

XIII. "Further Remarks on the Organo-metallic Radicals, and Observations more particularly directed to the isolation of Mercuric, Plumbic, and Stannic Ethyl." By GEORGE BOWDLER BUCKTON, Esq., F.R.S. Received June 17, 1858.

Before again entering on the subject of the organo-metals, the author wishes to call attention to the remarks he has previously made* on the difficulties which presented themselves at that time in the preparation of mercuric ethyl. Secondary decompositions, induced by the nature of the materials employed and the high temperature necessary to the reaction, showed themselves even in the more easily prepared mercuric methyl, and reduced the quantity obtained considerably below that pointed out by theory.

The loss sustained in the similar operation of distilling together cyanide of potassium and iodide of mercurous ethyl, $C_4H_5Hg_2I$, is yet more marked; and it may be remembered that the portion obtained did no more than suffice for a cursory examination of its most marked characters. A new mode of operating was therefore desirable, and it was not long before the following considerations presented themselves.

The powerful and well-defined affinities of zinc-ethyl have already furnished a valuable key to the explanation of several chemical problems, and seem to be well suited for experiment in the present case. Bearing in mind its well-known reactions on water and hydrochloric acid, there appeared to be well-grounded reasons for supposing that interesting decompositions might be effected with various oxides, chlorides, and iodides.

Through the instrumentality of zinc-ethyl the author has succeeded in isolating, in a neat and efficient manner, several of the organo-metals, and he indulges a hope that they may, when taken as starting-points of investigation, prove of service in fixing exact formulæ to some of those bodies, the composition of which, at present, appear doubtful from their complexity.

Action of Zinc-ethyl on Mercuric Chloride.

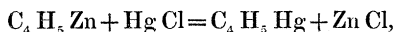
Corrosive sublimate acts with great energy on zinc-ethyl; so much

* Phil. Trans. Roy. Soc.; Proc. Roy. Soc. vol. ix. p. 91.

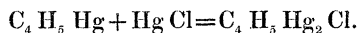
so, as to render it necessary to cool the apparatus in water, and add the well-dried salt by degrees. An excess of the latter must be avoided, since chloride of mercurous ethyl would be formed, as was formerly shown to be the case in the methyl series.

After the two bodies have been brought together in their proper proportions, heat is applied, and the radical passes over by distillation as a heavy, colourless, and nearly inodorous liquid; the slight excess of zinc-ethyl is then decomposed by the addition of water, and just sufficient dilute hydrochloric acid added as will dissolve the precipitated oxide of zinc.

The two transformations may be seen in the equations,



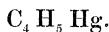
and again,



The pure radical boils at a temperature between 158° and 160°C . It burns readily, with a luminous and somewhat smoky flame, with disengagement of mercurial vapour. It is almost wholly insoluble in water. Alcohol dissolves it rather sparingly, but it mixes freely with ether.

The behaviour of acids towards mercuric ethyl is strictly analogous to that shown by mercuric methyl. With dilute acid there is but little change, but warm concentrated hydrochloric or sulphuric acid liberates hydride of ethyl in sufficient quantity to permit of its inflammation through a gas jet. The salts of mercurous ethyl remain in solution.

The specific gravity of a specimen boiling between 158° and 160°C . was found to be 2.444, and the same sample when submitted to analysis, gave numbers agreeing accurately with the formula



The correctness of this formula was further confirmed by an appeal to the vapour-density.

The first experiment failed, from the circumstance that the vapour decomposes with a slight explosion, when heated a few degrees above 205°C . In this experiment metallic mercury was deposited on the walls of the glass balloon as a grey film, and the other contents consisted of an inflammable gas. Mercuric methyl appears therefore to be resolved at this temperature into ethyl gas and mercury.

Another experiment was more successful, and gave the number 9.97 for the vapour-density.

The equivalent weight of mercuric ethyl is 129, which, being divided by the former figures, gives $\frac{129}{9.97} = 12.94$. If the constituents of this radical be condensed into two volumes of vapour, the more accurate number 14.86 should have been obtained.

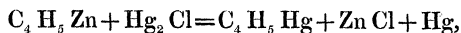
The theoretical density of mercuric ethyl, thus calculated, is equal to $\frac{129}{14.86} = 8.68^*$.

This portion of the subject would be incomplete unless a few words were added on the behaviour of zinc-ethyl towards mercurous chloride.

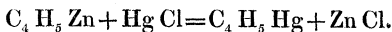
It has been mentioned, that all attempts to reduce iodide of mercurous methyl to the form of a radical containing one equivalent of methyl and two equivalents of mercury have hitherto failed.

Reasoning *a priori*, we should not expect to find a departure in the present case, neither does such appear. Mercurous chloride reacts with vigour on zinc-ethyl, but metallic mercury is formed simultaneously with chloride of zinc and mercuric ethyl.

The decompositions of mercurous and mercuric chlorides or iodides, are thus shown:—



and



Having succeeded, by these simple means, in effecting a replacement in zinc-ethyl through the ordinary metallic chlorides, there remained yet one point untouched, viz. the behaviour of various organo-metallic salts, under similar treatment.

