions of sodium, a yellow precipitate is formed, the amount of which increases until one atom of sodium has been added per atom of bromine in the compound. Reaction takes place as follows: $(CH_3)_2SnBr_2 + 2Na = 2NaBr + (CH_3)_2Sn$. The yellow precipitate is the free group, $(CH_3)_2Sn$, in a polymerized condition. The degree of polymerization is not known and probably varies with the conditions under which reduction is carried out.

On further addition of sodium, the yellow precipitate combines with the metal to form an orange-red solution. When one atom of sodium has been added per atom of tin, the precipitate has disappeared and the solution is a dark red. Reaction takes place according to the equation, $2(CH_3)_2Sn + 2Na = NaSn(CH_3)_2.Sn(CH_3)_2Na$. Thus, on addition of metal, the disodium salt, $Na_2Sn(CH_3)_2$, is not formed but rather a compound

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[6] Kraus and Sessions, This Journal, **47**, 2361 (1925).

in which two dimethyl tin groups appear in combination, each group being at the same time combined with a sodium atom. In fact, it was shown that the disodium salt, $Na_2Sn(CH_3)_2$, reacts with the free group, $Sn(CH_3)_2$, according to the equation, $Na_2Sn(CH_3)_2 + Sn(CH_3)_2 = NaSn(CH_3)_2.Sn(CH_3)_2Na$. On further addition of sodium, reaction takes place as follows: $NaSn(CH_3)_2.Sn(CH_3)_2Na + 2Na = 2Na_2Sn(CH_3)_2$. This reaction, then, is a reversible one.

Disodium dimethylstannide is readily soluble in liquid ammonia, yielding an intensely red solution which is opaque at higher concentrations. It is not possible by visual observation to determine the end-point of the final reduction process, for which reason the solution is stirred for an hour or more after addition of the necessary quantity of sodium.

When a solution of the disodium salt is treated with methyl iodide, reaction occurs according to the equation: $Na_2Sn(CH_3)_2 + 2CH_3I = Sn(CH_3)_4 + 2NaI$.

To 2.406 g. of dimethyltin dibromide were added 0.717 g. of sodium and, when this reaction was completed, 2 molecular equivalents of methyl iodide. A liquid was immediately precipitated. This liquid was washed repeatedly with ammonia to remove inorganic salts and finally, after all but a trace of ammonia had been drawn off as liquid, the remaining solvent was removed with a vacuum pump at liquid-ammonia temperature. The liquid was then allowed to come to room temperature and the density of its vapor determined.

Mol. wt. Subs., 353 cc. (27°, 45 mm.), weighed 0.1669 g. Calcd. for $Sn(CH_3)_4$: mol. wt., 187.8. Found: 180.4.

This reaction establishes the presence of the disodium salt in solution.

Disodium Tetramethylstanno-ethane.—As has already been stated, when the dimethyltin group is treated with sodium, a compound (in solution), containing one atom of sodium per atom of tin, is formed. It is scarcely conceivable that a free group of the type NaR_2Sn exists in solution, and we may therefore conclude that reaction takes place as follows: $2(CH_3)_2Sn + 2Na = NaSn(CH_3)_2.Sn(CH_3)_2Na$. The resulting compound is disodium tetramethylstanno-ethane.

In order to characterize this compound, methyl iodide was added to the solution. A white solid was immediately precipitated whose properties were found to correspond to those of hexamethylstanno-ethane or the free trimethylstannyl group.

Sodium was added to dimethyltin dibromide in the ratio of three atoms of sodium per molecule of bromide. A red solution resulted in which no precipitate was present. To this was added an equivalent quantity of methyl iodide. The white solid which precipitated was washed with water. This solid melted to a heavy oil above 25° and solidified below 18°. It was clearly the free trimethyltin group which melts at 23°. It was evidently formed according to the reaction, $Na(CH_3)_2Sn.Sn(CH_3)_2Na + 2CH_3I = 2\ NaI + (CH_3)_3Sn.Sn(CH_3)_3$.

Disodium Hexamethylstannopropane.—When dimethyltin dibromide is added to a solution of disodium dimethylstannide, reaction takes place immediately, the opaque red color of the disodium stannide disappears, and an orange-red, transparent solution is formed. Reaction takes place according to the following equation: $2Na_2Sn(CH_3)_2 + (CH_3)_2SnBr_2 = 2NaBr + NaSn(CH_3)_2.Sn(CH_3)_2.Sn(CH_3)_2Na$. The end product of the reaction, aside from sodium bromide, is disodium hexamethylstanno-propane, which is readily soluble and is chemically very reactive. The compound was characterized by various reactions which will be described below.

