LXX.—*Action of Mercurous Nitrate on Chloroauric Acid.*

By WILLIAM BRANCH POLLARD.

THE action of mercurous nitrate on chloroauric acid has been stated to give (1) gold, or a mixture of gold and mercurous chloride (Proust, *Nicholson's J.*, 1806, **13**, 244), (2) a combination of aurous and mercuric oxides (Fischer, *Schweigger's J.*, 1829, **56**, 363), (3) aurous oxide (Figuier, *Ann. Chim. Phys.*, 1844, **11**, 336).

The author has studied the reaction under two distinct conditions; first, the reaction which occurs when an excess of some halide is present, and, secondly, the reaction which occurs in the absence of halides.

EXPERIMENTAL.

Action of Mercurous Nitrate on Chloroauric Acid in Presence of Halides.—Mercurous nitrate was prepared by shaking a solution of mercuric nitrate in dilute nitric acid with excess of mercury, a little carbamide being added to prevent the formation of nitrites. The solution was titrated as described below, and then diluted until 50 c.c. reduced exactly 0·5 g. of gold.

Gold (0·5 g.) was dissolved in 4 c.c. of aqua regia (3 : 1). The fumes were blown out with a current of air, but the excess of nitric and hydrochloric acids was not removed. The solution was diluted with 50 c.c. of water, 1 c.c. of concentrated hydrochloric acid was added, and mercurous nitrate solution run in. The black colour of the precipitate of metallic gold that instantly formed slowly changed to brown. The particles of the precipitate cohered on shaking, leaving the liquid clear. As the end-point was approached, the yellow colour of the chloroauric acid disappeared, the precipitate took on a transient purple tint, and finally white, mercurous chloride formed. During the titration, no evidence of reduction to the aurous state was obtained, even when a large amount of alkali-metal chloride was present (Diemer, *J. Amer. Chem. Soc.*, 1913, **35**, 552). Addition of such chlorides or of bromides or iodides appears to increase the velocity of the reaction. The amount of mercurous nitrate required to precipitate the gold when in combination with chlorine, bromine, or iodine was, however, practically identical in the three cases, provided there was sufficient halide to combine with the whole of the mercury present.

In order to obtain the quantitative relation between mercurous nitrate and chloroauric acid, the volume of solution required to precipitate 0·5 g. of pure gold was taken and precipitated with sodium chloride. The resulting mercurous chloride was equivalent to 2·0039 g. of mercurous nitrate as against 1·9947 g. required by the equation :

$$HAuCl_4 + 3HgNO_3 + 2HCl = 3HgCl_2 + 3HNO_3 + Au.$$

To test whether this relation held at very great dilutions, the mercurous nitrate and chloroauric acid were titrated at a dilution one hundred times as great as that employed above. The gold separated in the red, colloidal condition. It was flocculated with a little hydrochloric acid, and the end-point found by addition of *o*-tolidine (*Trans. Inst. Min. Met.*, 1923, **32**, 242), which gives a yellow colour with one part of chloroauric acid in twenty million parts of solution. At this dilution, the relationship found above still held.

From this experiment it is inferred that the precipitate which forms when strong solutions react consists of colloidal gold which has been flocculated by the acids and salts present in the liquid, and this would also account for the very marked adsorption effects which have been observed.

When 0·5 g. of the precipitated gold was shaken with a solution containing a few mg. of chloroauric acid, this substance was so completely adsorbed that it could not be detected in the solution.

The adsorbed substance reacted quite readily with solutions of reducing agents when these were applied to the precipitate.

When solutions of certain dyes were shaken with the precipitate, these became colourless, and in the case of methyl-red this was adsorbed more readily in an acid than in an alkaline solution.

In the course of these experiments it was noticed that if a very small amount of brucine or one of the quinine alkaloids was added to the chloroauric acid before precipitation with mercurous nitrate, the gold remained dispersed through the liquid and did not flocculate. Up to the present this result has not been observed except with the class of substances mentioned.

