LIII.—*The Action of Acetylene on Aqueous and Hydrochloric Acid Solutions of Mercuric Chloride.*

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THE recent publication of papers by Bilz and Mumm (*Ber.*, 1905, 37, 4417) and by Karl Hofmann (*loc. cit.*, p. 4459) on the production of trichloromercuriacetaldehyde makes it desirable that the author should record experiments on the action of acetylene with mercuric chloride in aqueous solution and in solutions containing hydrochloric acid on which he has been engaged for the last four years.

Aqueous Solutions.

Several constitutions have been suggested by different observers for the white precipitate obtained when acetylene is passed into aqueous solutions of mercuric chloride, but Bilz and Mumm, and also Hofmann, seem to have settled fairly conclusively that it is trichloromercuriacetaldehyde, $C(HgCl)_3 \cdot CHO$, and analyses made by the author some

three or four years ago are in fair agreement with such a constitution.

Hofmann regards the action as proceeding through two stages, first the formation of $C_2Hg_3Cl_4$ (*Ber.*, 1899, **32**, 810), and then the hydrolysis of this compound to yield the foregoing aldehyde derivative. He ascribes the high analytical results obtained for chlorine by himself and other observers to small amounts of the former substance which remain undecomposed. It does not appear to have been noted, however, that accompanying the trichloromercuriacetaldehyde, there are almost always small amounts of another substance, $Cl \cdot CH:CH \cdot HgCl$, first described by Biginelli (*Ann. Farm. Chim.*, 1898, **16**), to which further reference is made, and that the presence of this substance increases the percentage of chlorine present and lowers the percentage of mercury. This acetylene-mercuric chloride is easily removed by two or three extractions with alcohol in a reflux apparatus. Even after its complete removal, however, analyses made by the author invariably gave too high values for chlorine, and too low values for mercury.

It must, indeed, be pointed out that whilst there is close agreement between the analytical results for this substance made by different observers, there is a considerable difference between these results and the values calculated for $C(HgCl)_3 \cdot CHO$, and for the purpose of comparison the details are summarised below, so far as they are available, together with the values calculated from various suggested formulæ. The numbers in brackets give the number of experiments from which the mean values were obtained.

	Analytical values.				Calculated values.			
	Keiser.	Bilz and Mumm.	Hofmann.	Brame.	Kutcheroff.	Keiser (<i>Amer. Chem. J.</i> , 1893, 15 , 535).	Peratoner (<i>Gazzetta</i> , 1894, 24 , [ii], 36).	Hofmann—Bilz and Mumm.
Hg ...	79·34 (3)	79·24 (2)	80·08	79·27 (3)	79·33	79·38	80·72	80·28
Cl.....	14·56 (2)	14·69	14·82	14·72 (6)	14·06	14·08	14·30	14·23
C	—	3·28 (5)	—	3·10	3·17	4·76	1·61	3·21
H	—	0·30 (3)	—	0·28	0·26	0·19	0·13	0·13

The values for Kutcheroff's formula are really deduced from the constitution ascribed by him to the corresponding allylene mercury compound, $3HgCl_2, 3HgO, (C_2H_2)_2$ (*J. Russ. Chem. Soc.*, 1882, **14**,

326), but which Bilz and Mumm state to be trichloromercuriacetone, $\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{HgCl})_3$.

The agreement between the analytical results and those calculated for such a constitution is really better than for the compound $\text{C}(\text{HgCl})_3 \cdot \text{CHO}$, except that the chlorine is abnormally high, but one would expect, if a formula based on Kutcheroff's allylene compound were correct, that acetylene would be liberated on heating, which is not actually the case. The formula indicated by Hofmann and by Bilz and Mumm is, therefore, most likely correct, but the author hopes to conduct further experiments in order to ascertain whether the analytical methods are at fault or whether the substance operated on is impure.

Hofmann (*loc. cit.*) states that there is no precipitation in the presence of a large excess of sodium chloride, but at least with a ratio of five molecules of salt to one molecule of mercuric chloride the precipitate is slowly formed.

Hydrochloric Acid Solutions.