Diethylhexamethylstannopropane.—This compound was prepared from disodium hexamethylstannopropane by the following reaction: $NaSn(CH_3)_2.Sn(CH_3)_2.Sn(CH_3)_2Na + 2C_2H_5Br = 2NaBr + C_2H_5Sn(CH_3)_2.Sn(CH_3)_2.Sn(CH_3)_2C_2H_5$.

To 5.19 g. of dimethyltin dibromide was added 1.526 g. of sodium to form disodium dimethylstannide, and to this solution in turn was added 2.56 g. of dimethyltin dibromide which resulted in the formation of disodium hexamethylstannopropane. On addition of 1.81 g. of ethyl bromide an oil was immediately precipitated while the solution became colorless. After evaporation of the ammonia, absolute ether was added and the solution allowed to stand. The supernatant liquid was then siphoned into a special tube from which the ether was evaporated in an atmosphere of ammonia vapor. The residual ether was removed by means of a vacuum pump. The resulting product, which was an oily liquid, was sealed in small weighed tubes, each having a volume of 2 or 3 cc. The samples thus obtained were employed for analysis and molecular-weight determinations.

Anal. Subs., 0.4155, 0.3303, 0.3763: SnO_2, 0.3699, 0.2591, 0.3337. Calcd. for $Sn_3(CH_3)_6(C_2H_5)_2$: Sn, 70.5. Found: 70.12, 69.66, 69.85.

Mol. wt. Subs., 2.4410, 0.7473, 0.6990; in benzene, 29.37, 27.59, 28.87: Δt, 0.838, 0.300, 0.290. Calcd. for $Sn_3(CH_3)_6(C_2H_5)_2$: mol. wt., 504. Found: 495, 458, 534, av. 499.

The stannopropane is not stable in air, oxidation taking place slowly. It may be distilled under reduced pressures at a temperature from 80° to 100°, but apparently decomposition occurs, presumably with the formation of other chain compounds. After such distillation, the molecular weight of the product was found to be 350 in place of 499 for the original compound.

Dodecamethylstannopentane.—This compound may be prepared according to the following reaction: $NaSn(CH_3)_2.Sn(CH_3)_2.Sn(CH_3)_2Na + 2(CH_3)_3SnBr = 2NaBr + (CH_3)_3Sn.Sn(CH_3)_2.Sn(CH_3)_2.Sn(CH_3)_2.Sn(CH_3)_3$.

To 5.98 g. of dimethyltin dibromide was added 1.78 g. of sodium to form disodium dimethylstannide and to this, in turn, was added 2.99 g. of dimethyltin dibromide, which formed a solution of disodium hexamethylstannopropane; 5.0533 g. of trimethyltin bromide was then added to this solution. Precipitation occurred immediately on addition of the monobromide and, when an equivalent quantity of the bromide had been added, the color characteristic of the sodium salt had disappeared. The product of the reaction was an oily liquid. This was dissolved in ether and handled in a manner similar to that described in the preceding paragraph.

Anal. Subs., 1.445, 0.9987: SnO_2, 1.1103, 0.9541. Calcd. for $Sn_5(CH_3)_{12}$: Sn, 76.69. Found: 76.41, 76.11.

Mol. wt. Subs., 2.3345, 3.4939; in benzene, 33.43, 33.43: Δt, 0.443, 0.658. Calcd. for $Sn_5(CH_3)_{12}$: mol. wt., 774. Found: 799, 805, av. 802.

The preparations described above not only illustrate the marked chaining tendency of tin atoms but also serve to establish the existence of sodium salts of certain of these chains, particularly disodium tetramethylstannoethane and disodium hexamethylstannopropane.

Reaction of Disodium Dimethylstannide with Methylene Chloride.—When disodium dimethylstannide is treated with methylene chloride, we might expect reaction to take place as follows: $Na_2Sn(CH_3)_2 + CH_2Cl_2 = (CH_3)_2Sn:CH_2 + 2NaCl$. It thus should be possible to obtain tin doubly bonded to carbon. There is reason for believing, however, that the reaction is much more complex than that given above.

On treating disodium dimethylstannide with methylene chloride in liquid ammonia, the color characteristic of this salt disappears when one molecular equivalent of chloride has been added to two of the disodium salt. The resulting solution is red and no precipitate is present. This clearly indicates the presence of a compound in which the tin groups are simultaneously combined with carbon and sodium. Probably reaction takes place as follows: $2Na_2Sn(CH_3)_2 + CH_2Cl_2 = 2NaCl + NaSn(CH_3)_2.CH_2.Sn(CH_3)_2Na$. While this compound has not been characterized, its existence is rendered probable, in view of the corresponding reaction between disodium dimethylstannide and dimethyltin dibromide.

