99. *Alkylmercuric Derivatives. Oxides, Carbonates, and Trismethylmercurioxonium Salts.*

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A number of trismethylmercurioxonium salts have been prepared (*a*) from bismethylmercuric oxide by partial neutralization, addition of a methylmercuric salt, and reaction with silver nitrate, and (*b*) from trismethylmercurioxonium perchlorate by double displacement with potassium salts. By the last method trismethylmercurioxonium hydroxide has also been obtained. The neutralization of aqueous and methanolic solutions of bismethylmercuric oxide with various acids is discussed on the basis of conductimetric titration curves. The substance hitherto described as methylmercuric hydroxide is actually trismethylmercurioxonium hydroxide or its dehydration product, bismethylmercuric oxide, as deduced from chemical evidence and infrared spectra. Some alkylmercuric oxides and carbonates have been prepared and examined.

IN an earlier paper [1] we reported that the product previously described [2] as methylmercuric hydroxide could be easily dehydrated to bismethylmercuric oxide. We described a simple method for the preparation of bismethylmercuric oxide by dissolving methylmercuric hydroxide in dry benzene and then reducing the volume of the solution by distillation: the oxide separated after cooling. We had not enough data at that time to decide whether the product described as "methylmercuric hydroxide" was a mixture of hydroxide and oxide, or more or less pure trismethylmercurioxonium hydroxide. Further study showed that trismethylmercurioxonium hydroxide and bismethylmercuric oxide were the only derivatives which could be isolated. All our attempts to prepare methylmercuric hydroxide failed and we concluded that it does not exist as a chemical compound but that, in accordance with the neutralization experiments, it might occur only in dilute aqueous solution as the dissociation product of trismethylmercurioxonium hydroxide. We succeeded in preparing the latter by double displacement of trismethylmercurioxonium perchlorate with potassium hydroxide in methanol. It is a white

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[1] Grdenić and Zado, *Croat. Chem. Acta*, 1957, **29**, 425.
[2] Slotta and Jacobi, *J. prakt. Chem.*, 1929, **120**, 249.

crystalline substance, m. p. 88°, which is dehydrated slowly in a vacuum desiccator to give pure bismethylmercuric oxide, m. p. 139°.

Consequently, the product which one obtains from methylmercuric bromide, by the action of either potassium hydroxide [2] or silver oxide,[3] is a mixture of bismethylmercuric oxide and trismethylmercurioxonium hydroxide in various proportions. This explains the inconsistency in the melting points for methylmercuric hydroxide, quoted [3,4,5,2] as 95°, 93°, 110°, and 137°, respectively. The last value was found for the compound which was described by Slotta and Jacobi as methylmercuric hydroxide and had been specially purified by recrystallization from pyridine. This substance was actually bismethylmercuric oxide which had been formed by dehydration during the recrystallization. Evidence for this has also been obtained from infrared spectra. Freshly prepared " methylmercuric hydroxide " gave characteristic absorption bands for O–H at 3410 cm.$^{-1}$ and for H • • • O–H at 3290 cm.$^{-1}$. The loss of weight of the sample in a desiccator was accompanied by a gradual decrease in the absorption in this region until its complete disappearance after five days, at which time the spectrum was identical with that of bismethylmercuric oxide. The loss in weight of the " hydroxide " in a desiccator has not been measured exactly because of the high volatility of bismethylmercuric oxide.

We are of the opinion that the higher members of the series behave similarly, although we did not investigate them as extensively as the methyl derivative. By dehydration in boiling benzene we obtained, in addition to bismethylmercuric oxide, m. p. 139° (137°), bisethylmercuric oxide, m. p. 47° (37°), bispropylmercuric oxide, m. p. 98° (78°), bisisopropylmercuric oxide, m. p. 135°, and bisbutylmercuric oxide, m. p. 74° (68°). The values in parentheses are those given by Slotta and Jacobi for the products described by them as alkylmercuric hydroxides.