A solution of mercuric chloride in dilute hydrochloric acid has been recommended by Bergé and Reyhler (*Bull. Soc. chim.*, 1897, 17, 218) as a purifying agent for acetylene, on which they say it has no action. This agent is certainly of considerable value as a test for impurities in that gas, and having frequently employed it for that purpose, the author observed after some hours the formation of fine, needle-shaped crystals, the gas washing-bottle being still full of acetylene. On referring to the literature of the subject, it was found that Biginelli (*Ann. Farm. Chim.*, 1898, 16) had obtained a similar result, and from estimations of mercury and chlorine only, ascribed to it the formula $\text{CHCl} \cdot \text{CH} \cdot \text{HgCl}$. The author has prepared several pure specimens and complete analyses are in good agreement with this.

In addition to the properties already described, it may be mentioned that the material produces intense irritation of the skin, especially on the face, and when dissolved in water, in which it is slightly soluble, gives only a white precipitate with potassium iodide, which serves as a valuable test for the freedom of the product from mercuric chloride. This white precipitate soon undergoes a change to a yellow substance, but all attempts to collect some and purify it for examination have so far failed. When perfectly pure, the dry substance is not darkened by ammonia. On heating, acetylene is given off, this being a point of some importance as supporting the constitution suggested by Biginelli.

Action of Water and Sodium Hydroxide on $\text{CHCl}:\text{CH}\cdot\text{HgCl}$.

On boiling with water, a white powder is produced to which Biginelli ascribed the formula $\text{CH}_2:\text{CH}\cdot\text{HgCl}$. The author of this paper has prepared several specimens, but the analytical results do not agree in the slightest with such a constitution.

The crystalline acetylene-mercuric chloride was heated in the water-bath with fresh portions of water until no turbidity was obtained on adding silver nitrate, and only a straw colour on passing sulphuretted hydrogen through the wash water. Acetaldehyde is always produced, the solution becoming strongly acid.

The following results were obtained, the mercury and chlorine being determined at the same time by the lime method:—

		Hg.	Cl.
I.	{ 1.2823 gave 1.0463 Hg	= 81.57	—
	{ „ „ 0.7360 AgCl	= —	14.19
II.	{ 0.6864 „ 0.5576 Hg	= 81.24	—
	{ „ „ 0.4040 AgCl	= —	14.55
III.	{ 0.7964 „ 0.6416 Hg	= 80.56	—
	{ „ „ 0.4652 AgCl	= —	14.44
IV.	{ 0.9728 „ 0.7895 Hg	= 81.15	—
	{ „ „ 0.5712 AgCl	= —	14.52
V.	{ 1.1616 „ 0.9469 Hg	= 81.52	—
	{ „ „ 0.6844 AgCl	= —	14.57

Combustions.

		C.	H.
2.2910	gave 0.2344 CO_2 ; 0.0383 H_2O	= 2.79	0.18
2.1526	„ 0.1616 „ 0.0241 „	= 2.05	0.13
2.5425	„ 0.1868 „ 0.0254 „	= 2.00	0.11

Mean values from above = Hg = 81.21 ; Cl = 14.45 ; C = 2.28 ; H = 0.13 per cent.

$4\text{HgCl}, \text{C}_2\text{HO}$ requires Hg = 81.40 ; Cl = 14.43 ; C = 2.44 ; H = 0.10 per cent.

Biginelli's $\text{C}_2\text{H}_3\cdot\text{HgCl}$ requires Hg = 76.21 ; Cl = 13.51 ; C = 9.14 ; H = 1.14 per cent.

There can be little doubt but that the substance is a mixture of trichloromercuriacetaldehyde and mercurous chloride in almost molecular proportions, and its behaviour fully bears out this view. On warming with dilute hydrochloric acid in a water-bath, the substance nearly all dissolves with the production of acetaldehyde and mercuric chloride, but a small amount of mercurous chloride remains, which by

the action of the acetaldehyde soon becomes reduced to metallic mercury.

The presence of the mercurous chloride in the first place is easily accounted for by the action of the acetaldehyde liberated on the mercuric chloride also set free on hydrolysis, and must be regarded as accidental, the true product being exactly the same as is produced on passing acetylene into aqueous mercuric chloride.

