CLXXIV.—*The Oxidising and Reducing Properties of Sulphur Dioxide. Part I. Mercury Chlorides.*

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THAT sulphur dioxide can function either as an oxidising or a reducing agent has been shown in the case of certain chlorides, sulphates, and phosphates (T., 1920, **117**, 1093, 1241; this vol., p. 210). The concentration of the acid plays an important part in many of these reactions, for by varying the amount of acid present the sulphur dioxide can be made either to oxidise or to reduce.

The chlorides of mercury seem to afford an interesting case for investigation, for the fact that mercuric chloride is quantitatively reduced by sulphur dioxide to the mercurous salt only under very specific conditions has been noticed by investigators since the time of Vogel and Wohler. Sartorius (*Annalen*, 1855, **96**, 335) showed that the question of concentration of the initial mercuric chloride solution is of great importance in determining whether the yield of mercurous chloride shall be quantitative or not. He showed that when a solution of mercuric chloride (1 : 80), saturated with sulphur dioxide at 70—80°, is maintained at that temperature for a prolonged period, the yield of mercurous chloride is almost theoretical. This conclusion was confirmed by Bolley.

The most recent contribution to this subject was made by Sanders (*Z. angew. Chem.*, 1915, **28**, 9), who concluded that the oxidation of sulphur dioxide by mercuric chloride takes place in accordance with equation (iv). It was quantitative, however, only when the solution contained not more than two grams of sulphur dioxide per litre. With greater concentrations, the gas escaped unoxidised from the boiling solution.

Smythe and Wardlaw (*Proc. Durham Phil. Soc.*, 1914, **5**, 187) have shown that sulphur dioxide oxidises mercurous chloride quantitatively to the mercuric salt in accordance with the equation :

$$SO_2 + 4HCl + 2Hg_2Cl_2 = 4HgCl_2 + 2H_2O + S \quad . \quad . \quad (i)$$

Evidently the reactions of sulphur dioxide with mercury chlorides are of a diverse nature, and the following experiments were carried out with the object of further investigating the conditions for these reactions.

EXPERIMENTAL.

Reactions of Mercurous Chloride with Sulphur Dioxide.

The method used in studying the reaction quantitatively was as follows :

A definite weight of mercurous chloride was covered with a known volume of hydrochloric acid of varying concentration containing dissolved sulphur dioxide, the mercurous chloride being white at this stage of the experiment. The flask was immersed in an oil-bath maintained at a constant temperature of 95°, and a slow stream of sulphur dioxide was passed through the mixture for twelve hours. The residue was filtered on a Gooch crucible, washed with dilute hydrochloric acid and with water respectively, dried, and weighed. The preliminary washing with hydrochloric acid removed sulphur dioxide which would have otherwise reduced the calomel to mercury on washing with water. The contents of the crucible were then extracted with chloroform in a Soxhlet tube, the sulphur being recovered by evaporation of the chloroform and weighed.

TABLE I.

Weight of mercurous chloride = 2·9376 grams.
Duration of experiment = 12 hours.

Normality of hydrochloric acid.	Unchanged mercurous chloride. Grams.	Sulphur. Calc. Gram.	Sulphur. Found. Gram.	Remarks.
8·64	nil.	0·0998	0·0989	No darkening.
4·75	1·9040	0·0351	0·0363	,,
4·32	2·1408	0·0271	0·0293	,,
2·16	2·6862*	0·0085	0·0070	Slight darkening.
1·73	2·7674	0·0058	0·0045	Appreciable darkening.
1·44			nil.	Appreciable darkening and no sulphur.

* Duration, 7 hours.

The first point of note in connexion with these experiments is the fact that mercurous chloride remains white in the presence of sulphur dioxide and high concentrations of hydrochloric acid. Had the hydrochloric acid, initially employed, not contained sulphur dioxide, the acid alone would have decomposed the mercurous salt. Richards (*Z. physikal. Chem.*, 1897, **24**, 39) observed that mercurous chloride is appreciably decomposed into mercuric chloride and mercury in the presence of other chlorides, and Richards and Archibald (*ibid.*, 1902, **40**, 385) found that the system reaches a definite equilibrium and that the amount of mercuric chloride in the solution increases with increase in the chloride concentration, the increase being approximately proportional to the square of the concentration of the chlorine ions in the solution. If mercurous chloride is covered with sulphurous acid alone and warmed at 95°, darkening immediately occurs. Evidently, therefore, in our experiments with high concentrations of acid, the normal behaviour of the acid and sulphur dioxide respectively is in abeyance and the two substances act as an oxidising medium whereby mercuric chloride is formed and sulphur deposited, in accordance with equation (i).

