CLXXX.—*The Decomposition of Hyponitrous Acid in Presence of Mineral Acids.*

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Hyponitrous acid has been isolated by Hantzsch and Kaufmann, who have also described some of its important properties and its decomposition products (*Annalen*, 1896, **292**, 317). In continuation of our work on the decomposition of silver and mercurous hyponitrites we have recently studied the action of mineral acids on these salts at the ordinary temperature, namely, 25—29°. It will be shown that the hyponitrous acid which is set free decomposes simultaneously according to the two equations:

$$2HNO = H_2O + N_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$5HNO = 2H_2O + HNO_3 + 2N_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Silver Hyponitrite and Nitric, Hydrochloric, and Sulphuric Acids.

Method of Experiment.—In order to avoid unnecessary repetition the details of experiments will be given here once for all. The substance was weighed in a tube, and another tube, much narrower in diameter, and containing from 1 to 2 c.c. of dilute nitric acid, was placed in it. The apparatus, after exhaustion by means of a Sprengel pump, was gently tilted so as to bring the salt and the acid into contact with each other. Brisk effervescence at once set in. The gaseous product which was found to be free from nitric oxide was analysed in the following manner. It was repeatedly shaken up with tap water,* changing the water if necessary, until no more absorption took place. The remaining gas which was unaffected by alkaline pyrogallate was taken to be nitrogen. The residue in the tube did not respond to Nessler's or Fehling's solution and was thus absolutely free from ammonia and hydroxylamine. It was also found to be free from nitrite. The amount of nitrate in it was estimated by making it up to a given volume and treating an aliquot portion by the Crum-Frankland method. An example will make the point clear. Let us assume that the first reaction which set free hyponitrous acid was according to the equation:

$$5AgNO + 5HNO_3 = 5AgNO_3 + 5HNO \quad . \quad . \quad . \quad (1)$$

and that the second reaction which gave rise *de novo* to nitric acid was that conforming to:

$$5HNO = HNO_3 + 2H_2O + 2N_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

In the experiment in question 1 c.c. of dilute nitric acid was used. As a blank test, 1 c.c. of this acid was made up to 20 c.c., of which 1 c.c. again gave 3·9 c.c. of nitric oxide. The residual product was also made up to the same bulk (20 c.c.) and 1 c.c. of it yielded 4·1 c.c. of nitric oxide. The difference was 0·2 c.c. of nitric oxide. Now (20 × 0·2) c.c. or 4 c.c. was the total amount of nitric oxide and half of it, namely, 2 c.c., as nitrogen, represented the nitric acid generated according to the equation (2). The free nitrogen which was measured according to the process described above was actually found to be

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* That is, with water saturated with respect to nitrogen at the ordinary temperature and pressure. By blank experiments we have satisfied ourselves that it is a fairly trustworthy method of estimating the proportion of nitrous oxide and nitrogen in a mixture of the two gases.

8·2 c.c. at the same temperature and pressure; hence the ratio of nitrogen in nitric acid to nitrogen in the free condition was as 1 : 4. When sulphuric or hydrochloric acid was used no blank experiment was, of course, necessary.*

Decomposition of Silver Hyponitrite.

(*a*) *With nitric acid* (1 c.c. = 0·179 gram of HNO_3).

Expt. I.—0·1764 gave 11·5 c.c. N as such, 2·88 c.c. N as HNO_3, and 2·0 c.c. N_2O;† $t = 25°$; $p = 760$ mm.

Expt. II.—0·1016 gave 6·1 c.c. N as such, 1·5 c.c. N as HNO_3, and 1·9 c.c. N_2O; $t = 25°$; $p = 760$ mm.

Expt. III.—0·1218 gave 8·2 c.c. N as such, 2·05 c.c. N as HNO_3, and 1·3 c.c. N_2O; $t = 27°$; $p = 760$ mm.

(*b*) *With hydrochloric acid* (1 c.c. = 0·153 gram of HCl).

Expt. I.—0·2144 gave 13·4 c.c. N as such, 3·4 c.c. N as HNO_3, and 3·1 c.c. N_2O; $t = 26°$; $p = 760$ mm.

(*c*) *With sulphuric acid* (1 c.c. = 0·366 gram of H_2SO_4).