First in order was tried

* Here it is fitting to mention an error that has crept into the calculation of the vapour-density of mercuric methyl as it appears printed in the ‘Proceedings of the Royal Society.’ A false figure in the denominator of one of the fractions, causes the experimental density to appear as 14.86, whereas the true experimental density observed was 8.29. The theoretical density of mercuric methyl calculated for two volumes, equals $\frac{115}{14.46} = 7.95$.

The Action of Zinc-ethyl on Iodide of Mercurous Ethyl.

Carbonic acid, or ordinary coal-gas, was slowly passed through the neck of a retort; and when the atmospheric air was displaced, about two ounces of zinc-ethyl, nearly free from ether, and wholly so from iodide of ethyl, was introduced. Iodide of mercurous ethyl was then added, by degrees, through the tubulure, and the whole mixed by agitation. The zinc-ethyl at first dissolves the iodide, but subsequently a cake of iodide of zinc is formed. Distillation was then commenced, the heat being raised by degrees until gaseous products appeared. The distillate, after being well washed, was rectified by the thermometer, and in this manner the radical was obtained in a state of purity. Iodide of mercurous ethyl may be formed so easily by diffused daylight, and its action is so gentle on zinc-ethyl, that its use offers greater conveniences to the operator than are afforded by any of the substances previously mentioned.

For obvious reasons, a similar choice of materials is recommended for preparing mercuric methyl.

Action of Zinc-ethyl on Chloride of Lead.

The close relations which exist between the three metals, lead, mercury, and silver, in their equivalent weights, salts, and other characters, lead the author to anticipate success in forming their ethyl bases.

The existence of the lead radical might indeed be considered as certain, since various salts of complicated structure have been made known to chemists through the experiments of M. Löwig, on the alloy of lead and sodium, under treatment with iodide of ethyl.

The principal product obtained by him, and the only one apparently analysed, had a grouping similar to a sesquichloride. The formula ascribed by him to the radical plumbethylium is $\text{Pb}_2(\text{C}_4\text{H}_5)_3$. I have attempted to form the iodide of this radical by exposing sealed tubes, containing granulated lead and iodide of ethyl, to the sun's rays, but without success. No better result was obtained by substituting bromide of ethyl for the iodide, and no change could be induced even when these tubes were heated strongly with high-pressure steam.

M. Löwig's method was not resorted to, from the supposition that the action of zinc-ethyl on a mixture would only give rise to radicals of

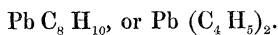
various constitution, which it might be impossible afterwards to separate, except by working on a large scale, which, considering the costliness of the materials, had its disadvantages. Perhaps success might attend the use of one of Dr. Frankland's mirrors for concentrating the sun's rays.

For obtaining the lead-radical, recourse was had to well-dried chloride of lead, which was introduced into a flask containing zinc-ethyl. The chloride immediately turned black, from the deposit of metallic lead, whilst moderate heat was disengaged. An excess of chloride was used, and the mass incorporated by stirring with a glass rod. After applying a gentle heat for a few minutes, the floating clear liquid was pipetted off. This substance is apparently a compound of zinc-ethyl and the lead radicals. It fumes slightly in the air, and no digestion with chloride of lead appeared to resolve it entirely into the lead base.

A great part of the zinc-ethyl, however, is removed by subsequent distillation; but the temperature should not be permitted to rise above 140° or 150° C. The substance in the retort is then treated with water and dilute hydrochloric acid, when the radical separates, and sinks in the form of colourless drops. When distilled cautiously, the thermometer soon rises to 200° ; but beyond this point the vapour is very prone to decomposition, with deposit of metallic lead.

From this tendency to change, there is some difficulty in obtaining the substance wholly pure from bodies with lower boiling-points. The larger portion came over between 198° to 202° . Its specific gravity was found to be 1.55.

Analysis led to the formula



It should, however, be noticed that a trifling excess in the percentage of carbon obtained, showed an increase rather than a decrease in the number of equivalents of ethyl.

This radical, for which the provisional name of plumbic bis-ethyl is suggested, is a colourless fluid, possessing little or no odour. It is insoluble in water, but perfectly miscible with ether. It burns readily with a beautiful orange-coloured flame, edged with blue, and gives off fumes of oxide of lead.

The radical appears to be incapable of forming salts without a

partial decomposition. With weak acids there is no perceptible action; but when they are concentrated and gently heated, a gas is given off, and crystalline salts are produced.

The chloride is insoluble in water, but soluble in alcohol and in ether, from which last liquid it crystallizes in satiny needles, which are very volatile and provoke sneezing and lachrymation. It burns with the characteristic lead flame, and by long digestion with concentrated hydrochloric acid, is converted into chloride of lead and volatile products.

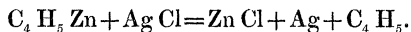
The sulphate also appears as a crystalline mass when plumbic-bis-ethyl is gently warmed with a few drops of concentrated sulphuric acid. It is conveniently prepared by agitating the materials in a stoppered bottle, an exit being made from time to time for the gas which is liberated.

