LXIV.—*The Reaction between Iodine and Sulphurous Acid.*

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IT is stated in most text-books of analytical chemistry that in the estimation of sulphurous acid by means of iodine correct results are obtained only when the sulphurous acid has been added to the iodine; and that when iodine solution has been added to sulphurous acid the results are invariably low.

The following experiments were undertaken with the object of forming a decision in respect of the several explanations that have been given of this phenomenon, and of determining whether the complex formed between sulphur dioxide and hydrogen iodide (Péchard, *Compt. rend.*, 1900, **130**, 1188) has any influence on the reaction.

EXPERIMENTAL.

The solutions of sulphurous acid employed were prepared by passing sulphur dioxide from a siphon into air-free water until the solutions were of the desired strength.

In the titrations, stoppered bottles were employed; and when the reaction was almost complete, the stopper was inserted, and the bottle shaken.

Since the concentration of the sulphurous acid solution quickly decreased on keeping, only the experiments performed at the same time gave comparable results. These are recorded in the same horizontal line in Table I.

TABLE I.

Exp.	C.c. of *N*/10-iodine.	C.c. of H_2SO_3 required.	Conc. of SO_2. Grams per litre.	C.c. of H_2SO_3.	C.c. of *N*/10-iodine required.	Conc. of SO_2. Grams per litre.
1	10	19·00	1·673	20	9·95	1·581
2	,,	20·50	1·551	,,	9·75	1·550
3				,,	26·30	
4				,,	,,	
5	20	21·00	3·080	,,	19·05	3·081
6	,,	14·90	4·320	,,	26·80	4·313
7	,,	15·00	4·291	,,	26·45	4·258
8	,,	14·95	4·293	,,	26·70	4·296
9	,,	,,	,,	,,	,,	,,

Results similar to that of experiment 2 were frequently obtained, especially when the iodine solution was added quickly. When stronger solutions of sulphurous acid than the above were employed, concordant results were not obtained, addition of the iodine solution to the sulphurous acid invariably giving lower values than those obtained by inverting the order of the addition.

When the sulphurous acid was approximately *N*/5 or stronger, a yellow coloration was produced on adding *N*/10-iodine. This coloration was due, not to free iodine (Péchard, *loc. cit.*; compare also Fox, *Z. physikal. Chem.*, 1902, **41**, 458), but to the formation of the compound SO_2,HI. On adding more iodine, the colour deepened up to a point, and then became paler again, the solution being colourless when the titration was nearly completed. Thus it would appear that the compound SO_2,HI did not interfere with the reaction, the sulphurous acid being oxidised by the iodine in the usual way. When more sulphurous acid was added to the liquid, the yellow coloration again developed. The solution was then kept for twenty-four hours, but no separation of sulphur took place. The yellow colour deepened on the addition of hydriodic acid, but sulphur was not deposited. This disproves Volhard's theory (*Annalen*, 1888, **242**, 93) of the reduction of sulphurous acid to sulphur in solutions up to about *N*/5.

Experiments 3 and 4 were performed under comparable conditions in an atmosphere of carbon dioxide; in the former, 5 c.c. of hydriodic acid were added before titrating.

A solution of sulphur dioxide in air-free water was stored in a bottle filled with carbon dioxide, oil being placed on the surface of the liquid to prevent loss of sulphur dioxide by evaporation. An atmosphere of carbon dioxide was maintained in the bottle, and in the burette, with which the bottle was connected. An attachment was made to the nozzle of the burette, so that the sulphurous acid was delivered at the bottom of the receiving vessel. Titrations performed in an atmosphere of carbon dioxide gave the results recorded in experiment 5. The erratic results often obtained under other experimental conditions would therefore appear to be due either to loss of sulphur dioxide by evaporation or to oxidation of sulphurous acid by air.

These suppositions were tested by means of titrations made with (experiment 6) and without (experiment 7) the burette attachment; in both cases the bottles were filled with carbon dioxide. In experiment 7 the results differed by approximately 1 per cent., and were lower than those obtained in experiment 6, which agreed within the limits of experimental error. Thus it would appear that the loss of sulphur dioxide by evaporation is appreciable.

The titrations were repeated, the bottles being filled with air. The burette attachment was employed (experiment 8).

At the same time, the experiments were repeated, the bottles being first filled with carbon dioxide (experiment 9).

From these results it is apparent that the erratic and low results obtained by titrating sulphurous acid with iodine are due wholly to loss of sulphur dioxide by evaporation. It was also observed that the stronger the sulphurous acid, the greater was the difference between the results of the two methods of titration; and the more quickly the iodine was added, the smaller was the difference.