All bisalkylmercuric oxides described in this paper are very soluble in water and alcohol, the solubility decreasing for higher members of the series. Ethyl, propyl, and butyl derivatives change slowly into viscous colourless masses which cannot be recrystallized, but the methyl and the isopropyl compound are stable. The CH_2 group attached to mercury seems to be responsible for this change. Aqueous solutions of bisalkylmercuric oxides are alkaline and can be titrated with acids to Methyl Orange, but the result of the neutralization depends on the concentration of the solution. Neutralization of a dilute aqueous solution (5×10^{-3}N) of bismethylmercuric oxide with perchloric, nitric, or sulphuric acid proceeded as if methylmercuric hydroxide had been dissolved, the end-point being reached at the equivalent ratio of 1 : 1, as was the case with the conductimetric titration curves shown in Fig. 1. On the other hand, the neutralization of a 50% aqueous solution of bismethylmercuric oxide with 10% perchloric acid caused an abundant separation of colourless needles of trismethylmercurioxonium perchlorate.

Neutralization of a concentrated solution of bismethylmercuric oxide in methanol or acetone always gave the crystalline oxonium salt and only one-third of the acid equivalent was employed. The reaction proceeds apparently according to the following scheme:

$$(CH_3{\cdot}Hg)_2O + HX \rightleftarrows [(CH_3{\cdot}Hg)_2OH]^+X^- \qquad (1)$$

$$[(CH_3{\cdot}Hg)_2OH]X + (CH_3{\cdot}Hg)_2O \rightleftarrows [(CH_3{\cdot}Hg)_3O]^+X^- + CH_3{\cdot}Hg{\cdot}OH \qquad (2)$$

$$CH_3{\cdot}Hg{\cdot}OH + (CH_3{\cdot}Hg)_2O \rightleftarrows [(CH_3{\cdot}Hg)_3O]^+OH^- \qquad (3)$$

$$[(CH_3{\cdot}Hg)_3O]OH + HX \rightleftarrows [(CH_3{\cdot}Hg)_3O]^+X^- + H_2O \qquad (4)$$

provided that the neutralization of trismethylmercurioxonium hydroxide is complete.

The neutralization of a dilute methanolic solution (5×10^{-3}N) of bismethylmercuric oxide can be followed conductimetrically only when nitric, phosphoric, acetic, or

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[3] Cannon, Sneed, and Maynard, *J. Amer. Chem. Soc.*, 1922, **44**, 2942.

[4] Enklaar, *Rec. Trav. chim.*, 1923, **42**, 1000.

[5] Hinkel and Angel, *J.*, 1927, 1948.

trichloroacetic acid is used; with fluoroboric, perchloric, or sulphuric acid the equivalence point cannot be detected at all. With the first three acids a stepwise reaction is apparent (Fig. 2). The initial increase in conductivity is due to the formation of an ionized oxonium salt according to reaction (4), until one-third of the acid equivalent is consumed. The curve for nitric acid shows a marked additional inflexion which corresponds to the equivalent ratio (1 : 2) of the acid to bismethylmercuric oxide according to reaction (1).

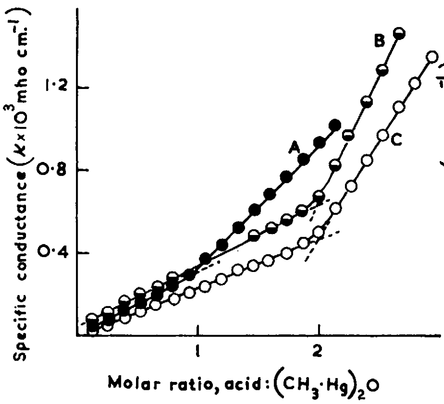

FIG. 1.

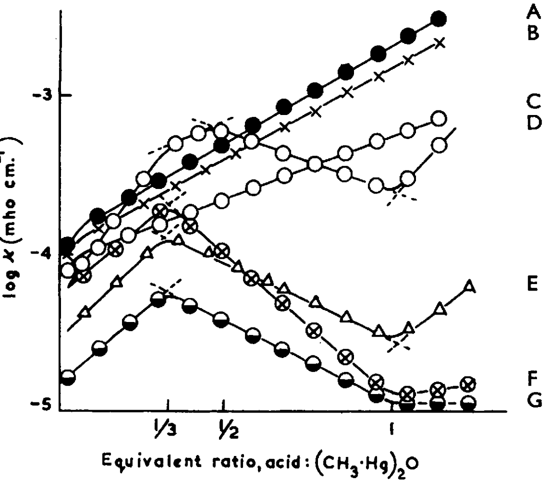

FIG. 2.

