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XXVIII.—Metallic Derivatives of Acetylene. I. Mercuric Acetylide.

By R. T. PLIMPTON, Ph.D., and M. W. TRAVERS, B.Sc.

IN a preliminary notice by one of us (Plimpton, Proc., 1892, 109), an account was given of certain silver and mercury derivatives of acetylene. These and other similar compounds have now been more fully studied, and in this paper we give the results of the investigation of the mercuric acetylide formed in alkaline solutions.

Berthelot (Ann. Chim. Phys., [4], 9, 386) obtained an explosive mercuric acetylide by the action of acetylene on a solution of mercuric iodide in potassium iodide made alkaline with ammonia; this he regarded as being similar in constitution to the copper and silver compounds, and accordingly named it oxide of mercuracetyl. He does not seem, however, to have made an analysis of the subtance.

Bassett (*Chem. News*, **19**, 28), by passing acetylene through Nessler's solution, obtained a pale yellow, slightly explosive product containing iodine, to which he gave the formula C_2 HHgI,HgO.

Towards the end of 1892, in the course of our study of the metallic derivatives of acetylene, we were able to prepare Berthelot's explosive compound in a pure state by various methods, and to examine it with some completeness. We delayed the publication of the results of our investigation, however, while experiments were in progress with regard to its possible technical value.

The preliminary notice on the silver and mercury compounds, published in the Proceedings and already referred to, was occasioned by the appearance of Dr. E. H. Keiser's paper on the silver and copper derivatives (*Amer. Chem. J.*, 14, 285), and it was stated that the examination of the mercuric and other metallic derivatives would be continued.

Keiser appears to have overlooked this preliminary communication, and has recently, in the November number of the same journal, published the results of some work on the mercury acetylides. As our results, which were completed before the appearance of his paper, do not in some respects agree with those of Dr. Keiser, and as we have made a somewhat more extended study of those substances, we desire to lay an account of our work before the Society.

Mercuric Acetylide.

We have been able to prepare this substance in a pure state in several ways. By subjecting freshly precipitated mercuric oxide, suspended in water, to the action of acetylene, it is slowly converted into a white, explosive powder; several days are, however, required for complete conversion of the oxide. In this respect, acetylene has an action similar to that of allylene, which, according to Kutscheroff, acts on mercuric oxide forming the compound $(C_3H_3)_2Hg$.

Ammoniacal solutions of mercuric salts are only partially precipitated by acetylene, the product consisting of explosive mercuric acetylide in a state of purity. From mercuric cyanide mixed with ammonia only about one-third of the mercury is precipitated, the ammonium cyanide formed tending to redissolve the precipitate.

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The same incomplete precipitation is observed in the case of the sulphate and acetate.

When, however, such mixtures as mercuric cyanide with copper sulphate and ammonia, or mercuric sulphate with zinc chloride and ammonia, are used, the whole of the mercury is thrown down as acetylide. The precise action of the salts added has not been fully ascertained, but it seems probable that in the decomposition of mercuric cyanide the cuprammonium sulphate serves to dispose of the hydrogen cyanide. A sparingly soluble ammonium copper cyanide separates in small, blue crystals on standing.

The best method of preparing the compound is as follows:— Freshly precipitated mercuric oxide is dissolved in strong ammonia, adding powdered ammonium carbonate; at first the oxide was treated with ammonia to convert it into the white amido-compound, and this was then dissolved in solution of ammonium carbonate, but it was subsequently found that the two processes might be combined in one operation. The filtered solution is moderately diluted and saturated with acetylene, preferably in a bottle fitted with a cork and glass stopcock and previously exhausted. The absorption takes place rapidly on shaking, fresh acetylene being admitted from time to time until precipitation is complete. The acetylide separates as a heavy, white powder, which is washed by decantation, and finally on a filter until free from ammonia. It may be kept an indefinite time under water without changing, and on account of its highly explosive character is conveniently stored in this condition.

The preparations used for analysis were made in the above way, and dried at first over oil of vitriol, and finally in the air bath at 100° until of constant weight. Pure mercuric acetylide at this temperature remains white, and shows no sign of decomposition. Analysis of three preparations gave the following results.

0 [.] 204 gave	• 0·2065 HgS.	Hg = 87'3.			
0·313 ,	0.3165 "	Hg = 87.1.			
0.258 ,,	0.2605 ,,	Hg = 86.8.			
0.161 "	0.163 "	Hg = 87.2.			
0.5405 "	0·199 CO ₂ .	C = 10.1.			
0 [.] 3595 "	0.1365 "	C = 10.3.			
C_2Hg requires $Hg = 89.3$; $C = 10.7$.					
$3C_{2}Hg, H_{2}O$ requires $Hg = 87$; $C = 10^{\circ}4$.					
$2C_2Hg,H_2O$ requires $Hg = 85.8$; $C = 10.3$ per cent.					

The determinations of mercury were made by warming the substance with excess of ammonium sulphide, which easily decomposes it, collecting the mercuric sulphide on a Gooch filter, and extracting with alcohol and chloroform. The filtrate was free from mercury. No difficulty was experienced in burning the substance when well mixed with sufficient powdered copper oxide; on exploding it in a vacuum, gas was not given off.

