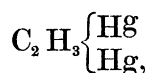


VIII. *On the Isolation of the Radical, Mercuric Methyl.*By GEORGE BOWDLER BUCKTON, *Esq.*, *F.R.S.*

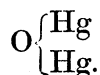
Received December 4, 1857,—Read January 7, 1858.

DR. FRANKLAND, in his memoir communicated to the Royal Society, has described the iodide of an organic base containing mercury, to the hypothetical radical of which he gave the name of hydrargyromethylum. At the same time he pointed out, that in common with zincethyl and analogous bodies, it might be regarded as formed upon the type of the metallic oxides, the oxygen of which, he considered, was represented by methyl, ethyl, &c.

Hydrargyromethylum,



according to this view, corresponds to mercurous oxide,



Notwithstanding the various ingenious theories advanced with reference to the constitution of these organic metals, the opinion of chemists upon the subject has remained divided; any addition therefore to our knowledge of their decompositions and transformations will be regarded with interest.

DÜNHaupt, and more recently STRECKER, examined and analysed the salts of hydrargyromethylum and hydrargethylum, but hitherto no successful attempt appears to have been made to convert these bases from the mercurous to the mercuric type.

In an experiment connected with an examination of the nitriles made by Dr. Hofmann and myself, iodide of hydrargyromethylum was acted upon by an aqueous solution of cyanide of potassium, under the impression that cyanide of hydrargyromethylum would be produced. After a digestion for twelve hours in a sealed tube, the chief product consisted of a double salt of iodide and cyanide of the two bases, a compound which readily crystallized in large plates on cooling. The tube also contained an inflammable gas, ammonia, a little reduced mercury, and a few drops of a heavy liquid, which at the time was regarded as regenerated iodide of methyl.

The investigation in this direction was then abandoned, but I have since returned to the subject, with the special view of effecting a partial reduction of the metallic element in the base.

The iodide of hydrargyromethylum was formed in the usual manner by sunlight, in long horizontal tubes, which gave a large surface of mercury for contact with the iodide of methyl. After sufficient exposure, the contents of the tubes were heated to 100° C.

to drive off the iodide of methyl, and the crystalline mass, after separation from the excess of mercury by pressure in a cloth, was powdered and exposed to the air for some hours to remove every trace of iodide of methyl.

This crude mass was generally employed in the following experiments, but the pure compound may be expeditiously obtained by dissolving the crystals in hot aqueous potash. By the addition of weak hydrochloric acid, which must not be in excess, the substance is again precipitated. A subsequent washing in water, in which it is almost insoluble, yields it pure and colourless.

Aqueous cyanide of potassium acts very slowly upon iodide of hydrargyromethylum, and requires a temperature approaching to 200° C. before mercury is reduced.

The volatile matters formed, exert a pressure that few glass tubes can resist, even when assisted by an atmosphere of steam. Much better results were obtained by the following method.

Dry iodide of hydrargyromethylum was rubbed in a mortar with finely divided cyanide of potassium, and distilled in flasks over the naked gas flame.

Small charges and frequent operations are better than acting on large portions. A gas passes with an odour something like that of trimethylamine; also water, ammonia, and finally, a heavy liquid which is not miscible with water. The residue in the flask contains iodide and carbonate of potassium, paracyanogen, and metallic mercury. A portion of iodide of hydrargyromethylum always sublimes.

The distillate was agitated with water, and the lower stratum, which was comparatively small in amount, was twice rectified over chloride of calcium at the temperature of the water-bath.

This liquid has the following properties:—It is colourless, highly refractive to light, and almost wholly insoluble in water. When pure, it has a faint and somewhat sweetish odour, but the crude product is contaminated with the offensive body that always accompanies the decomposition of methyl compounds when heated with cyanide of potassium. The odour may be entirely removed by agitation with very dilute sulphuric acid.

This liquid is very combustible, and burns with a luminous flame and abundant evolution of mercurial vapour. It is soluble in all proportions in alcohol and in ether, from the former of which it is precipitated on addition of water. The vapour detonates loudly when exploded with oxygen gas.

This preparation began to boil at 93°, at which point it remained constant until about $\frac{5}{6}$ ths of the whole had passed over; the remainder came over between 93° and 96° C.

The specific gravity of the former portion was found to be 3.069, from which it appears to be the heaviest of known non-metallic liquids. A solid glass rod floats freely on its surface*.

The pure substance contains neither iodine nor cyanogen; still it is very difficult to separate every trace of iodide of hydrargyromethylum which volatilizes with the vapour.