FIG. 1. Conductimetric titration of a dilute aqueous solution of bismethylmercuric oxide with acids.

A, H_2SO_4. B, $HClO_4$. C, HNO_3.

FIG. 2. Conductimetric titration of a methanolic solution of bismethylmercuric oxide with acids in methanol.

A, H_2SO_4. D, HNO_3. F, $CCl_3{\cdot}CO_2H$. G, $CH_3{\cdot}CO_2H$. B, $HClO_4$. C, HBF_4. E, H_3PO_4.

The decrease in conductivity during the next step is due to the decomposition of trismethylmercurioxonium ion with formation of a less ionized methylmercuric salt, which is complete when the equivalent ratio (1 : 1) of the acid has been added to the bismethylmercuric oxide. The result of the titration with fluoroboric, perchloric, and sulphuric acid is not completely understood, since the corresponding oxonium salts exist as stable compounds. The linear dependence of the conductivity might be explained by assuming that sulphuric, perchloric, or fluoroboric acid does not act upon trismethylmercurioxonium ion. In fact, this means that methylmercuric ions, formed by dissociation of trismethylmercurioxonium ion, *viz.*:

$$(CH_3{\cdot}Hg)_3O^+ \rightleftharpoons CH_3{\cdot}Hg^+ + (CH_3{\cdot}Hg)_2O \qquad (5)$$

do not recombine with the anions of the added acid and thus are not removed from the equilibrium mixture. The explanation involves necessarily a high degree of dissociation for methylmercuric sulphate, perchlorate, or fluoborate, and this was confirmed by an approximate determination based on the conductivity measurements. Moreover, it was shown that trismethylmercurioxonium perchlorate and fluoroborate can be isolated from acid solutions, even at pH ~3, without decomposition, since they are less soluble than the corresponding methylmercuric salts. Nevertheless, much more work is required for a system as complex as that of a trismethylmercurioxonium salt before its chemical behaviour can be satisfactorily explained.

Trismethylmercurioxonium ion is stable in alkaline solution. Conductimetric titration of trismethylmercurioxonium nitrate and sulphate with potassium hydroxide in methanol gave a sharp equivalence point corresponding to the formation of trismethylmercurioxonium hydroxide (Fig. 3). Even when a large excess of alkali was added no sign of decomposition was noticed. This observation led us to the isolation of pure trismethylmercurioxonium base by double displacement between potassium hydroxide and trismethylmercurioxonium perchlorate in methanol. Trismethylmercurioxonium hydroxide crystallizes from benzene solution as fine needles which slowly lose one mol. of water in a dry atmosphere (giving bismethylmercuric oxide) and rapidly absorb carbon dioxide, giving trismethylmercurioxonium carbonate.

Both addition of a methylmercuric salt to bismethylmercuric oxide (in benzene or methanol) and partial neutralization of bismethylmercuric oxide (in methanol or acetone), described previously in principle,[1] are convenient methods for the preparation of trismethylmercurioxonium salts. In this paper results are given for oxonium carbonate and sulphate prepared by the addition method, as well as for oxonium perchlorate, nitrate, dichromate, and trichloroacetate prepared by partial neutralization; the oxonium bromide and fluoroborate were described in our previous paper. In addition, we found that the reaction of bismethylmercuric oxide with silver nitrate in methanol is a very convenient method for the preparation of trismethylmercurioxonium nitrate.* Furthermore, trismethylmercurioxonium perchlorate in methanolic solution can be employed for the preparation of trismethylmercurioxonium salts in good yield by double displacement with a corresponding potassium salt. Trismethylmercurioxonium hydroxide, permanganate, and hexafluorophosphate have been prepared by this method.

