#### STUDIES IN THE MALONIC ACID SERIES. 1013

# CIV.—Mercury Perchlorates. By Masumi Chikashigé, B.Sc.

HAVING, at the suggestion of Dr. Divers, prepared mercuric and mercurous perchlorates, with the object of examining their behaviour when heated, I found that their properties were not quite the same as those described by Serullas, and by Roscoe (*Proc. Roy. Soc.*, 1862, 11, 502, and *Liebig's Annalen*, 1862, 121, 346). The earlier memoir, which appeared in 1830 (*Ann. Chim. Phys.*, [2], 45, 270), I have not seen, and my statements as to its contents are on the authority of the larger works on chemistry.

Most of the hydrated perchloric acid, used in my experiments, was prepared, as Roscoe directs, by treating potassium chlorate with hydrofluosilicic acid, but some of it by the more convenient process of precipitating barium chlorate with sulphuric acid. Although not mentioned by Roscoe, it is tolerably well known that the hydrated acid is slightly decomposed when it is distilled, becoming contaminated with chlorine and hydrochloric acid. I find, however, that the distilled acid can be easily freed from these impurities by heating it for a short time in the air.

### Mercuric Perchlorate.

Mercuric perchlorate is formed when mercuric oxide is triturated with aqueous perchloric acid until the solution begins to grow turbid from the presence of basic salt; it is then filtered, preferably through asbestos, mixed with a few drops of perchloric acid, and concentrated at a gentle heat. Evaporation is then continued over sulphuric acid at the ordinary temperature until the salt crystallises. If necessary, it may be recrystallised, dissolving it in a very little water. It is **VOL. LXVII.** 3 **Y**  quite stable, but needs some care to dry it, for it slowly effloresces in a desiccator, whilst in the air it very quickly deliquesces (Serullas), and a slight rise of temperature causes it to melt. Preserved for a day or two in bottles, however, its upper layers become dry by draining, and may then be quickly pressed between folds of paper.

Mercuric perchlorate crystallises in slender rectangular prisms, as described by Serullas, but being exceedingly soluble in water, as well as very hygroscopic, its slender crystals rapidly liquefy when exposed to the air. It reddens litmus (Serullas), but its freedom from acid can be shown by adding excess of sodium chloride to its solution, which renders it neutral. It shows a slight tendency to decompose with water, and in absence of any excess of acid, its solution deposits basic salt if evaporated by the aid of heat. Moreover, its slow efflorescence in the desiccator is the result of loss of acid as well as of water: so that the effloresced salt leaves some insoluble basic salt when dissolved in water.

Alcohol decomposes it still more easily. The effect of this agent has been described by Serullas. I find that alcohol at once decomposes the crystals of the salt, leaving a white basic salt undissolved; this again is decomposed by water which leaves impure mercuric oxide. Alcohol, also, added to an aqueous solution of mercuric perchlorate, gives an orange precipitate, mainly mercuric oxide. As to the formation of mercurous oxide or mercurous salt, which is mentioned in the handbooks as taking place on evaporating the mother liquor, that happens to a small extent only, and because mercuric salts are reduced by hot alcohol.

Of the composition of mercuric perchlorate all that is known is that, on the authority of Serullas, it is expressed by  $Ag(ClO_4)_k$ ; it passes for an anhydrous salt (Roscoe and Schorlemmer's Treatise. Muir and Morley's Watt's. Dictionary, &c.). It is, however, a hydrated salt, with as much as 6H<sub>2</sub>O, which, though it can be readily removed from the salt by heat, cannot well be directly estimated, since perchloric acid is liberated along with it from the The composition of the salt was determined by precipitating first. the mercury as sulphide and obtaining the perchloric acid from the filtrate as its potassium salt, with the precautions given in Roscoe's The formation of a very little sulphuric acid in removing naper. the excess of hydrogen sulphide, cannot be avoided, and this comes out in the potassium perchlorate and, small as it is, has to be taken In the second of the analyses here given, the mercury into account. was precipitated by gaseous hydrogen sulphide without addition of acid; in the first, it was precipitated by adding, at once, excess of hydrogen sulphide solution, and then 1 c.c. of dilute sulphuric acid to aggregate the mercury sulphide. The total sulphuric acid having

1015

## CHIKASHIGÉ: MERCURY PERCHLORATES.

been determined, the corresponding quantity of potassium sulphate was deducted from that of the potassium perchlorate and sulphate together. In consequence of what has just been stated, this procedure introduced no complication, while the use of hydrochloric acid was precluded, as interfering with the determination of the perchloric acid. The calculation is for  $Hg(ClO_4)_{2,6}GH_2O$ .

	Calc.	Ι.	II.
Mercury	39.45	39.26	38.95
Perchlorate radicle	39.25	38.90	38.82
Water	21.30		

Behaviour of Mercuric Perchlorate when Heated.—Mercuric perchlorate, as dry as possible, melts at about  $34^{\circ}$  in dry air. Heated in a long, narrow tube, closed only at its lower end, the salt melts to a colourless liquid, which boils freely, without noticeable change, even in a bath of boiling sulphur. In reality it is decomposed, and at temperatures far below this, but since the products of its decomposition, which boil off, condense and flow down again, the salt is recovered when the tube is cooled.