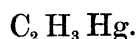
* The specific gravity of bromine at 15° is 2.98. Selenic acid, with one equivalent of water, MITSCHERLICH found to have a density of 2.85.

This impurity is not easily detected until the liquid is burnt with oxide of copper, when a little subiodide of copper generally appears. To this cause is referred the circumstance that the following analyses are slightly below the theoretical value:—

- I. 0.9774 grm. burnt with oxide of copper, gave 0.2335 grm. water and 0.3508 grm. carbonic acid.
 II. 0.8082 grm. burnt with oxide of copper, gave 0.1895 grm. water and 0.2870 grm. carbonic acid.
 III. 0.7800 grm. burnt with soda-lime, gave 0.6718 grm. mercury.
 IV. 1.2405 grm. burnt with oxide of copper, gave 1.0680 grm. mercury.
 These numbers correspond to the per-centages—

	I.	II.	III.	IV.
Carbon	9.78	9.68	—	—
Hydrogen	2.65	2.60	—	—
Mercury	—	—	86.11	86.09

and accord with the formula



	Theory.		Mean of Experiment.
2 equivs. of Carbon . .	12	10.43	9.73
3 equivs. of Hydrogen . .	3	2.60	2.63
1 equiv. of Mercury . .	100	86.97	86.10
	115	100.00	

If the materials be dry, the decomposition of iodide of hydrargyromethylum by cyanide of potassium is very simple, and may thus be expressed by equation,—



I do not find, however, any advantage in using the materials absolutely dry. A little moisture disintegrates the cyanogen, and the resulting gaseous products assist in removing the vapour of the new body from the seat of decomposition.

From the constitution of this compound the name mercuric methyl is proposed. Should this appellation be accepted by chemists, Dr. FRANKLAND'S radical would be styled mercurous methyl.

As a corroboration to the foregoing analysis, an experiment was made to ascertain the specific gravity of the vapour, after the method of DUMAS.

	Grammes.	Pressure.	Temperature.
Weight of globe filled with vapour . .	10.3245	769 mm.	117° C.
Weight of globe filled with air . .	9.9705	770 mm.	14° C.

$$\text{Difference} = P = 0.3540$$

$$\text{Capacity of the globe} = V = 57.0 \text{ cubic centimetres.}$$

$$\text{Volume of mercury entering the globe} = 56.5 \text{ cubic centimetres.}$$

$$\text{Difference } v = 0.5$$

n_t = weight of one cubic inch of air at 14° C. = 0.001230.

n_t = weight of one cubic inch of air at 117° C. = 0.000905.

By introducing these numerical values into MÜLLER'S formula, we have

$$\left. \begin{array}{l} \text{Specific gravity} \\ \text{of the vapour} \end{array} \right\} = \frac{P + Vn_t}{(V - v)n_v} = \frac{0.42411}{0.05113} = 8.29.$$

The weight represented by the formula $C_2 H_3 Hg$, divided by the experimental density, gives the quotient $\frac{115}{8.29} = 13.87$. Supposing the constituents of mercuric methyl condensed into two volumes of vapour, the more accurate number 14.46 should have been obtained.

The theoretical density of the vapour of mercuric methyl is $\frac{115}{14.46} = 7.95$.

Although the salts of mercurous methyl are remarkably stable, the sulphate for instance resisting for some time the action of boiling sulphuric acid, they may be made to part with a portion of their mercury by a variety of means. The action of sodium on mercuric methyl is very slow, and it is only after long boiling that the sodium becomes amalgamated, with the liberation of a gas which is doubtless methyl. The action of sodium, on the other hand, upon iodide of mercurous methyl, is sufficiently great to cause explosion when gently heated. If the sodium be previously amalgamated, and reduced to small pieces, the volatile products will be found to contain a considerable quantity of mercuric methyl. The same decomposition is also effected through lime or hydrate of potassa. A higher temperature appears to be required to induce the change, and accordingly the amount of mercuric methyl obtained is comparatively small.

Marsh-gas is liberated in the decomposition according to the equation



Decompositions of Mercuric Methyl.

Mercuric methyl exhibits no tendency to unite with the electro-negative elements, such as oxygen and chlorine. All attempts to produce such compounds lead to the destruction of the substance.

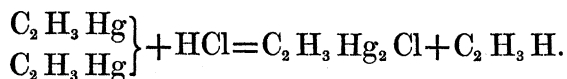
Mercuric methyl sinks in concentrated sulphuric acid, and liberates bubbles of a gas which burns with a pale non-luminous flame. This evolution is assisted by a gentle heat.