The crystalline acetylene-mercuric chloride is soluble in alkalis, and on heating the solution a greyish-white precipitate is deposited, which, when examined under the microscope, generally shows globules of finely divided mercury. Biginelli (*loc. cit.*), from apparently one mercury estimation, assumed that this substance was a di-acetylide, $(C_2H_2)_2, HgO$.

In order to obtain the substance as free as possible from metallic mercury, a large number of experiments were made by the author, and ultimately it was found that the best results were obtained by shaking the mercuric compound in small quantities at a time with sodium hydroxide solution and filtering through glass wool into a large volume of hot water. After washing by decantation with hot water until the washings were free from chlorine, the material was dried on porous plates and then under diminished pressure over sulphuric acid, finally being kept for several weeks in a vacuum over phosphoric oxide. The substance ultimately lost weight very slowly, and the drying is therefore a lengthy process. Heating is inadmissible, for the thoroughly dried material steadily loses weight in the water-oven and changes in character.

The dry substance is bluish-white, free from chlorine, and very explosive either when heated or rubbed in a mortar. With the exception of any free mercury, the material is soluble in dilute hydrochloric acid, and this gives a fairly good method of ascertaining the purity, samples which showed more than a trace of the latter being rejected.

Much trouble was experienced in making satisfactory estimations of the mercury, neither the action of sulphuretted hydrogen in hydrochloric acid solution nor the direct decomposition of the substance by ammonium sulphide giving satisfactory results. Ultimately, the method of Frankland and Duppá (*J. Chem. Soc.*, 1863, 15, 417) was adopted. The material was carefully mixed with copper oxide in the combustion tube, the latter drawn out about five inches from the exit end, a boat containing phosphoric oxide slipped in, and a tapped calcium chloride tube attached, the whole apparatus being exhausted to a few millimetres pressure, dry air was admitted, and the tube again exhausted daily for some three weeks. To make quite sure that no mercury vapour passed into the sulphuric acid tube during combustion, a few strips of silver foil were inserted in the small side tube.

The analytical data for the three purest specimens are :—

		Hg.	C.	H.
1.0570	gave	0.9162 Hg ; 0.3824 CO ₂ ; 0.0360 H ₂ O.	86.68	9.86 0.38.
1.1040	„	0.9694 Hg ; 0.3904 CO ₂ ; 0.0334 H ₂ O.	87.25	9.64 0.34.
1.0609	„	— ; 0.3826 CO ₂ ; 0.0239 H ₂ O.	—	9.83 0.25.
		Mean	86.96	9.77 0.32.

Biginelli's (C₂H₂)₂HgO requires Hg, 74.63 ; C, 17.91 ; H, 1.49 per cent.
 Travers and Plimpton's 3C₂Hg₂H₂O requires Hg, 86.96 ; C, 10.43 ;
 H, 0.29 per cent.

It will be seen that the compound gives results agreeing very closely with those required for the acetylide described by Travers and Plimpton (*Trans.*, 1894, **65**, 264), except that the carbon is unaccountably low. Moreover, the substance generally agrees in its properties with the other acetylide, and there is every reason to believe that it is identical with this, although perhaps it is not quite pure.

Keiser (*Amer. Chem. J.*, 1893, **15**, 535) describes an anhydrous acetylide, HgC₂, but Travers and Plimpton (*loc. cit.*) were unable to obtain the substance free from water, and as Keiser's work seems to be unconfirmed the author is at present engaged in attempting to prepare an anhydrous acetylide.

Conclusions.

There seems good reason for believing that the first action of acetylene on either aqueous or dilute acid solutions of mercuric chloride is the formation of the compound Cl·HC·C·HgCl by direct addition together with acetaldehyde. This additive compound has been shown to undergo decomposition with water, producing acetaldehyde, mercuric chloride, free hydrochloric acid, and some trichloro-mercuriacetaldehyde. The latter is decomposed by hydrochloric acid, and in the presence of much acid is therefore not isolated. It remains to be proved whether it is an intermediate substance concerned in the production of acetaldehyde, or whether it is a secondary substance derived from the aldehyde.

It is hoped to study the exact mechanism of the reaction further, for it should throw considerable light on the remarkable influence exerted by mercury salts in bringing about the formation of acetaldehyde from acetylene in the presence of water.

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