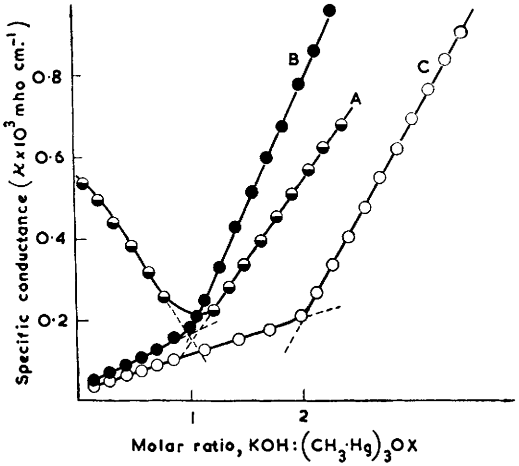

FIG. 3. Conductimetric titration of a methanolic solution of trismethylmercurioxonium perchlorate, nitrate, and sulphate with potassium hydroxide in methanol.
A, $[(CH_3{\cdot}Hg)_3O]ClO_4$. B, $[(CH_3{\cdot}Hg)_3O]NO_3$. C, $[(CH_3{\cdot}Hg)_3O]_2SO_4$.

All of the trismethylmercurioxonium salts described dissolve easily in water, except for the dichromate which is slightly soluble and the permanganate which is insoluble. The stability of their aqueous solutions, which are slightly acid, depends upon the nature of the anion, *e.g.*, the bromide decomposes with separation of methylmercuric bromide which is almost insoluble in water, and the solutions become alkaline owing to the dissociation equilibrium,

$$[(CH_3{\cdot}Hg)_3O]X \rightleftharpoons (CH_3{\cdot}Hg)_2O + CH_3{\cdot}HgX \qquad (6)$$

the constant of which is a measure of the stability of trismethylmercurioxonium salts in the solution. It follows that those oxonium salts which give insoluble $CH_3{\cdot}HgX$, *e.g.*,

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* Bismethylmercuric sulphide behaves similarly, but the resulting sulphonium nitrate reacts further with silver nitrate. Thus, for preparative purposes, the exact stoicheiometric ratio of the compounds should be employed (unpublished result).

halides, are easily decomposed in solution and thus cannot be prepared by partial neutralization. On the other hand, if $CH_3{\cdot}HgX$ is soluble, which is always the case for compounds with pronounced salt-like properties ($CH_3{\cdot}Hg^+X^-$), the corresponding oxonium compound is not decomposed in solution and can be easily prepared by the methods described. The members of the latter group are also differentiated by their behaviour in aqueous solution in which they are more or less hydrolyzed. An aqueous solution of the acetate, for instance, cannot be concentrated by evaporation because of the volatility of the acetic acid, while at the same time the sulphate can be separated from an aqueous solution by evaporation *in vacuo*. The stability of an aqueous solution of trismethylmercurioxonium dichromate should be particularly mentioned; this salt can be recrystallized from hot aqueous solution. Trismethylmercurisulphonium dichromate behaves similarly.[6]

During the work with bismethylmercuric oxide we noticed that it rapidly absorbs carbon dioxide from the air to form the carbonate. Since alkylmercuric carbonates had not previously been described, it seemed worthwhile to prepare some members of the series, and we found that the most convenient method is to pass carbon dioxide through a concentrated methanolic solution of a bisalkylmercuric oxide.

Alkylmercuric carbonates are white crystalline substances, and are very soluble in water and alcohol. Like oxides they change slowly to colourless viscous masses, the most stable being methylmercuric carbonate. Aqueous solutions of carbonates can also be readily titrated with acid, with Methyl Orange as indicator. We expected that alkylmercuric carbonates would be easily converted into oxides by gentle heating, but they decomposed, even in boiling toluene, with the formation of an unidentified amorphous yellowish organic material which contained mercury.

EXPERIMENTAL

Conductimetric titrations were carried out at 25° in a simple cell provided with a thermometer and platinized platinum electrodes in connection with a RLC-Siemens bridge (800 Hz). Conductivity water and methanol with average specific resistivity of 10^6 and 3×10^7 ohm cm.$^{-1}$, respectively, were obtained by redistillation in a Pyrex-glass still. The concentration was 5×10^{-3} mole per l. for bismethylmercuric oxide and 0·1N for acids.

