

vestigation that the odorous constituents of the apple consist chiefly of amyl esters, and it has also afforded further information respecting the substance which imparts to some apples a distinctly rose-like odor. Although the proportion of this substance, even in the McIntosh apple, is extremely small, it has nevertheless been possible to determine with a considerable degree of certainty that it consists of the aliphatic terpene alcohol geraniol $C_{10}H_{18}O$. The evidence for this conclusion may be adduced from the fact that by the hydrolysis of the esters of the apple a product was obtained which possessed, in addition to the odor of amyl alcohol, a rose-like fragrance, and that by the oxidation of this product it yielded, besides valeric acid, a substance which had the characteristic odor and other properties of the aldehyde citral. At the same time the formation in very small amounts of the further oxidation products of geraniol or citral, which are acetone and levulinic acid, was decisively indicated. It is probable that geraniol, either in the free state or in the form of esters, is contained in varying amounts in all the numerous varieties of the apple, although to the greatest extent in those which possess its distinctive odor.

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THE PREPARATION OF METHYLMERCURIC ACETATE AND THE ISOLATION OF METHYLMERCURIC HYDROXIDE¹

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During the course of an investigation of the thermal decomposition of mercurous acetate in a non-oxidizing atmosphere (nitrogen) the formation of a small quantity of an organic mercury derivative was noted. A further study of the reaction led to the conclusion that the substance in question might be methylmercuric acetate. However, a comparison of its physical properties with those of the "methylmercuric acetate" first prepared and described by Otto² showed such a wide variation that the two substances could not be regarded as identical.

A consideration of the method by which Otto prepared his methylmercuric acetate cast some doubt upon the purity of his product. He heated mercury dimethyl with acetic acid in a sealed tube at 120° for 1 hour.² The reaction presumably took place in accordance with the general expression, $R_2Hg + HX = RHgX + RH$. In the presence of acetic acid, a further reaction may take place. This would result in the decomposition of the organomercuric acetate. Thus, it has been shown

¹ Presented before the American Chemical Society at the Birmingham Meeting, April, 1922.

² Otto, *Z. Chem.*, [2] 6, 25 (1870); *Ann.*, 154, 199 (1870).

that, when mercury diethyl is heated in a sealed tube with glacial acetic acid at 190°, the chief products of the reaction are ethane, metallic mercury, and ethyl acetate.³ The two last-named products evidently result from the decomposition of the ethylmercuric acetate formed in the primary reaction (1).



Mercury di-*iso*-amyl and mercury dibenzyl react similarly with acetic acid at elevated temperatures. The chief products are in each case a hydrocarbon, metallic mercury and an ester of acetic acid.³

However, the reaction of mercury dimethyl with acetic acid is apparently more complex than the decompositions of the mercury alkyls and aryls previously noted. When mercury dimethyl is heated to 250° with glacial acetic acid, one of the methyl groups is completely eliminated as methane; the other products are metallic mercury and a large quantity of a brown amorphous material of undetermined composition.³ Thus the removal of the second methyl group complicates the reaction in some unexplained manner. In view of this fact, it was deemed advisable to attempt the preparation of the true methylmercuric acetate by reactions which would exclude the possibility of the separation of the second methyl group.

Four methods were selected as being suitable; in each case the possibility of the decomposition of the desired organomercuric salt is remote.

(1) The action of mercuric acetate on mercury dimethyl: $(CH_3)_2Hg + Hg(OAc)_2 = 2CH_3HgOAc$. This type of reaction is general for the mercury alkyls and aryls.

(2) The formation of methylmercuric acetate by the neutralization of the parent mercury base with acetic acid: $CH_3HgOH + HOAc = CH_3HgOAc + H_2O$.

(3) The action of methylmercuric hydroxide on ethyl acetate: $CH_3HgOH + C_2H_5OAc = CH_3HgOAc + C_2H_5OH$. This reaction has been employed successfully in the preparation of mercury derivatives which are not readily obtainable in acid solutions.⁴

(4) The simple metathetical reaction between methylmercuric iodide and silver acetate: $CH_3HgI + AgOAc = CH_3HgOAc + AgI$. This reaction also is well adapted to the preparation of organomercuric salts which are decomposed by the action of acids:⁵ $RHgX + HX = HgX_2 + RH$.