With decrease in the acid concentration the oxidising action of the sulphur dioxide becomes less pronounced and darkening occurs, indicating decomposition of the mercurous salt. The fact that no sulphuric acid can be detected shows that the mercurous chloride decomposes solely as

$$Hg_2Cl_2 \rightleftharpoons Hg + HgCl_2 \quad . \quad . \quad . \quad . \quad . \quad (ii)$$

and that no reduction by the sulphur dioxide occurs. Reduction by sulphur dioxide could take place in two ways :

$$Hg_2Cl_2 + SO_2 + 2H_2O = 2Hg + 2HCl + H_2SO_4 \quad . \quad . \quad (iii)$$

$$2HgCl_2 + SO_2 + 2H_2O = Hg_2Cl_2 + 2HCl + H_2SO_4 \quad . \quad (iv)$$

In both cases sulphuric acid would be produced.

TABLE II.

Weight of mercurous chloride = 2·9376 grams.
Duration of experiment = 12 hours.

Normality of hydrochloric acid.	Remarks.
0·785 0·360	Slight darkening at the end of the experiment. Mercuric chloride was detected, but not sulphuric acid.
*0·108	Remained white.
0·072 0·052 0·036	Darkening just perceptible.
0	Immediate darkening. Sulphuric acid was produced in quantity.

With decrease in the concentration of the hydrochloric acid the amount of mercurous salt decomposed diminishes until it seems to reach a minimum (in the experiment denoted by the asterisk in Table II), and then increases again. The reason for this result in the experiment referred to will be dealt with later. It seems, however, well established that the reducing power of sulphur dioxide, so well-defined in aqueous solutions, is almost inoperative in the presence of very dilute hydrochloric acid. Further experiments amply confirmed this view, which, moreover, serves to explain some observations of earlier investigators. Vogel has stated that mercurous chloride is converted by sulphurous acid into a grey sub-chloride. Divers and Shimidzu (T., 1886, **49**, 557), however, state that they observed very slight decomposition to occur in the cold. They summarise their conclusions as follows :

"Ordinary calomel becomes a little greyish when suspended in a small quantity of water through which sulphur dioxide is passed . . . only traces of hydrochloric acid are found in the mother-liquor. We doubt whether there is any reaction at all between true mercurous chloride and sulphurous acid, for when mercurous chloride is precipitated by sulphurous acid itself, it is of dazzling whiteness." The last observation of Divers and Shimidzu, in view of our experiments, is not a satisfactory proof that mercurous chloride does not react with sulphurous acid. During its precipitation from the mercuric salt, hydrochloric and sulphuric acids would be produced, and as we have shown that a small quantity of acid inhibits the reducing effect of sulphurous acid, no reaction with the precipitated mercurous chloride would be expected. These experimental observations of Divers and Shimidzu, however, support the view that traces of hydrochloric acid have a very marked inhibiting effect on the reducing action of sulphur dioxide on mercurous chloride.

Reactions of Mercuric Chloride with Sulphur Dioxide.

It is well known that mercuric chloride in nearly boiling solution is converted by sulphur dioxide into mercurous chloride, hydrochloric and sulphuric acids. This reaction does not take place in the cold, but Divers and Shimidzu (*loc. cit.*) have shown that, even so, the two substances are not indifferent to one another. Mercuric chloride dissolves much more readily in aqueous solutions containing sulphur dioxide than in water alone. This increased solubility in sulphurous acid is not observed in the presence of much sulphuric acid. The above authors have explained the reduction of mercuric chloride as proceeding in stages. The first stage results in the intermediate formation of mercuric hydrogen sulphite (v). This undergoes partial hydrolysis in the presence of a small but sufficient quantity of acid into mercurosic sulphite (vi), which is decomposed by the hydrochloric acid (vii).

$$HgCl_2 + 2H_2SO_3 = Hg(HSO_3)_2 + 2HCl \quad . \quad . \quad . \quad . \quad (v)$$

$$3Hg(HSO_3)_2 + H_2O = Hg_3(SO_3)_2 + H_2SO_4 + 3H_2SO_3 \quad . \quad (vi)$$

$$Hg_3(SO_3)_2 + 4HCl = HgCl_2 + Hg_2Cl_2 + 2H_2SO_3 \quad . \quad . \quad (vii)$$

Divers and Shimidzu explain the limited reduction of mercuric chloride by sulphur dioxide as being due to the fact that in the course of the reduction so much sulphuric acid is formed that it prevents the remainder of the mercuric chloride from forming the essential intermediate mercuric hydrogen sulphite and thereby brings the reaction to a close. This represents one explanation of the facts first recorded by Sartorius and mentioned in the introduction to this communication. The influence of the hydrochloric acid liberated in the reduction, however, requires consideration in view of the small ionisation of mercuric chloride even in aqueous solution, and especially on account of the formation of complexes with this acid. Le Blanc and Noyes (*Z. physikal. Chem.*, 1890, **6**, 401) showed that the complex H_2HgCl_4 is formed from mercuric chloride and hydrochloric acid and that it is a strong acid dissociating to about the same extent as hydrochloric acid.

