XXXVIII.—*Cuprous Formate.*

By ANDREA ANGEL.

IN the course of an investigation by the author of the decomposition by heat of cupric formate, the question of the existence of cuprous formate arose, and attempts were therefore made to prepare this substance by different methods, but although definite indications of its existence were obtained, all endeavours to prepare it in quantity failed. The preparation by Pechard (*Compt. rend.*, 1903, **136**, 504) of cuprous acetate by a new method, namely, the acidification with acetic acid of an ammoniacal solution of cupric acetate which had been reduced with an aqueous solution of hydroxylamine sulphate, seemed to indicate a possible way of preparing cuprous formate. Working in a similar way, using an ammoniacal solution of cupric formate decolorised by hydroxylamine sulphate and acidifying with formic acid, a white precipitate was momentarily produced. This, however, could not be separated from the liquid, as it decomposed almost immediately with the precipitation of metallic copper and the formation of the cupric salt. No modification of the conditions of the experiment could be found which would render the precipitate stable. It seemed, however, probable that cuprous formate could exist, but that in the presence of water or formic acid it underwent decomposition. It was thought, therefore, that if the precipitation could be brought about in a solvent other than water the decomposition might be prevented or delayed. Alcohol seemed a suitable liquid, but then the reduction method became inapplicable, since cuprous chloride was precipitated if hydroxylamine hydrochloride were used for the reduction; or if the sulphate were used, ammonio-cuprous sulphate, which is insoluble in alcohol, as Péchard found, was precipitated. Hydrazine sulphate gave equally unsatisfactory results. The reduction method was therefore abandoned, and eventually the process described below was devised.

In the meantime, however, Joannis (*Compt. rend.*, 1904, **138**, 1498), by the action of liquefied ammonia on ammonium formate and cuprous oxide in a sealed glass apparatus previously exhausted with air, obtained a compound having the formula $Cu_2(O_2CH)_2,4NH_3,\frac{1}{2}H_2O$, which he described as "cuprous formate." The present author, however, considers that this substance would more appropriately be described as "ammonio-cuprous formate," since it differs considerably in properties from the compound which he has obtained by the method described below, and which is the free cuprous formate corresponding to the formula $Cu_2(O_2CH)_2$.

Instead of reducing the cupric salt, cuprous oxide was made the starting point. When an aqueous solution of ammonium formate is heated with cuprous oxide and a little strong ammonia solution under a layer of light petroleum to minimise oxidation, a blue solution is obtained (since some oxidation does occur) which contains a cuprous salt, probably an ammonio-cuprous formate. If this liquid is diluted with alcohol, no precipitation occurs, but on adding formic acid to this alcoholic solution and cooling under the tap, colourless crystals are precipitated which have all the appearance of a cuprous salt and which are fairly stable, the alcohol arresting the decomposition which occurs in an entirely aqueous solution. The decomposition, however, is only delayed and not entirely prevented by the alcohol, for if the crystals are allowed to remain for a long time in the liquid they decompose as before into copper and the cupric salt.

It was therefore necessary to find some means of rapidly separating the crystals from the mother liquor in an air-free atmosphere and also of finding a liquid with which they might be washed without decomposition occurring. Here, again, much difficulty was encountered. Various forms of filtering apparatus were devised, but the only one which proved satisfactory was a method of reverse filtration; for in all cases of direct filtration, the filter soon became blocked, and the crystals on prolonged contact with the mother liquor decomposed. Further, the ease with which the crystals decompose renders the washing a difficult matter. Water immediately hydrolyses them to cuprous oxide. Ether, chloroform, benzene, petroleum, and absolute methyl and ethyl alcohols were tried with unsatisfactory results; absolute alcohol causes hydrolysis. Formic acid decomposes the crystals with precipitation of copper. Partial success was obtained by using as a washing liquid absolute alcohol containing a little formic acid. Any attempt, however, to prepare more than a small quantity of the crystals resulted in failure, for if the washing liquid was too acid, copper was precipitated, whilst if insufficient acid were used the crystals gradually became yellowish-red during the drying owing to the hydrolysing action of the alcohol. These results suggested that possibly ethyl formate might cause neither of these two decompositions. This was found to be the case; further, the greater volatility of ethyl formate hastens the drying, and its use as a washing liquid has enabled the author to prepare cuprous formate as a comparatively stable substance.