Both these salts require analyses to fix their composition, the details of which the author hopes shortly to be able to communicate.

The Action of Zinc-ethyl on Chloride of Silver.

These substances react with some violence, and a black substance sinks in the liquid, which proved to be a mixture of chloride and metallic silver. The zinc-ethyl seems partly to escape decomposition, even when the chloride is in excess and considerable heat is applied. On the addition of water, effervescence sets in, and chloride of zinc is alone found in solution.

In another experiment dry ether was employed instead of water, under a supposition that a solid compound might be formed, soluble in that menstruum. The only reaction, however, appeared to be that expressed by the equation,



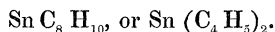
A similar negative result was obtained when zinc-ethyl was made to react on protochloride of platinum, Pt Cl . The action is violent, and the platinum is thrown down in the form of platinum-black.

The same remark also applies to protochloride of copper, $\text{Cu}_2 \text{Cl}$, when similarly treated; no combination of copper and ethyl could be thereby eliminated.

Action of Zinc-ethyl on Iodide of Stan-ethyl.

This iodide, C_4H_5SnI , was readily obtained by heating sealed tubes containing excess of tinfoil and iodide of ethyl from 150° to 160° C. The pure transparent crystals which were obtained by a little management, were introduced, in a melted state, into a retort containing zinc-ethyl. It is necessary to cool the apparatus with water. After breaking up the resulting mass, the retort was heated until the thermometer marked 210° C., and the distillate, which contained a slight excess of zinc-ethyl, was agitated with water, and treated with dilute acid, as before described.

The resulting heavy liquid was again distilled, and fractionized with the thermometer. By far the larger portion came over between 170° and 180° as a clear and colourless body, insoluble in water, but soluble, like the other radicals, in ether. That section which possessed a boiling-point between 176° and 180° C., was taken for examination, and was found, when burned with oxide of copper, to give the formula



This compound, for which the name stannic bis-ethyl is proposed, has a specific gravity of 1.192. In its external and more prominent characters it resembles plumbic bis-ethyl; but an exception may be made, that it is more stable. It is very combustible, burning with a coloured flame and scintillation like that exhibited by the metal tin under the flame of the hydro-oxygen blowpipe.

This radical appears to differ in several particulars from the organo-metal stan-ethyl, C_4H_5Sn , obtained by Dr. Frankland by acting on sheet-zinc with a salt of stan-ethyl. This last body is described as a thick, oily substance, possessed of a powerful odour, and having a specific gravity of 1.55. It differs also in its lower boiling-point, which is about 150° C.

Pure stannic bis-ethyl is perfectly limpid, inodorous, and is acted upon by hydrochloric acid with difficulty. A gas is slowly evolved on the application of heat, and a chloride is formed which seems to be richer in tin than the radical itself.

The chloride appears to crystallize with difficulty, and at usual temperatures has the consistence of an oil. It possesses a powerfully pungent odour, and when heated, a vapour which painfully attacks the skin of the face, and produces fits of sneezing.

A corresponding bromide is formed when bromine is added to stannic bis-ethyl. It is an oily body, with an irritating odour. When acted upon by ammonia, an oxide is precipitated, which with acids forms beautiful crystallizable salts, readily soluble in water.

A complete history of these salts, and their decompositions with zinc-ethyl, will possess much interest, and may prove of value in referring to a few simple radicals the numerous complex bodies described by Löwig, &c.

The author is at present engaged on this branch of the inquiry, a detailed account of which he hopes to embody in a communication to the Royal Society, the present paper being intended only as an outline to be hereafter filled in.

In conclusion, the author would remark that a rich harvest can scarcely fail to be reaped, from submitting to the action of zinc-ethyl the metallic compounds of other groups, such as arsenic, bismuth, and antimony.

XIV. "Preliminary Notice of Additional Researches on the Cinchona Alkaloids."—Part III. By W. BIRD HERAPATH, M.D. &c. Communicated by Professor STOKES, Sec. R.S.
Received June 17, 1858.

Since the author had the honour of presenting to the Royal Society his paper entitled "Researches on the Cinchona Alkaloids," Parts I. and II., he has been much occupied with a continuation of the subject, and he has arrived at important results, which, although in an unfinished state, he hastens to lay before the scientific world, in order to assure himself of the priority of discovery.

Having had occasion to make some experiments upon the rotatory power of the β -quinidin mentioned in the first part of his paper, he arrived at the conclusion that some other feebly dextro-gyrate alkaloid accompanied it, and of a more soluble and less crystallizable character. Consequently, on its further purification by frequent recrystallization from alcohol, the quinidin was obtained perfectly pure; it then had the molecular rotation assigned to it by Pasteur, namely $250^{\circ} \cdot 75^{\nearrow}$. Two examinations have given the following elements:—

I. Its solution having been made in rectified spirit of $\cdot 836$ by boiling,