On further addition of methylene chloride, a white precipitate is formed and the solution is decolorized when the total chlorine added as chloride is equivalent to the sodium present, so that the final product of the reaction is a compound whose composition corresponds to the formula $(CH_3)_2SnCH_2$.

At ordinary temperatures, the compound is a liquid that does not crystallize but becomes very viscous and ultimately practically solid at low temperatures. It is fairly readily oxidizable in air, forming an insoluble white powder. It is readily soluble in ether, petroleum ether and other organic solvents. On standing, the liquid gradually increases in viscosity and, in the course of time, becomes solid. This solid becomes fluid at higher temperatures at a fairly definite point. In many respects its behavior is similar to that of ordinary rosin. The properties of the compound continue to change for a longer period of time.

A quantity of the compound was prepared by treating disodium dimethylstannide with methylene chloride in liquid ammonia as described. After evaporation of the ammonia, ether was added to dissolve the compound, and the supernatant liquid siphoned off and evaporated in a stream of ammonia gas. The last traces of ether or ammonia were removed with a vacuum pump. The product was then sealed in small sample tubes of known weight as already described.

Anal. Subs., 0.2904, 0.2752, 0.3844, 0.2981: SnO_2, 0.2706, 0.2543, 0.2613, 0.3671. Calcd. for $Sn(CH_3)_2CH_2$: Sn, 72.93. Found: 73.40, 72.78, 73.91, 72.64.

The analyses are thus in substantial agreement with the proposed formula.

Numerous attempts were made to determine the molecular weight of the compound in benzene, at the boiling point as well as the freezing point. In no case was the molecular weight found to correspond, even roughly, to the monomolecular formula. Indeed, in many instances practically no change was observed in the boiling point or freezing point of the solvent. The result of a typical molecular-weight determination follows: subs., 0.6322; benzene, 20.05 g.: Δt (lowering), 0.0158°; mol. wt., 1011. This molecular weight corresponds approximately to that of a compound containing six formula weights. Consistent results could not be obtained, which indicates that the degree of polymerization of the compound is not fixed. This is further indicated by the gradual change observed in the properties of the pure substance. Apparently the process of polymerization goes on steadily with time and the substance ultimately reaches a condition approaching that of a colloid.

The chemical properties of the compound are, in part at least, in agreement with the proposed formula. When the compound was treated with hydrochloric acid, a white solid was obtained which was found to melt at 35° and which was identified as trimethyltin chloride. Another compound was also obtained which melted at 107° and was identified as dimethyltin dichloride. The first compound is probably formed according to the reaction: $(CH_3)_2Sn{:}CH_2 + HCl = (CH_3)_3SnCl$. Trimethyltin chloride so formed reacts with hydrochloric acid with the formation of dimethyltin dichloride, which accounts for the presence of the dichloride found.

On treatment of the compound with bromine it might be expected that methylene bromide and dimethyltin dibromide would be formed. While bromine reacts fairly readily with the compound, neither of these substances was found among the products of bromination. Methyl bromide was identified as one of the products. Another product formed was not identified.

The Free Group $(R_2Sn)_x$.—The free group, $(R_2Sn)_x$, was prepared by two methods. (A) An ammonia solution of dimethyltin dibromide was treated with a quantity of sodium equivalent to the bromine present. A yellow precipitate was formed, presumably the group R_2Sn. (B) An ammonia solution of the salt disodium dimethylstannide was treated with one molecular equivalent of dimethyltin dibromide, the group R_2Sn being precipitated as a yellow solid.

The compound was purified by being washed repeatedly with liquid ammonia to remove the inorganic salts and other impurities soluble in liquid ammonia. While the compounds made by the two methods have the same appearance, they are not identical in properties, the product prepared according to Method B being much more readily oxidizable than that prepared according to Method A. In all likelihood, both compounds are polymers of the group $(CH_3)_2Sn$. The free diphenyltin group has been obtained as a liquid,[3] and it was to be expected that the free dimethyltin group would likewise be a liquid in the monomolecular or possibly even bimolecular condition. In the method of preparation here employed we have reactions between dihalides and compounds containing chains of tin atoms. The initial product is, therefore, a complex one when precipitated. Without doubt, the complexity of the product obtained depends upon the procedure followed in its preparation.

Preparation A.—The compound was obtained as a yellow solid by the method described above. Using a specially designed reaction tube, the solid was introduced into weighed bottles in an inert atmosphere. These samples were then exposed to slow oxidation. When the bottles reached constant weight, the products formed were analyzed for tin.