One volume of this gas, when exploded in the eudiometer with a mixture of oxygen and air, gave, after due correction for pressure and temperature, a contraction equal to two volumes, and subsequently by potash, an absorption equal to one volume of carbonic acid.

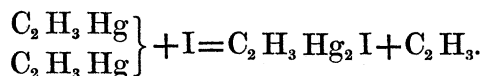
This deportment shows the gas to be hydride of methyl or marsh-gas.

After the decomposition of mercuric methyl by an acid, the solution contains an abundance of that salt of mercurous methyl which corresponds to the acid employed.

Thus with hydrochloric acid we obtain the chloride, and with sulphuric acid the sulphate of mercurous methyl,



On adding bromine to the liquid, a violent action results, and the white and crystalline bromide is formed. Iodine also unites with mercuric methyl with a loud hissing noise. If the reaction be conducted under water, bubbles of gas are disengaged, which prove to be pure methyl gas,



The mercury in these bodies is retained with remarkable tenacity, in what may be called organic combination. The strongest acids fail in reducing them to ordinary inorganic mercury salts. They are indifferent also to sulphide of ammonium, at usual pressures and temperatures.

Both compounds are however decomposed, with deposition of mercury, by the action of clean zinc and a dilute acid.

Mercuric methyl is a ready solvent of resins and caoutchouc, but it retains in solution only a small quantity of sulphur even at the boiling heat. The liquid dissolves phosphorus almost in every proportion, but no transformation is effected by subjecting the two bodies to a temperature of 160° C. in a sealed tube.

The solution, when allowed to evaporate on filter paper, leaves the phosphorus in a state so finely divided as to cause spontaneous ignition.

Mercuric methyl furnishes with bichloride of tin a crystalline compound which readily decomposes on the addition of water. Thin colourless plates are formed, which after being well washed with water from the soluble tin salt, were analysed. The crystals were dried over sulphuric acid, and sublimed between watch-glasses.

0·7105 grm. of substance gave with nitrate of silver 0·4090 grm. of chloride of silver. The salt proved therefore to be nothing but chloride of mercurous methyl.

$\text{C}_2 \text{H}_3 \text{Hg}_2 \text{Cl}$ requires—

	Theory.	Experiment.
Chlorine	14·18	14·22

An analogous reaction is effected by a similar treatment with terchloride of phosphorus.

Some interest attaches also to the circumstance that mercuric iodide combines directly with mercuric methyl, to form iodide of mercurous methyl.

The change is effected quietly when assisted by a gentle heat.

Mercuric methyl is indifferent to the action of the iodides of lead and silver, the metals most nearly allied to mercury in their general properties.

Mercuric Ethyl.

The foregoing experiments left little doubt of the existence of a corresponding body in the ethyl series. There appears, however, to be some difficulty in obtaining it in quantity, from the ease with which the body undergoes decomposition at a high temperature.

Although little less than one pound of iodide of mercurous ethyl was digested with cyanide of potassium, the distillate obtained was too small in quantity to permit of more than a general examination.

The greater part of the new body is resolved by the heat employed into mercury, paracyanogen, and gaseous matters, of an offensive odour. The product in the receiver was distilled in a water-bath until all iodide of ethyl was driven off. A watery liquid remained having a substratum of an oily consistence, which strongly greased the sides of the retort. At an advanced heat this substance passed over as a colourless, heavy fluid, quite unmiscible with water.

Although unable to obtain an analysis, I have no doubt of this substance being mercuric ethyl. The boiling-point, as before noticed, is above that of water. It burns with a lurid flame, which appears to be smoky from the disengagement of mercurial vapour.

Its behaviour towards acids is just what we might expect from a body so little removed in composition from mercuric methyl. Hydride of ethyl is liberated instead of marsh-gas, as in the former case, and salts of mercurous ethyl are deposited from the acid solutions.

A question now arises as to whether the above-described substances represent, in their respective series, the sole radicals of the organo-mercurial bases.

Up to the present time the radical of mercurous methyl, &c. has not been isolated. Should it indeed exist, its discovery would add weight to GERHARDT'S views with reference to the different conditions of mercury, as mercuricum and mercuriosum.

I propose to submit to similar treatment the salts of stanethylium and zincethyl. I have already made some preliminary experiments on the former, and the results seem to give promise of subjects of interest.

December 2, 1857.