Infrared spectra were determined, for mulls with hexachlorobutadiene, by using a Perkin-Elmer model 221 spectrophotometer with sodium chloride optics.

Bisalkylmercuric Oxides.—The starting material for the preparation of a given bisalkylmercuric oxide was the product described by Slotta and Jacobi [2] as alkylmercuric hydroxide, and it was obtained by the reaction of alkylmercuric bromide with potassium hydroxide according to the method proposed by them. As previously described for bismethylmercuric oxide,[1] the solution of a given hydroxide (5—10 g.) in benzene (~100 ml.) was reduced by distillation to about one-quarter of its initial volume. The crystalline oxide which separated after cooling was filtered off and washed with dry ether, precautions being taken to exclude carbon dioxide. The mercuric oxides prepared were: *bismethyl-*, fine needles, m. p. 47°, which changed even *in vacuo* to a thick viscous mass (Found: Hg, 84·0%; equiv., by titration, 239·2. $C_4H_{10}Hg_2O$ requires Hg, 84·4%; equiv., 237·6); *bispropyl-*, needles, m. p. 98°, which changed slowly to a viscous mass (Found: Hg, 80·2%; equiv., by titration, 249·0. $C_6H_{14}Hg_2O$ requires Hg, 79·8%; equiv., 251·6); *bisisopropyl-*, needles, m. p. 135°, unchanged *in vacuo* (Found: Hg, 79·4%; equiv., by titration, 253); and *bisbutyl-*, needles, m. p. 74° (Found: Hg, 75·4%; equiv., by titration, 264·2. $C_8H_{18}Hg_2O$ requires Hg, 75·6%; equiv., 265·6).

Trismethylmercurioxonium Salts.—(a) *By partial neutralization of bismethylmercuric oxide.* A solution of bismethylmercuric oxide (5 g.) in methanol (~20 ml.) was neutralized (Merck Universal indicator) by dropwise addition of acid diluted with methanol. For the preparation of the *perchlorate*, 70% perchloric acid in methanol (1 : 3) was used and a crystalline product was obtained by precipitation with absolute ether; it had m. p. 148° (decomp.) (Found: Hg, 79·4; ClO_4, 12·9. $C_3H_9ClHg_3O_5$ requires Hg, 79·4; ClO_4, 13·1%). *Trismethylmercurioxonium nitrate* was prepared in the same way by using 65% nitric acid in methanol (1 : 3); it formed

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[6] Grdenić and Markušić, *J.*, 1958, 2434.

needles (from 2 : 1 benzene–ethanol), m. p. 188° (decomp.) (Found: Hg, 83·2; NO_3, 8·7. $C_3H_9Hg_3NO_4$ requires Hg, 83·0; NO_3, 8·5%). *Trismethylmercurioxonium trichloroacetate* was precipitated by addition of light petroleum to a dioxan solution of the dry residue which remained after evaporation of the neutralized solution (10% methanolic solution of trichloroacetic acid) *in vacuo*; it had m. p. 88° (decomp.) (Found: Hg, 73·0. $C_5H_9Cl_3Hg_3O_2$ requires Hg, 72·9%). For the preparation of *trismethylmercurioxonium dichromate* a 10% aqueous solution of chromium(VI) oxide was employed. The precipitate, after recrystallization from the warm aqueous solution, formed orange-red prisms, m. p. 124° (decomp.) (Found: Cr, 6·8; Hg, 78·2. $C_6H_{18}Cr_2Hg_6O_9$ requires Cr, 6·6; Hg, 77·9%).

(b) *By addition of methylmercuric salts to bismethylmercuric oxide.* Bismethylmercuric oxide and the corresponding methylmercuric salts were dissolved in methanol in the stoicheiometric ratio, the solution was heated to boiling and then cooled, and separation of crystals was promoted by the addition of absolute ether. *Trismethylmercurioxonium sulphate* formed prisms, m. p. 176° (decomp.) (Found: Hg, 84·3; SO_4, 6·6. $C_6H_{18}Hg_6O_6S$ requires Hg, 84·7; SO_4, 6·7%). *Trismethylmercurioxonium carbonate* formed fine needles, m. p. 105° (decomp.) (Found: Hg, 86·7; CO_3, 4·2. $C_7H_{18}Hg_6O_5$ requires Hg, 86·8; CO_3, 4·3%).