Anal. Subs., 0.8170, 0.4328. Calcd. for $(CH_3)_2SnO$: O_2 absorption, 0.0878, 0.0466. Found: 0.0858, 0.0490.

Subs., 0.3750, 0.3851: SnO_2, 0.3150, 0.3476. Calcd. for $(CH_3)_2SnO$: Sn, 72.05. Found: 71.34, 71.10.

The compound was brominated under benzene. It was found that two atoms of bromine are taken up per molecule of the dimethyltin group. On evaporating the benzene a compound was obtained melting at 76°. Evidently the dibromide was formed.

Preparation B.—This compound is very much more sensitive to oxidation than is that prepared according to Method A. In fact, it is so sensitive to the action of oxygen, that, even at low pressures of oxygen, explosion may take place. It is clear from this that, while the two preparations are otherwise identical, they differ markedly in the ease with which they may be oxidized, and therefore in their constitution.

Anal. Subs., 0.9356. Calcd. for $(CH_3)_2SnO$: O_2 absorption, 0.1006. Found: 0.0817.

The oxygen absorbed is probably low since, if oxygen is introduced too rapidly, the sample is lost, while on slow oxidation a long time is required.

It was shown that the compound contains no bromine by determining the sodium bromide formed in the course of reaction. From 3.2595 g. of dimethyltin dibromide, treated with an equivalent amount of sodium and then with a corresponding weight of dimethyltin dibromide, 6.667 g. of sodium bromide was recovered as compared with 6.834 g. calculated. Considering the fact that certain losses of bromine were unavoidable in manipulation, it is evident that the compound contains no bromine.

The compound was brominated in benzene solution at ordinary temperatures. Bromine reacted readily at first, but toward the end bromination appeared to be slower than in the case of Preparation A. On evaporation of the benzene, the greater portion of the residue melted at 76° while a small quantity of another product melted at 200°. Melting point as well as analysis of the lower-melting compound identified it as dimethyltin dibromide.

Anal. Subs., 0.5512, 0.5274: AgBr, 0.6702, 0.6396. Calcd. for $(CH_3)_2SnBr_2$: Br, 51.80. Found: 51.74, 51.69.

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Summary

1. Disodium dimethylstannide, $Na_2Sn(CH_3)_2$, has been prepared by treating dimethyltin dibromide with four atomic equivalents of sodium in liquid ammonia. On treating the same compound with three atomic

equivalents of sodium, disodium tetramethylstanno-ethane, $NaMe_2Sn.SnMe_2Na$, is formed. On treating two molecular equivalents of disodium dimethylstannide with one of dimethyltin dibromide, disodium hexamethylstannopropane, $NaSn(CH_3)_2.Sn(CH_3)_2.Sn(CH_3)_2Na$, is formed.

2. Diethyl hexamethylstannopropane has been prepared by treating disodium hexamethylstannopropane with ethyl bromide. Dodecamethylstannopentane has been prepared by treating the same disodiumstannopropane with trimethyltin bromide. Both compounds are difficultly volatile liquids which oxidize in the atmosphere.

3. The free dimethyltin group, $[Sn(CH_3)_2]_x$, in the polymerized form has been prepared by two different methods. Both products are yellow solids, insoluble in organic and inorganic solvents and oxidizing readily, one being spontaneously inflammable.

4. The stanno-ethylene, $(CH_3)_2Sn:CH_2$, has been prepared by the action of methylene chloride on disodium dimethylstannide. This compound is a liquid at ordinary temperatures which oxidizes slowly in air and is reactive toward the halogens. Its properties undergo change with time, apparently due to polymerization. The molecular weight in benzene solution indicates a high degree of polymerization.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE CALIFORNIA FRUIT GROWERS EXCHANGE]

THE VOLATILE CONSTITUENTS OF VALENCIA ORANGE JUICE

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General

The purpose of this investigation was to discover the nature of the substances responsible for the characteristic aroma of freshly prepared orange juice. This juice aroma appears to be due to certain substances existing in the juice itself, which are distinctly different from the "Oil of Orange," which occurs only in the peel.

This was demonstrated in the following manner: 135 liters of juice was prepared by means of Sunkist Extractors from halved oranges without crushing the oil cells. This juice was distilled under conditions to be described, and from the distillate about 0.75 cc. of a fragrant oil was obtained whose odor was distinctive and quite different from that of peel oil.

Since the flavor of orange juice changes very rapidly after removal from the fruit, it was practically impossible by the use of Sunkist Extractors to get a sufficient quantity of burred juice for this investigation without appreciable changes taking place in the first runnings by the time enough