Dr. Keiser's analyses of mercuric acetylide, obtained from mercuric iodide dissolved in potassium iodide solution mixed with potash, gave 88.94, 88.42, and 89.14 per cent. of mercury, and he accordingly regards the acetylide as free from water (calculated for C_2Hg , 89.3). We, however, have not been able to obtain the substance free from water, even by drying it during many hours at 100°. Drying at a higher temperature is impracticable, as the substance decomposes at about 110°. In the case of silver acetylide, the analyses of preparations from ammoniacal silver nitrate and from silver acetate always showed a certain quantity of water (see note in Proceedings), and the regularity of the results obtained with the mercuric compound leads us to believe that its composition is represented by the formula $3C_2Hg,H_2O$.

Properties.—Mercuric acetylide is a heavy, white powder, which, under the microscope, does not appear to be crystalline. Its relative density at 16° compared with water at the same temperature is 5.3.

It is insoluble in water, alcohol, and ether. A solution of ammonium accetate dissolves the freshly precipitated substance; potassium cyanide dissolves even the dried substance with ease.

When heated gradually in an oil bath, mercuric acetylide, from its point of decomposition at about 110°, slowly breaks up into mercury and soft, black carbon, a little water being given off at the same time. In one experiment, in which the temperature was not raised above 150°, decomposition was complete at the end of three weeks. In another experiment the substance was heated gradually to 300° in about two hours; on cooling, some acetylide remained undecomposed.

When heated rapidly, the substance explodes violently, leaving a residue of carbon; and when dropped on to the bottom of a heated metal cylinder explosion took place at all temperatures above 230°. Although it explodes when struck smartly, it can be handled with safety.

When allowed to stand in contact with an alcoholic solution of mercuric chloride, or when boiled for a short time with an aqueous solution of this substance, mercuric acetylide is converted into a nonexplosive white compound which behaves exactly like the precipitate obtained by passing acetylene into a solution of mercuric chloride. This substance gives calomel and carbon on heating, no acetylene with hydrochloric acid, and no C_2I_2 with iodine. It belongs to a separate class of non-explosive acetylides, of which several have been prepared, and which will be described in a separate paper. Action of Acids.—Cold hydrochloric acid has little action on mercuric acetylide; on warming, mercuric chloride is formed, acetylene being evolved; part, however, of the latter is hydrolysed to aldehyde, the action being similar to the conversion of allylene into acetone by hydration, which, as Kutscheroff (Ber., 13, 17) has shown, takes place when that hydrocarbon is passed into a warm solution of mercuric chloride.

The proportion of acetylene evolved depends on the conditions in some experiments; about three-fifths of the calculated quantity was obtained. Nitric acid readily dissolves the acetylide; strong sulphuric acid causes it to explode; the dilute acid has little action, and appears to give aldehyde rather than acetylene.

Action of the Halogen.—Chlorine and bromine, when brought in contact with mercuric acetylide, cause explosion. A solution of chlorine in chloroform acts on it, forming mercuric chloride and a substance which is probably C_2Cl_6 . The action is accompanied by a sharp, crackling noise.

Bromine water, in excess, on warming, yields a white, crystalline substance, insoluble in water, volatile with steam, and melting at 53°, which, on analysis, proved to be tetrabromethylene.

	Ι.	11.	Calculated for C ₂ Br ₄ .
Bromine	92.7	92.9	93

Iodine in potassium iodide solution readily attacks mercuric acetylide; the first product of the action is the compound C_2I_2 ; at least the smell of this substance is instantly noticed when the substances are brought together.

The action is not complete, owing to the acetylide becoming coated with the insoluble organic iodide, unless heat be applied; when, however, the acetylide is heated with iodine solution in excess for 24 hours at 100—120°, it is completely decomposed, taking up the quantity of iodine needed to form C_2I_4 and mercuric iodide.

I. 0.741 gram acetylide took up 2.312 grams iodine,

II. 0·359 " " " 1·212 "

or one molecular porportion of $3 HgC_2, H_2O$ required 17 and 18.3 atoms of iodine instead of 18.

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The melting point of the tetraiodethylene was 185° . Iodine found, 95.5; calculated for C₂I₄, 95.5. A solution of iodine in ether, shaken with excess of the acetylide, is decolorised, and, on filtering and allowing the ether to evaporate, leaves a residue which consists of mercuric iodide and needles having the intolerable odour of diiodacetylene; on treating with chloroform and filtering, a solution is obtained which, on adding more iodine, yields crystals of C₂I₄.

It is possible that additive compounds of C_2Hg with iodine are also

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formed, which are decomposed by more iodine, yielding mercuric iodide and C_2I_2 or C_2I_4 , but the smell of diiodacetylene is always perceptible, however large may be the excess of acetylide present.

Mercuric acetylide appears to be strictly analogous to the silver and cuprous compounds. Like these, it is explosive, and yields acetylene with hydrochloric acid, and C_2I_2 or C_2I_4 with iodine. It differs entirely from the substance obtained by precipitating mercuric acetate solutions with acetylene, which has been briefly described (Proc., *loc. cit.*), and which gives aldehyde when treated with hydrochloric acid and iodoform with iodine.

The acetylene used was made either from the copper compound or by the method described in the Proceedings for 1893, 15.

University College, London.