In many cases the titration of sulphurous acid with iodine appeared to be finished, the yellow colour (due to free iodine) persisting when the bottle was merely rotated. On inserting the stopper, however, and shaking the bottle, the colour disappeared, and an appreciable amount of iodine solution had still to be added before the oxidation of the sulphurous acid was completed. This showed the presence of an appreciable quantity of sulphur dioxide in the space above the liquid in the bottle.

The foregoing experiments were repeated with sulphurous acid of different strengths; the values given above are typical results.

Sodium Sulphite Solution.

When iodine solution is added to sodium sulphite solution, lower results are obtained than in the reverse process. In this case the lowness of the results appears to be due to oxidation of sodium sulphite by air. This was demonstrated by performing the titrations in an atmosphere of (1) air, (2) carbon dioxide.

In the former case the result obtained by adding the iodine solution to the sodium sulphite solution was lower than that obtained by adding the sodium sulphite to the iodine.

In case (2) similar results were obtained by both methods, and they agreed with those obtained by titrating iodine solution (acidified with hydrochloric acid) with sodium sulphite solution; and also with those obtained by an indirect titration.

In the following experiments the sodium sulphite solution was prepared by dissolving crystallised sodium sulphite in air-free water and storing the solution in a bottle connected with a two-way burette; an atmosphere of carbon dioxide was maintained in the bottle and in the burette.

1. *In an atmosphere of air.*

(*a*) 22·45 C.c. of sodium sulphite required 21·55 c.c. of *N*/10-iodine. Concentration of Na_2SO_3 = 6·049 grams per litre.

(*b*) 20·20 C.c. of *N*/10-iodine required 20·85 c.c. of sodium sulphite. Concentration of Na_2SO_3 = 6·105 grams per litre.

(*c*) 19·05 C.c. of *N*/10-iodine + 16·77 c.c. of sodium sulphite required 2·85 c.c. of *N*/10-thiosulphate. Concentration of Na_2SO_3 = 6·088 grams per litre.

(*d*) 15·96 C.c. of *N*/10-iodine + 14·80 c.c. of sodium sulphite + 1 gram of sodium hydrogen carbonate, titrated immediately, required 1·63 c.c. of *N*/10-thiosulphate. Concentration of Na_2SO_3 = 6·101 grams per litre.

(*e*) 16·10 C.c. of *N*/10-iodine + 16·20 c.c. of sodium sulphite + 1 gram of sodium hydrogen carbonate, titrated after fifteen minutes, required 0·43 c.c. of *N*/10-thiosulphate. Concentration of Na_2SO_3 = 6·096 grams per litre.

2. *In an atmosphere of carbon dioxide.*

(*a*) 22·10 C.c. of sodium sulphite required 21·42 c.c. of *N*/10-iodine. Concentration of Na_2SO_3 = 6·108 grams per litre.

(*b*) 21·25 C.c. of *N*/10-iodine required 21·95 c.c. of sodium sulphite. Concentration of Na_2SO_3 = 6·101 grams per litre.

Results 1 (*d*) and (*e*) differ from those of Rupp (*Ber.*, 1902, **35**, 3694), who states that keeping of the solution for fifteen minutes is necessary for the complete oxidation of sodium sulphite in the presence of sodium hydrogen carbonate, as the rate of oxidation of sodium sulphite is slower than that of sulphurous acid, or free sulphur dioxide. This is contrary to experience, sulphur dioxide being more easily oxidised in presence of alkali (Raschig, *Z. angew. Chem.*, 1904, **17**, 577). Addition of sodium hydrogen carbonate also seems unnecessary, since the reaction $Na_2SO_3 + I_2 + H_2O = Na_2SO_4 + 2HI$ is not reversible.

Conclusions.

Sulphurous acid is quantitatively oxidised to sulphuric acid by *N*/10-iodine, without the separation of sulphur. The intermediate formation of the yellow compound, SO_2,HI, which occurs in solutions of moderate concentration, has no influence on the final result.

The low results obtained when sulphurous acid is exposed to the air during the titration are due entirely to evaporation of sulphur dioxide, the amount of atmospheric oxidation being negligible.

Sodium sulphite solution is more readily oxidised than sulphurous acid; consequently atmospheric oxidation is a disturbing factor when sodium sulphite solution is titrated with iodine. Since the reaction between sulphurous acid and iodine is not reversed under the state of dilution obtaining in volumetric analysis, the addition of sodium hydrogen carbonate to neutralise hydriodic acid, as when solutions of arsenious compounds are being titrated, is unnecessary; and since a sulphite solution is so quickly oxidised, it is not necessary to allow a time interval for such oxidation by iodine to be completed.

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