A consideration of the results obtained by the use of all these methods shows that the true methylmercuric acetate was formed in each case.

³ Jones and Werner, *THIS JOURNAL*, **40**, 1270 (1918).

⁴ Whitmore, *ibid.*, **41**, 1844 (1919).

⁵ Otto, *J. prakt. Chem.*, [2] **1**, 180 (1870).

Method 1.—When mercuric acetate was added to a methanol solution of mercury dimethyl the greater part of the salt dissolved immediately, while gentle heating sufficed to bring the remainder into solution. The reaction product was then free from mercuric ion. Evaporation of the solution to dryness yielded crystals of a colorless solid which was found to be identical with the organic mercury compound obtained in the course of the thermal decomposition of mercurous acetate. Analyses showed that the product conformed to the composition demanded by methylmercuric acetate, $\text{CH}_3\text{HgOCOCH}_3$.

Method 2.—Upon a study of this method, the problem at once assumed a new angle. A search through the literature revealed the fact that the base, CH_3HgOH , from which the methylmercuric salts are derived, had never been isolated. However, since the corresponding ethyl derivative, $\text{C}_2\text{H}_5\text{HgOH}$, had been obtained by the action of moist silver oxide on ethylmercuric iodide,⁶ the preparation of methylmercuric hydroxide was undertaken in an analogous manner: $2\text{CH}_3\text{HgI} + \text{Ag}_2\text{O} + \text{H}_2\text{O} = 2\text{CH}_3\text{HgOH} + 2\text{AgI}$. Prepared in this way, the base was obtained as a colorless, crystalline solid. Its identity was confirmed by analyses, and by its chemical behavior. The conversion of the hydroxide into methylmercuric acetate by this method involved no difficulties.

A methanol solution of methylmercuric hydroxide was treated with the theoretical quantity of glacial acetic acid. Upon evaporation of the resulting solution to dryness, a colorless, crystalline solid was obtained. After purification, analysis and melting point showed it to be identical with the product obtained by use of Method 1.

Method 3.—When a solution of methylmercuric hydroxide in ethyl acetate was refluxed for 12 hours, a substance was obtained which was identical with the organomercuric salt obtained by the foregoing reactions.

Method 4.—The addition of silver acetate to a methanol solution of methylmercuric iodide caused an immediate precipitation of silver iodide at the ordinary room temperature. The methanol held in solution a substance whose melting point and analysis showed it to be identical with the mercury derivative prepared by the use of the preceding methods.

Mixed melting points were taken with the 4 products obtained as described above, and with the mercury derivative formed in the decomposition of the mercurous acetate. Each determination gave a melting point⁷ of 128° .

Portions of the 5 products prepared by the different methods were treated separately in aqueous solutions with dil. hydrochloric, hydrobromic and hydriodic acids. Identical methylmercuric halides were obtained from each sample of methylmercuric acetate: $\text{CH}_3\text{HgOAc} +$

⁶ Dunhaupt, *Ann.*, **92**, 381 (1854).

⁷ All melting points given in this article are uncorrected.

$\text{HX} = \text{CH}_3\text{HgX} + \text{HOAc}$. The properties of the salts so prepared were in agreement with descriptions given for methylmercuric chloride, bromide, and iodide.⁸ The identity of each of these methylmercuric halides has been definitely established. These metathetical reactions of the methylmercuric acetate prepared by us show, therefore, that the mercury-carbon linkage was not broken by any one of the four methods of preparation employed.

Methylmercuric acetate is described as crystallizing from acetic acid in thin, rhombic platelets, m. p. 142–143°, practically *insoluble* in boiling water and cold acetic acid, but more soluble in hot acetic acid and in alcohol.²

Methylmercuric acetate as prepared by us crystallizes from glacial acetic acid in thin, satiny platelets, m. p. 128°. It is very soluble at ordinary temperatures in water, in acetic acid, and in ethyl alcohol.