Even at the common temperature, as already mentioned, mercuric perchlorate very slowly decomposes in dry air, but in a current of dried air at 120°, the evolution of water and perchloric acid becomes manifest in the shape of white fumes. By raising the temperature gradually, and then maintaining it at 150° until the weight of the residue becomes constant, a homogeneous, and apparently definite This compound, oxymercuric perchlorate, is white compound is left. and amorphous; it is not changed by the heat of boiling mercury, and only slowly affected by that of boiling sulphur. Heated to a point a little below that at which mercuric oxide freely decomposes, it is completely changed into oxygen and chlorine gases, sublimates of mercuric and mercurous chlorides, and a residue of mercuric oxide. By water it is decomposed into mercuric perchlorate and mercuric oxide, besides insignificant quantities only of chloride and chlorate. In a quantitative experiment, it was found to yield to water, mercury 12.64, and perchlorate radicle, 12.90 per cent. of the original weight of the salt heated. Therefore, water dissolves out normal mercuric perchlorate, and, since 12.90 is almost exactly the third part of 39.25. the percentage amount of perchlorate radicle in the original salt, and the change effected by heat, may be formulated thus,

 $3[Hg(ClO_4)_2, 6H_2O] = O_2Hg_3(ClO_4)_2 + 4HClO_4 + 16H_2O_4$ 

 $O_2Hg_3(ClO_4)_2$  expressing the composition of the oxymercuric perchlorate. 1016

CHIKASHIGÉ: MERCURY PERCHLORATES.

# Mercurous Perchlorate.

Mercurous perchlorate can be very quickly prepared by violently shaking a solution of mercuric perchlorate with mercury for a few minutes, after which nothing but the mercurous salt will be found in Such a solution cannot be left for days, or heated long the solution. on a water bath, without some basic salt being deposited, but a concentrated solution can be evaporated in a vacuum desiccator fast enough to avoid this. With rapid evaporation, the salt is obtained in fine needles, as described by Serullas; these are flat, and, with slower evaporation, develop into flattened prisms or plates of considerable size. The salt is exceedingly soluble in water, and causes a sensible fall in temperature in dissolving, the solution being neutral to litmus; with a large quantity of water, it is often decomposed. Serullas found the salt to be unchanged by exposure to air, and must therefore have been working in very dry weather, for it is as Roscoe states, very deliquescent, though less so than the mercuric salt. According to Roscoe, it does not lose water, either at 100°, or in a vacuum over sulphuric acid; but this is not really the case, although the loss of weight is slow enough to be easily overlooked ; when kept for about two weeks in a vacuum desiccator, the loss reaches nearly 6 per cent., and then ceases. This loss, though mainly that of water, includes also that of a little acid; a loss of half its water would amount to 5.36 per cent. of its weight. At 100°, in a current of dry air, it loses about 2 per cent. of water in six hours, a mere trace of acid also escaping, as was proved by placing litmus paper in the issuing current of air; in another six hours, it loses about 2 per cent. more in weight, including now a notable amount of acid.

As already stated, the salt is gradually decomposed by water; and when the white, basic salt thus produced is washed with water, it becomes black from loss of acid. Alcohol decomposes the solid salt into soluble acid salt and white basic salt, which is also blackened by washing with water, but not by alcohol. Alcohol added to an aqueous solution of the salt has no immediate effect.

In analysing the salt, the perchloric acid was determined in the same way as in the case of the mercuric salt, after removal of the mercury as sulphide, whilst the mercury was estimated in a separate portion of the salt by precipitation as mercurous chloride. The composition of the salt has been given by Roscoe as  $(HgClO_4)_2, 6H_2O$ , he having found the mercury to be 56.60 per cent. as required by that formula. I have assured myself, however, by examining different preparations, that the crystals I obtained only contained 4 mols. water when not visibly moist, the formula being  $(HgClO_4)_2, 4H_2O$ .

CHIKASHIGÉ :	MERCURY	PERCHLORATES.	101	7
CHIKASHIGÉ:	MERCURY	PERCHLORATES.	101	

	Calc.	Ι.	II.	III.	IV.
Mercury	59.61	59.00	58.90		
Perchlorate radicle	29.66			29.60	29.50
Water	10.73	_	—		

It might seem from our respective results that we had examined different hydrates, but in the several preparations I made of the salt, I never met with but one form of crystal which, with rapid evaporation in the vacuum desiccator, was that of fine needles, as described by Serullas and as got by Roscoe presumably, for he makes no mention at all of the form of his crystals. By somewhat slower evaporation in the desiccator, much larger crystals were obtained, and these were found to be preferable for analysis as they were more easily freed from mother liquor. For analysis, however, I used the fine needles as well as the plates. Of the three samples analysed, marked above II, III, IV, one consisted of fine needles that had formed the first crop, whilst the other two were larger crystals of the second crop from the same preparation; sample I was another preparation. If Roscoe's salt were a higher hydrate than that I obtained, it could not have been heated at 100°, even for a short time, or exposed to the dry air of a desiccator without loss, as he found it to do.

Behaviour of Mercurous Perchlorate when Heated.-Mercurous perchlorate, unlike the mercuric salt, has no melting point. Quickly raised to about 190°, the salt becomes partly liquid for a short time, but only from the presence of unvolatilised acid along with basic salt; when gradually heated, the salt does not show even this false fusion. At 100°, the crystals of the salt decrepitate; but it loses acid only very slowly at this temperature, and is still completely soluble in a little water, even after two or three hours' heating in an open tube. At about 150°, the crystals slowly intumesce and become opaque, basic salt being formed and also a little mercuric salt and a trace of chloride. Heated at 170° for some hours, its decomposition goes further; more mercuric salt is formed and a good quantity of chloride, as well as some chlorate (detected by decomposing with hydrochloric acid), whilst at 200° white fumes escape containing mercuric chloride. The more the salt is heated, the more basic it becomes, the redder and the larger is the residue left on treating it with water, and the less mercurous nitrate this residue yields when dissolved in nitric acid. Heated to 357° it suffers no further change, but at 444° decomposes slowly. The products are then the same as those found on heating the residue from the mercuric salt, but only very little free chlorine can be detected; metallic mercury does not occur among the products.

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