215. *The Reduction of Nitrosylsulphuric Acid by Sulphur Monoxide.*

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Further work bearing on the reduction of nitrosylsulphuric acid by sulphur monoxide (cf. Wilkins and Soper, J., **1939**, 600) has shown that liberation of nitrogen is not due to reduction of nitric oxide, or to the intermediate formation of hydrazine or hydroxylamine. It has been found that nitrogen peroxide is reduced, though not irreversibly, by sulphur monoxide. The possibility of effecting the irreversible reduction of nitrosylsulphuric acid by sulphur compounds other than sulphur monoxide has been examined.

THE reducing action of sulphur monoxide on a nitrite dissolved in sulphuric acid (nitrosylsulphuric acid) was investigated by Wilkins and Soper (*loc. cit.*) and nitrogen was isolated as a product of the reduction. In a continuation of this work, an attempt was made to elucidate the mechanism of the reduction, and although this object was not realised, certain results are recorded, as the work cannot yet be completed.

The sulphur dioxide, with which the sulphur monoxide used was mixed, reduced the nitrosylsulphuric acid to the violet hydroxynitrosylsulphuric acid, which rapidly decomposed with the evolution of nitric oxide, so it was possible that a reaction had been occurring between sulphur monoxide and nitric oxide. Schenk (*Z. anorg. Chem.*, 1937, **233**, 385) has, however, reported that nitric oxide is unattacked by sulphur monoxide, and this is confirmed by the present observations. When sulphur monoxide and nitric oxide were kept in a dry bulb the latter could always be recovered within the limits of experimental error (Table I); hence no reduction to nitrogen had occurred in these circumstances.

The possible intermediate formation of hydrazine or hydroxylamine in the reduction of nitrosylsulphuric acid by sulphur monoxide has been examined, but experiments show that these substances are not intermediates because they both react with nitrosylsulphuric

TABLE I.

NO admitted, g.	NO recovered, g.	NO lost, g.	SO admitted, g.	Time of standing.
0·0253	0·0242	0·0011	(SO_2 only)	30 mins.
0·0154	0·0146	0·0008	(SO_2 only)	40 ,,
0·0188	0·0168	0·0020	0·045	50 ,,
0·0198	0·0184	0·0014	0·062	60 ,,
0·0138	0·0126	0·0012	0·038	13 hrs.
0·0276	0·0241	0·0035	(SO_2 only)	16 ,,
0·0236	0·0212	0·0024	0·061	16 ,,

acid giving nitrous oxide as well as nitrogen, and no nitrous oxide could be detected in the reduction of nitrosylsulphuric acid with sulphur monoxide.

In view of the interesting nature of this reduction to nitrogen, other reductions involving sulphur monoxide or nitrosylsulphuric acid were examined. Nitrogen peroxide was not irreversibly reduced by sulphur monoxide, though the latter had been largely destroyed after 2 hours' contact with the peroxide (Table II). Since nitrogen peroxide is reduced (though only slowly under the experimental conditions) by the sulphur dioxide with which the sulphur monoxide was mixed, the results do not show any relationship between the weight of sulphur monoxide destroyed and the weight of nitrogen peroxide introduced.

TABLE II.

SO admitted, g.	SO recovered, g.	SO lost, g.	NO_2 admitted, g.	Time of standing, hrs.
0·050	0·013	0·037	0·070	3
0·040	0·014	0·026	0·034	3
0·035	0·012	0·023	0·057	2¼
0·036	0·019	0·017	0·034	2

Experiments on the reducing action of sulphur compounds other than sulphur monoxide on nitrosylsulphuric acid indicated that neither sodium thiosulphate nor sodium tetrathionate carried the reduction below nitric oxide. Hydrogen sulphide and sodium hyposulphite each effected a small irreversible reduction accompanied by the formation of ammonia; although the former produced only a trace of ammonia, the latter reduced as much as 4% of the nitrogen to ammonia, but even so, the powerful reducing action of the hyposulphite ion was probably much limited by its decomposition by acid. Had sulphur monoxide been liberated by the action of acid on the salts used (cf. Foerster and Umbach, *Z. anorg. Chem.*, 1934, **217**, 175) a much greater irreversible reduction of the nitrosylsulphuric acid would have been expected because a considerable excess of reducing agent was used. The results also exclude the possibility that a decomposition of sulphur monoxide by water to yield hydrogen sulphide, sulphur dioxide, and thiosulphuric acid precedes the reaction with nitrosylsulphuric acid.

EXPERIMENTAL.