With the object of determining the influence of concentration of hydrochloric acid on the reduction of mercuric chloride by sulphur dioxide, the experiments recorded in Tables III and IV were carried out. Sulphur dioxide was passed for twelve hours through a solution of mercuric chloride in 120 c.c. of standard hydrochloric acid at 95°.

TABLE III.

Normality of hydrochloric acid = 0·48*N*.

Mercuric chloride. Grams.	Mercurous chloride produced. Grams.	Mercuric chloride. Grams.	Mercurous chloride produced. Grams.	Remarks.
5·1580	0·1058	1·0106	0·0070	Crystalline deposits of calomel were formed in every experiment and no darkening was observed.
2·9760	0·0278	0·3090	0·0020	
1·8968	0·0160			

TABLE IV.

Normality of hydrochloric acid = 2·64*N*.

Mercuric chloride. Grams.	Remarks.	Mercuric chloride. Grams.	Remarks.
9·8314	No precipitate at the end of the experiment	36·2810	Very minute deposit, thought to be sulphur.
14·7352	,,	46·3700	
25·7948	,,	62·8170	0·0437 gram of calomel produced.

With a definite concentration of acid, the yield of mercurous salt is dependent on the concentration of mercuric chloride present.

TABLE V.

In the undermentioned experiments two solutions, having either a constant acid or a constant mercuric chloride content (the values bracketed in the table), were subjected, concurrently, to the action of sulphur dioxide for a definite period, which differed in the various experiments.

Temperature = 95°.

Mercuric chloride. Grams.	Concentrated hydrochloric acid. C.c.	Water. C.c.	Mercurous chloride obtained. Grams.
3·3	5	115	0·0757
„	10	110	0·0063
3·3	6	114	0·0245
„	9·6	110·4	0·0090
6·6	4·8	115·2	0·4397
3·3	„	115·2	0·0870
6·6	4·8	115·2	0·2633
13·2	„	115·2	2·0852

These experiments confirm the idea that the amount of mercurous chloride deposited is dependent on the concentration of the acid itself and the initial concentration of the mercuric chloride. Debray (*Compt. rend.*, 1882, **94**, 1222) observed a similar behaviour of mercuric chloride in solutions of sodium chloride. This peculiarity of mercuric chloride in the presence of hydrochloric acid and alkali chlorides seems satisfactorily explained by the fact that mercuric chloride is only slightly ionised even in aqueous solution and that it forms complexes with hydrochloric acid and alkali chlorides. Before reduction of the mercuric chloride can occur, a certain concentration of free mercuric ions must be present. In hydrochloric acid of high concentration, no such mercuric ions will be formed. When mercuric chloride is taken up in the form of the complex, it will ionise mainly as $H_2HgCl_4 \rightleftharpoons 2H^{\cdot} + HgCl_4''$. Le Blanc and Noyes (*loc. cit.*) have shown that the actual hydrogen-ion concentration of hydrochloric acid is unaffected by addition of mercuric chloride. However, the concentration of the chlorine ion is affected by the formation of the complex, and as this is the important ion in determining the ionisation of the mercuric chloride into mercuric ions, it follows that a stage will be reached in the addition of the mercuric chloride to the acid when the chlorine-ion concentration will be sufficiently lowered to allow the necessary mercuric ion concentration to be present for reduction to proceed. Obviously, on this view, the conditions for reduction are, in agreement with the experimental results, dependent on the concentration of the acid and of the mercuric chloride.

The Quantitative Reduction of Mercuric Chloride.

Sulphur dioxide was passed for twelve hours into an aqueous solution (120 c.c.) at 95° containing the amount of mercuric chloride given in the first column in Table VI.

TABLE VI.