Thus, in view of the evidence presented, it will be seen that the substance prepared and described by Otto could not have been pure methylmercuric acetate. He does not support the identity of his "methylmercuric acetate" with analytical results, but merely states that the substance reacts with ammonium sulfide, with hydrochloric acid, and with iodine like the analogous aryl derivatives. In the absence of more definite data, we have not speculated upon the identity of the substance which he obtained.

Experimental

The Action of Mercuric Acetate on Mercury Dimethyl.—A solution of 5 g. of mercury dimethyl in 35 cc. of methanol was treated with 7.9 g. of mercuric acetate. The mixture warmed immediately, and nearly all of the mercuric acetate dissolved. Gentle warming sufficed to send the remainder into solution. After 10 minutes, the mercuric ion was shown to be absent from the reaction mixture by reason of the failure of sodium hydroxide to precipitate mercuric oxide from a test portion. (A solution of potassium iodide precipitated only methylmercuric iodide, m. p. 144°.) The main portion of the solution was then filtered, the filtrate was cooled in a freezing mixture, and 9.6 g. of methylmercuric acetate separated. Upon concentration of the mother liquor, a further yield of 2.1 g. of acetate was obtained. The total yield of pure substance was 97.5%. Methylmercuric acetate is very soluble at ordinary temperatures in water, glacial acetic acid, methanol, or ethyl alcohol. It is readily soluble in benzene, toluene, carbon tetrachloride, carbon disulfide, ethyl acetate, or pyridine. The acetate is only moderately soluble in ether, and in petroleum ether. It melts at 128°.

Methylmercuric acetate possesses a disagreeable odor which resembles somewhat that of mercury dimethyl. The acetate sublimes very readily, being slightly volatile even at the boiling point of ether. Thus, it is impossible to remove the last traces of the salt from a solvent by means of distillation. A persistent taste develops far back in the mouth after working for a short time with the salt or its solutions. The intensity of this disagreeable after-taste is greatly increased by the inhalation of tobacco smoke.

The determination of mercury in the acetate was carried out in the following manner. The substance was decomposed by boiling it for a half hour with a mixture of 3 parts

⁸ Crymble, *J. Chem. Soc.*, **105**, 668 (1914).

of conc. nitric acid and 1 part of sulfuric acid. After the resulting solution had been made nearly neutral by the careful addition of solid sodium bicarbonate, the mercury was precipitated by freshly prepared, colorless ammonium sulfide solution.

Analyses. Subs., 0.2010, 0.2558: HgS, 0.1711, 0.2158. Calc. for $C_3H_6O_2Hg$: Hg, 73.03. Found: 73.04, 72.87.

Subs., 0.1399, 0.3000: CO_2 , 0.0665, 0.1426. Calc. for $C_3H_6O_2Hg$: C, 13.10. Found: 12.93, 12.97.

The Preparation of Methylmercuric Hydroxide.—To 36.8 g. of methylmercuric iodide in 200 cc. of acetone-free methanol was added 25 g. of freshly prepared moist silver oxide. The mixture was stirred vigorously for an hour and then the silver iodide and unchanged silver oxide were filtered off. The filtrate was carefully evaporated to dryness in a vacuum below 55° since at this temperature decomposition of the mercury base sets in. The residue was then dissolved in the smallest possible amount of methanol. The solution was filtered, and the base was precipitated from the filtrate by the addition of a large quantity of cold, dry ether, in which methylmercuric hydroxide is nearly insoluble. The base is a colorless crystalline solid melting at 95° . It is exceedingly soluble in water and cannot be recrystallized undecomposed from this solvent. The base is very soluble in the usual organic solvents such as methanol, ethyl alcohol, benzene, toluene, carbon tetrachloride, pyridine, petroleum ether, or carbon disulfide.

Aqueous solutions of the base react alkaline to litmus, and acid to phenolphthalein.⁹

Methylmercuric hydroxide is a strong vesicant, and even dilute solutions produce blisters within a few hours.

Analyses. Subs., 0.2079, 0.6986: HgS, 0.2078, 0.6976. Calc. for CH_3OHg : Hg, 86.24. Found: 86.28, 86.10.