(c) *By reaction of bismethylmercuric oxide with silver nitrate.* A mixture of methanolic bismethylmercuric oxide (1·0 g. in 5 ml.) and silver nitrate (0·25 g. in 10 ml.) was set aside overnight and filtered, the filtrate was evaporated *in vacuo* to dryness and the residue (0·4 g.) was recrystallized from benzene–ethanol (2 : 1). Trismethylmercurioxonium nitrate had m. p. 188° (Found: Hg, 83·2; NO_3, 8·7. CH_3HgNO_4 requires Hg, 83·0; NO_3, 8·5%).

(d) *By double displacement between trismethylmercurioxonium perchlorate and potassium salts.* Trismethylmercurioxonium perchlorate and a potassium salt were dissolved in the stoicheiometric ratio in methanol (or acetone in the case of permanganate), the solution was kept for 2 hr., the precipitate filtered off, and the filtrate evaporated *in vacuo*. *Trismethylmercurioxonium acetate*, recrystallized from benzene, had m. p. 111° (decomp.) (Found: Hg, 83·5; OAc, 8·0. $C_5H_{13}Hg_3O_3$ requires Hg, 83·8; OAc, 8·2%). The neutralization method is not convenient for the preparation of the acetate, since the end-point cannot be easily detected under the conditions described in paragraph (a). *Trismethylmercurioxonium permanganate* was obtained as small dark red prisms which could not be recrystallized. They exploded at 183° (Found: Hg, 76·9; MnO_4, 11·4. $C_3H_9Hg_3MnO_5$ requires Hg, 76·9; MnO_4, 11·2%). *Trismethylmercurioxonium hexafluorophosphate* formed leaflets (from methanol–ether), m. p. 153° (Found: Hg, 74·5. $C_3H_9F_6Hg_3OP$ requires Hg, 74·6%). The double displacement of trismethylmercurioxonium perchlorate with potassium hydroxide was effected by the dropwise addition of a (methanolic) carbonate-free solution of potassium hydroxide to a methanolic solution of trismethylmercurioxonium perchlorate until the pH reached 7·5. After removal of potassium perchlorate by centrifuging, the clear solution was treated again with potassium hydroxide solution until the precipitation of perchlorate was complete (pH 8·5—9). The clear filtrate was evaporated to dryness in a vacuum desiccator over sodium hydroxide. *Trismethylmercurioxonium hydroxide* formed colourless needles (from benzene), m. p. 88° (Found: Hg, 88·9. $C_3H_{10}Hg_3O_2$ requires Hg, 88·5%).

Alkylmercuric Carbonates.—Carbon dioxide was bubbled slowly into a methanolic solution (about 5 ml.) of a bisalkylmercuric oxide (1—5 g.) cooled with ice-water. *Methylmercuric carbonate* formed needles (from methanol–ether), m. p. 110° (Found: Hg, 81·7; CO_3, 12·2. $C_3H_6Hg_2O_3$ requires Hg, 81·7; CO_3, 11·9%). *Ethylmercuric carbonate* formed leaflets (from acetone–methanol), m. p. 98° (Found: Hg, 77·2; CO_3, 11·3. $C_5H_{10}HgO_3$ requires Hg, 77·2; CO_3, 11·5%). *Propylmercuric carbonate* formed needles (from benzene–light petroleum), m. p. 77° (Found: Hg, 73·2; CO_3, 11·0. $C_7H_{14}Hg_2O_3$ requires Hg, 73·3; CO_3, 10·9%). *Isopropylmercuric carbonate* formed needles (from methanol–ether), m. p. 126° (Found: Hg, 73·3; CO_3, 10·7%). *Butylmercuric carbonate* formed needles (from methanol), m. p. 72° (Found: Hg, 67·3; CO_3, 10·3. $C_9H_{18}Hg_2O_3$ requires Hg, 67·7; CO_3, 10·1%).

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