Details of the Method of Preparation.

A strong solution of ammonium formate is made by dissolving 136 grams of the salt in 100 c.c. of distilled water. A separate solution of 30 grams of ammonium formate in 10 c.c. of water is then prepared, and in this 9 grams of pure cuprous oxide are dissolved (under a layer of light petroleum) with the aid of heat and the addition of just sufficient strong ammonia solution (sp. gr. 0·880) to enable the cuprous oxide to dissolve, forming a blue solution. For the above quantities, the amount of ammonia solution required should not exceed ·11 c.c.

The blue liquid so obtained is then diluted with half its own volume of the first solution of ammonium formate, transferred by reverse filtration through a pad of glass wool enclosed between silk (to remove any fine particles of cuprous oxide) to a tube similar to the tube *A* in Fig. 1, and preserved under petroleum.

For the precipitation, this blue liquid is diluted with ten times its volume of alcohol, and more light petroleum added, if necessary, to form a layer on top. Aqueous formic acid of sp. gr. 1·15 is then gradually introduced from a burette. The deep blue colour is discharged, the liquid becomes green, and, on cooling under the tap, colourless crystals of cuprous formate are deposited. About 15 c.c. of the blue liquid is a convenient quantity to take for a preparation, and after dilution with alcohol the formic acid required is about 8 c.c.

Much difficulty was encountered in finding the right conditions for the precipitation. If too much ammonia is used in preparing the blue solution, the heat evolved in the neutralisation causes local decomposition, and small particles of copper become mixed with the crystals and cannot afterwards be separated from them. If the blue solution is too dilute, the products of the hydrolysis of the salt, namely, cuprous oxide and formic acid, are obtained instead. If too much formic acid is used in the precipitation, the preservative influence of the alcohol and ammonium formate is counteracted and decomposition again occurs, whilst if the blue liquid is largely diluted with alcohol, the salt is found to be contaminated with ammonia and cupric salt owing to the small solubility of ammonium formate and cupric formate in alcohol.

For the separation of the crystals, the apparatus shown in Fig. 1 was employed. It consists of a vessel, *D*, made from part of a large test-tube about 3½ cm. in diameter, into which is fitted an india-rubber cork, *E*, with four holes, coated with a very thin layer of paraffin wax. Through two of the holes pass delivery tubes, *A* and *B*, fitted with taps; a third allows hydrogen to enter through a tube, and through the fourth and central hole passes the filter tube, *C*. This consists of a piece of quill tubing expanded at the bottom; over this is tied a single layer of silk. The upper end of *C* is connected by stout india-rubber tubing to a thick-walled flask attached to a water pump.

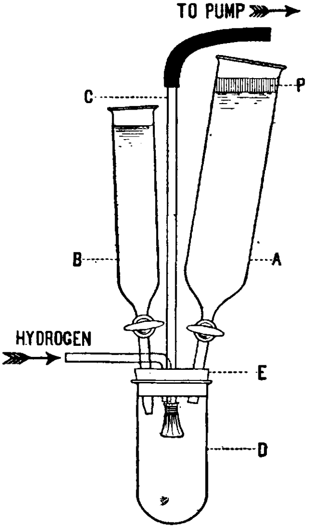
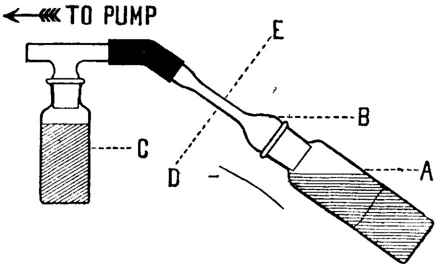


Fig. 1.

The hydrogen is prepared in a Kipp apparatus from zinc (free from arsenic and antimony) and dilute sulphuric acid, and is passed through a tower containing glass beads moistened with silver nitrate solution and then through U-tubes containing soda-lime and calcium chloride before entering the vessel *D*.