Action of Mercurous Nitrate on Chloroauric Acid in the Absence of Halides.—Gold (0·5 g.) was converted into chloroauric acid, and all excess of nitric and hydrochloric acids was removed; 50 c.c. of water were added and mercurous nitrate solution was run in. The precipitate did not "clear" on shaking and the end-point was difficult to find, but much less mercurous nitrate was needed to precipitate the gold completely in the absence of halides than in their presence.

To a fresh solution of chloroauric acid a little mercurous nitrate was added, in order to precipitate only a small part of the gold. The black precipitate, on standing over-night in the solution, was converted into metallic gold. The gold was separated from the solution, and a further amount of mercurous nitrate added. The black, colloidal precipitate which formed was centrifuged, and the clear solution, which had changed from yellow to reddish-brown, was further examined. When heated, a reddish-brown precipitate resembling ferric hydroxide formed, and the same substance was deposited when the solution was kept.

The substance was difficult to filter and wash, and after drying in a vacuum over sulphuric acid gained weight when exposed to the air. When heated, it gave off oxygen, water, and mercuric chloride, and left a residue of metallic gold. It dissolved in hydrochloric acid with the reformation of chloroauric acid.

If the equation for the reaction between mercurous nitrate and chloroauric acid is written omitting the hydrochloric acid from the left-hand side, this will require the addition of mercuric nitrate to the right-hand side:

$$HAuCl_4 + 3HgNO_3 = 2HgCl_2 + Hg(NO_3)_2 + HNO_3 + Au.$$

Now Proust (*loc. cit.*, p. 224) showed that when "gold chloride" was added to an excess of mercuric nitrate solution a yellow precipitate formed. This compound gave oxygen, water, mercuric chloride, mercurous chloride, and gold on heating. The brown compound prepared by the author gave no mercurous chloride when heated.

On adding a small amount of mercuric nitrate to chloroauric acid, a slight darkening of the solution occurred. Further additions produced a reddish-brown solution similar to that previously obtained after centrifuging. When heated, a brown, colloidal precipitate separated identical with that previously described. The brown substance is therefore formed when chloroauric acid is in excess and Proust's yellow substance is formed when mercuric nitrate is in excess.

Proust explained the formation of his compound as being due to the very strong affinity of mercury for chlorine, which it is able to displace even from chloroauric acid.

Jacobson (*Compt. rend.*, 1908, **146**, 1213) has shown that silver nitrate also can remove chlorine from chloroauric acid with formation of a brown basic compound :

$$HAuCl_4 + 4AgNO_3 + 3H_2O = Au(OH)_3,4AgCl + 4HNO_3.$$

Attempts to discover the exact composition of the brown substance failed, as different preparations did not show sufficient agreement among themselves, and it is doubtful whether it has been prepared as yet in a state of purity. The following results, obtained by heating the substance in a Penfield tube, may, however, be taken as an approximate indication of its nature : Loss on heating (oxygen), 9·42; H_2O, 7·18; $HgCl_2$, 19·71; Gold (by difference), 63·69%.

The black precipitate formed by the action of mercurous nitrate on chloroauric acid which had been centrifuged out of the solution was now examined to see whether it consisted of a mixture of gold and the brown substance. After washing and drying, it was heated and gave off oxygen, water, and mercuric chloride and left a residue of gold. When it was treated with hydrochloric acid, chloroauric acid passed into solution and a residue of metallic gold was left. The black precipitate may therefore be regarded as a kind of "Purple of Cassius" in which stannic acid is replaced by the brown substance. It results from two reactions occurring simultaneously, which explains why, in the absence of halides, less mercurous nitrate is required to remove the gold completely from solution.

The author takes this opportunity of thanking Professor Carpenter and the staff of the Royal School of Mines for all the facilities which he has been afforded.

ROYAL SCHOOL OF MINES,
SOUTH KENSINGTON.

[*Received, October* 17*th*, 1925.]