The Preparation of Methylmercuric Acetate by the Neutralization of Methylmercuric Hydroxide with Acetate Acid.—A methanol solution of 5 g. of methylmercuric hydroxide was treated with 1.5 g. of glacial acetic acid. The resulting solution was evaporated to dryness on a steam-bath, and the residue was dissolved in 75 cc. of hot carbon tetrachloride. The solution was allowed to cool slowly, whereupon 5.2 g. of long, colorless needles, m. p. 128° , separated. The mother liquor was cooled in a freezing mixture, and 0.5 g. more of the acetate was obtained; total yield, 96.6%.

Analyses. Subs., 0.3470: HgS, 0.2947. Calc. for $C_3H_6O_2Hg$: Hg, 73.03. Found: 73.21.

Subs., 0.3131: CO_2 , 0.1500. Calc. for $C_3H_6O_2Hg$: C, 13.10. Found: 13.09.

The Action of Methylmercuric Hydroxide on Ethyl Acetate.—A solution of 2.4 g. of methylmercuric hydroxide in 5 cc. of water was refluxed for 12 hours with 0.9 g. of ethyl acetate. At the end of this time the solution was allowed to cool, and it quickly solidified to a slightly brownish crystalline mass of methylmercuric acetate. This was recrystallized from carbon tetrachloride. The total yield was 2.7 g., or 94.7%.

Analysis. Subs., 0.3183: HgS, 0.2692. Calc. for $C_3H_6O_2Hg$: Hg, 73.03. Found: 72.94.

The Action of Silver Acetate on Methylmercuric Iodide.—When 4.9 g. of silver acetate was added to 10 g. of methylmercuric iodide in 30 cc. of methanol, the reaction took place immediately at room temperature. After the silver iodide had been filtered off, most of the methanol was evaporated on a steam-bath. The concentrated solution of the acetate was then set aside to crystallize. The product amounted to 7.6 g.; yield, 97.3%. This was of such purity that a recrystallization was unnecessary.

⁹ The weakness of the base is further shown by conductivity data included in results shortly to be published by J. L. Maynard and H. C. Howard, Jr., of Princeton University.

Analysis. Subs., 0.1065: HgS, 0.0903. Calc. for $C_2H_5O_2Hg$: Hg, 73.03. Found: 73.05.

Summary

1. The substance prepared and described by Otto was not pure methylmercuric acetate.
2. Pure methylmercuric acetate has been prepared by four different methods.
3. The parent base of the methylmercuric salts has been isolated.
4. Methylmercuric acetate is found to be one of the products formed by the thermal decomposition of mercurous acetate in an atmosphere of nitrogen.

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[CONTRIBUTIONS FROM THE OIL, FAT AND WAX LABORATORY, BUREAU OF CHEMISTRY,
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THE CHEMICAL COMPOSITION OF SOYA BEAN OIL

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Soya bean oil is reported by Matthes and Dahle¹ to contain palmitic acid 15%, oleic acid 56%, linolic acid 19%, and linolenic acid 4.8%. This is obviously not correct because the theoretical iodine number of such a mixture is 98.1, while the iodine number of soya bean oil is about 130. Keimatsu² examined a sample which he found contained about 12% of saturated acids and about 80% of unsaturated acids. He reports the saturated acid fraction consists of palmitic and stearic acids and the unsaturated acid fraction contains about 50% of an isomer of linolic acid, yielding a tetrabromide melting at 158°, about 15% of ordinary linolic acid and about 35% of oleic acid. W. B. Smith³ made an investigation of the composition of the unsaturated acids but not of the saturated acids. As a result he expresses the opinion that a soya bean oil having an iodine number of 134 contains approximately 2 to 3% of linolenic acid, 55 to 57% of linolic acid, 25 to 27% of oleic acid and 9 to 10% of saturated acids. The calculated iodine number of such a mixture agrees very well with that of the oil.

Experimental

The oil used in this investigation was expressed in this Laboratory from

¹ Matthes and Dahle, *Arch. Pharm.*, **249**, 424 (1911).

² Keimatsu, *Chem.-Ztg.*, **35**, 839 (1911).

³ Smith, *J. Ind. Eng. Chem.*, **14**, 530 (1922).