After the whole apparatus has been filled with hydrogen, the liquid containing the precipitated crystals is transferred, still under a layer of light petroleum, to the tube *A*. It is then run into *D*, excluding the petroleum layer *P*, the liquid drawn off, and the crystals repeatedly washed (lowering *C* when necessary and eventually inverting the whole apparatus to drain away the washing liquid), first with a mixture of four volumes of absolute alcohol with one volume of absolute ethyl formate, and finally with absolute ethyl formate delivered through the tube *B*. When the crystals are quite clean, any remaining liquid is poured out of *A* and *B*, and hydrogen is passed through the inverted apparatus for one and a half to two hours. The crystals form a cake on the round end of *D* and adhere until they are dry. They may then readily be detached from the glass by a slight tap and quickly transferred through a dry funnel to carefully dried bottles with ground tubular stoppers, which are then exhausted of air, left in connection with phosphoric oxide on the mercury pump, and then sealed off (Fig. 2).

Analysis.—The salt was quickly weighed out into a porcelain dish and decomposed with sodium carbonate solution. The dish and its contents were heated to boiling and then the liquid decanted from the precipitated cuprous oxide on to a filter, the filtrate being collected in a measuring flask. The oxide was repeatedly washed with distilled water, and the washings added to the filtrate and made up to 500 c.c. The cuprous oxide was dissolved in dilute nitric acid and the copper estimated as cupric oxide by precipitation with sodium hydroxide. The formic acid (as sodium formate) in the filtrate was estimated by Lieben's method, that is, by titration with potassium permanganate in alkaline solution, 50 c.c. of the filtrate being used for an estimation.



A = Bottle containing cuprous formate.
B = Tubular stopper, originally open at both ends, finally sealed off at *DE*.
C = Bottle containing phosphoric anhydride.

FIG. 2.

Analyses of three different preparations gave the following results:

Weight of substance taken.	Percentage of copper found.	Percentage of (O_2CH) found.
0·4085 gram	58·54	41·31
0·4051 ,,	58·34	40·79
0·4068 ,,	58·32	41·22

$Cu_2(O_2CH)_2$ requires Cu = 58·55; (O_2CH) = 41·45 per cent.

Properties of Cuprous Formate.—The compound described by Joannis under this name is said to consist of pale blue crystals, which become intensely blue in moist air and brownish-black in dry air, and when thrown into a dilute acid give immediately a precipitate of cuprous oxide.

Cuprous formate obtained as above consists of colourless, needle-like crystals, which are very light and appear white with a very faint pink tinge in a compact mass. The appearance of the crystals is very characteristic; they almost invariably occur associated in double or quadruple groups, as shown in the diagram in Fig. 3, whilst in some cases they appear to be grouped about the three axes of a cube, with the result that the whole complex has a globular appearance. This generally occurs when the precipitation is slow and in a solution which has been largely diluted with alcohol.

In moist air, the substance is rapidly decomposed, and assumes a brilliant orange-red colour owing to the formation of cuprous oxide. When treated with water, it is also hydrolysed to cuprous oxide and the liquid has an acid reaction. When dropped into strong ammonia solution, it is instantly decomposed with a slight hissing noise, and if sodium carbonate solution is poured on the dry substance it decomposes it with effervescence. When thoroughly dried, it is practically permanent in dry air, as it may be kept over sulphuric acid for weeks without any apparent change. Aqueous formic acid rapidly decomposes it into metallic copper and the cupric salt, and when it is thrown into dilute sulphuric acid metallic copper is immediately precipitated.

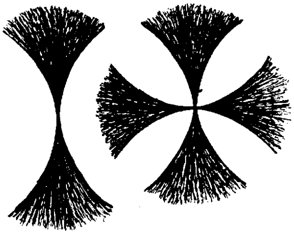


Fig. 3.

The difficulties met with in the preparation of cuprous formate have been chiefly due to the fact that formic acid decomposes it. In the case of the higher members of the same series of acids, this decomposition does not occur. Péchard showed that cuprous acetate is stable in presence of acetic acid. Preliminary experiments made by the author seem to show that this holds for other members of the series, since by a similar method, omitting, however, the addition of alcohol, white precipitates of cuprous salts were obtained with chloroacetic, propionic, and butyric acids.

In conclusion, the author wishes to express his thanks to Mr. Vernon Harcourt and Dr. Brereton Baker for their helpful interest in the work, and to the latter especially also for his kindness in allowing the author every facility in the use of the new research laboratory at Christ Church.

Dr. Lee's Laboratory,
Christ Church,
Oxford.