Mercuric chloride. Grams.	Mercurous chloride. Grams. Calc.	Mercurous chloride. Grams. Found.	Mercuric chloride. Grams.	Mercurous chloride. Grams. Calc.	Mercurous chloride. Grams. Found.
3·3791	2·9380	2·8862	2·6053	2·2650	2·2470
3·3000	2·8690	2·8236	2·5990	2·2600	2·2400

From the above figures it will be seen that the reduction is nearly quantitative when 2·6 grams of mercuric chloride are present under the special conditions of the experiment. Sartorius found that reduction was nearly quantitative at 70—80° in a solution containing 1 gram of mercuric chloride in 80 c.c. Sanders (*loc. cit.*), using boiling solutions, found that the reduction was quantitative only when not more than 2 grams of sulphur dioxide per litre were present. This corresponds with a reduction of 17 grams of mercuric chloride per litre. Our figure corresponds with 21·7 grams of mercuric chloride per litre reduced by sulphur dioxide. Reference to Table VI, however, indicates that reduction would only be complete in a somewhat lower concentration of mercuric salt. On Sanders's figure, the reduction results in the liberation of hydrochloric and sulphuric acids, the total concentration of which produces an acidity of 0·13*N*. Undoubtedly the production of a definite acidity brings the reaction to a close, for hydrochloric acid will react with the mercuric chloride to form complexes and un-ionised molecules.

To determine what effect approximately 0·13*N*- or less concentrated hydrochloric acid has on calomel, the following experiments were carried out.

TABLE VII.

The mercurous chloride was covered with 120 c.c. of the acid of strength specified in the first column, and sulphur dioxide was passed for varying periods, the temperature being 95°.

Normality of hydrochloric acid.	Remarks.
0·160	No darkening at the end of 20 hours.
0·020	Slightly grey at the end of 5 hours.
0·016	Dark at the end of 4 hours.
0·001	Distinctly black at the end of 4 hours.

These results serve to clarify those of Table II. Considering the results in Tables II and VII, it seems clearly established that in the reactions of mercurous chloride and sulphur dioxide in the presence of hydrochloric acid there is a definite stage of acid concentration where the calomel remains unaffected. The lower limit of this stage has been fixed by the experiments recorded in Table VI. The concentration of the hydrochloric acid liberated in the quantitative reduction of mercuric chloride was 0·065*N*; a similar concentration of sulphuric acid would also be liberated. With concentrations of acid ranging from this to about 0·02*N*, only very slight darkening was detected. With acid less concentrated than 0·02*N*, distinct reduction was noted, which became more pronounced as the acid reached zero concentration. This reduction takes place in accordance with equation (iii).

Above 0·065*N*-acid concentration, there is a range of acidity where the calomel is unaffected. Beyond this area, darkening occurs in accordance with equation (ii).

Reduction of Mercurous Chloride to Mercury.

To determine the acidity produced when mercurous chloride was quantitatively reduced to mercury by sulphur dioxide, calomel, covered with water, was subjected to the action of sulphur dioxide at 95° for twelve hours. It was found that the maximum amount of calomel that was quantitatively reduced to mercury under the conditions of the experiment was 0·2024 gram. The maximum amount of mercuric chloride (in 120 c.c. of water) that was reduced to mercury by sulphur dioxide under the same conditions was 0·154 gram. Calculating the acidity of the solutions produced by the reductions, it was found that the mercurous salt gave a 0·014*N*-acidity and the mercuric chloride a 0·019*N*-acidity. These results show a distinct agreement and seem to indicate that for complete reduction a very low acid concentration must be finally produced.

From these results it would seem that if an acidity of more than approximately 0·02*N* is developed in the reduction of the mercury chlorides, reduction to mercury will be incomplete. Reference to the various results obtained in the investigation of the influence of acid concentration on the reduction of calomel shows that only when the acidity was less than the above figure was appreciable darkening noted. Superficial darkening has been noticed in acid of higher concentration, but it may be due to experimental error and not to a definite reduction effect.

Summary.

The type of reaction that occurs when sulphur dioxide reacts at 95° with mercurous chloride in the presence of hydrochloric acid depends on the concentration of acid present.

Normality of hydrochloric acid.	Remarks.	Equation.
8—2	*Oxidation area.* Oxidation decreases with decreasing acid concentration.	(i)
2—0·16	*Decomposition area.* Darkening decreases with decrease in acid concentration.	(ii)
0·16—0·07	*Inert area.* Calomel unaffected.	
0·07—0·02	Minute reduction.	
0·02—zero	*Reduction area.* Reduction increases with decreased acid concentration.	(iii)

Quantitative reduction to mercurous chloride occurs when sulphur dioxide reacts for twelve hours at 95° with approximately 2·6 grams of mercuric chloride in 120 c.c. of water. Above this concentration of mercuric chloride, incomplete reduction occurs. The amount of reduction of mercuric chloride to mercurous chloride depends on the concentration of hydrochloric acid present and the initial concentration of mercuric chloride.

The small degree of ionisation of mercuric chloride in aqueous solution, and the fact that it forms complexes with hydrochloric acid, have an important bearing on the above reactions.

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