Reaction of Hydrazine and Hydroxylamine Sulphates with Nitrosylsulphuric Acid.—The reactants were contained in the limbs of a small inverted V-tube. Each limb carried a side arm so that the air could be swept out by a stream of sulphur dioxide. By tilting the tube the reactants were brought together, and the gases evolved were collected over mercury by sweeping out with more sulphur dioxide, which was then removed by a little concentrated alkali. Results of analyses of the sample to determine the relative proportions of nitrogen and nitrous oxide are given in Table III. In all experiments a considerable excess of nitrosylsulphuric acid was used.

TABLE III.

	Hydrazine sulphate.					Hydroxylamine sulphate.	
N_2, c.c.	2·80	2·27	2·20	3·04	N_2, c.c.	1·61	2·24
N_2O, c.c.	2·82	1·93	1·97	2·83	N_2O, c.c.	3·39	4·15

The fact that equal volumes of nitrogen and nitrous oxide are evolved from the reaction with hydrazine sulphate suggests that the Thiele reaction $N_2H_4 + 2HNO_2 = N_2 + N_2O + 3H_2O$ has taken place. This is usual in strongly acid solutions where an excess of nitrous acid is available. On the other hand, the ordinary reaction between nitrous acid and hydroxylamine, which yields nitrous oxide alone, has been disturbed by the particular experimental conditions here prevailing.

Action of Sulphur Monoxide on Nitric Oxide and Nitrogen Peroxide.—Two 5-l. bulbs were filled simultaneously with the mixture of sulphur monoxide and dioxide. One of them was an analysis bulb for determining the weight of sulphur monoxide available. Into the other, a reaction bulb, there was introduced a measured volume of dry nitric oxide from a gas burette. After the gases had remained together for the necessary time, air was admitted and alkaline peroxide run in from a tap funnel to recover unchanged nitric oxide. Since nitrogen peroxide cannot be manipulated over mercury, in those experiments where this gas was used, equivalent volumes of dry nitric oxide and oxygen were introduced, first into a small combination tube and then into the reaction bulb containing sulphur monoxide and dioxide. The combination tube was necessary because nitric oxide and oxygen combine but slowly at the low pressure used (40 mm.). In the experiments of Table II the procedure was similar except that 5N-alkali was run into both bulbs simultaneously, to absorb the sulphur monoxide remaining. The weight of sulphur monoxide present was calculated from the sulphide titre only. That the presence of the nitrogen oxides did not interfere either with the absorption of the sulphur monoxide by alkali or with the sulphide analysis was shown by a control experiment in which alkali was run into both bulbs immediately after the introduction of the nitric oxide; the sulphide titres were identical.

Action of Reducing Agents on Nitrosylsulphuric Acid.—The nitrosylsulphuric acid was run from a tap funnel on to 2—3 g. of the solid salts contained in an evacuated vessel, and the oxides of nitrogen evolved were retained according to the method previously described. In the case of hydrogen sulphide, the gas was passed through the acid. When a reaction was complete the acid in the reaction tube was neutralised by running in excess dilute alkaline peroxide, and the nitrate remaining therein was usually determined separately (by means of Devarda's alloy) from that which had collected in the absorbing vessels. In Table IV the nitrogen is calculated as NaNO$_2$.

TABLE IV.

Reducing agent.	Initial NaNO$_2$, g.	NaNO$_2$ left, g.	NaNO$_2$ carried over, g.	Total NaNO$_2$ recovered, g.	NaNO$_2$ lost, g.
Sodium sulphite (control) ...	0·2734	0·0067	0·2643	0·2710	0·0024
Sodium thiosulphate	0·2734	0·0082	0·2616	0·2698	0·0036
Hydrogen sulphide	0·2734	0·0192	0·2359	0·2551	0·0183
Hydrogen sulphide	0·2734	0·0157	0·2413	0·2570	0·0164
Sodium hyposulphite	0·2734	0·0157	0·2443	0·2600	0·0134
Sodium hyposulphite	0·2734	—	—	0·2567	0·0167
Sodium hyposulphite	0·2734	—	—	0·2565	0·0169
Sodium sulphite (control) ...	0·2734	—	—	0·2712	0·0022
Sodium hyposulphite	0·2734	—	—	0·2586	0·0148
Sodium tetrathionate	0·2734	0·0112	0·2618	0·2730	0·0004
Sodium tetrathionate	0·2734	0·0189	0·2520	0·2709	0·0025

It is seen that, within the limits of experimental error, the nitrite is completely recoverable after reaction with tetrathionate or thiosulphate. On the other hand, with hyposulphite or hydrogen sulphide, the nitrosylsulphuric acid suffers a small but definite reduction to some stage lower than nitric oxide as well as the above-mentioned reduction to ammonia, which (owing to the analytical method employed) does not manifest itself as a loss of sodium nitrite in the table.

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