Expt. I.—0·17 gave 5·2 c.c. N as such, 1·3 c.c. N as HNO_3, and 8·7 c.c. N_2O; $t = 27°$; $p = 760$ mm.

Expt. II.—0·115 gave 4·8 c.c. N as such, 1·2 c.c. N as HNO_3, and 4·9 c.c. N_2O; $t = 31°$; $p = 760$ mm.

The results of these experiments are tabulated below; the figures denote percentages:

No. of expt.	N as such.	N as HNO_3.	N as N_2O.	Total N found.	Total N (theory).
(*a*). With nitric acid:					
I.	7·25	1·81	1·26	10·32	10·14
II.	6·72	1·65	2·09	10·46	,,
III.	7·45	1·86	1·18	10·49	,,
(*b*). With hydrochloric acid:					
I.	6·95	1·74	1·61	10·30	10·14
(*c*). With sulphuric acid:					
I.	3·39	0·85	5·70	9·94	10·14
II.	4·52	1·13	4·58	10·23	,,

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* It may be noted here that as the Crum-Frankland method is not satisfactory in presence of a chloride the nitric acid in this case was tested by Pelouze's method.

† The gases were always measured in the moist state.

Mercurous Hyponitrite and Nitric, Sulphuric, and Hydrochloric Acids

The method of experiment was the same as described before, and no further prefatory remarks are called for. The only point to bear in mind is that a solution of mercurous hyponitrite in dilute nitric acid undergoes slow dissociation; thus: $Hg_2(NO)_2 = Hg + Hg(NO)_2$. As the acid was very dilute and as the reaction was completed in a few minutes there was no appreciable disturbance due to secondary reaction, namely, interaction between metallic mercury and excess of free nitric acid.

Decomposition of Mercurous Hyponitrite.

(*a*) *With nitric acid.*

Expt. I.—0·197 gave 6·3 c.c. N as such, 1·58 c.c. N as HNO_3, and 1·0 c.c. N_2O; $t = 28°$; $p = 760$ mm.

(*b*) *With hydrochloric acid.*

Expt. I.—0·115 gave 4·0 c.c. N as such, 1·0 c.c. N as HNO_3, and 1·6 c.c. N_2O; $t = 31°$; $p = 760$ mm.

Expt. II.—0·25 gave 9·3 c.c. N as such, 2·33 c.c. N as HNO_3, and 2·4 c.c. N_2O; $t = 30°$; $p = 760$ mm.

(*c*) *With sulphuric acid.*

Expt. I.—0·1955 gave 2·8 c.c. N as such, 0·7 c.c. N as HNO_3, and 5·2 c.c. N_2O; $t = 25°$; $p = 760$ mm.

The results are presented below in percentages in a tabulated form:

No. of expt.	N as such.	N as HNO_3.	N as N_2O.	Total N found.	Total N (theory).
(*a*). With nitric acid:					
I.	3·55	0·89	0·56	5·0	6·09
(*b*). With hydrochloric acid:					
I.	3·76	0·94	1·51	6·21	6·09
II.	4·05	1·01	1·05	6·11	,,
(*c*). With sulphuric acid:					
I.	1·60	0·4	2·98	4·98	6·09

NOTE.—The preparation and analysis of the samples of salts made use of in the experiments recorded in the above tables have been given at length in the previous memoirs on "Mercurous Hyponitrite" and "The Decomposition of Mercurous and Silver Hyponitrites by Heat" (this vol., pp. 1404, 1399).

Discussion of Results.

It will be seen that silver hyponitrite by reaction with the three mineral acids gives almost the theoretical yield of hyponitrous acid, which again breaks up into nitrous oxide, nitrogen, and nitric acid. According to Hantzsch and Kaufmann, ammonia and nitrous acid are among the decomposition products of hyponitrous acid, but under certain conditions they failed to detect either of these, obtaining instead traces of nitric acid, as, for instance, when they allowed hyponitrous acid to remain for twenty-four hours in contact with a few drops of hydrochloric acid. As these chemists contented themselves with proving, merely qualitatively, the existence of nitric acid, they erroneously concluded that it was derived from the oxidation of nitrous acid.* In fact, the following three sets of reactions are strictly comparable:

$$5HNO = HNO_3 + 2N_2 + 2H_2O,\dagger$$
$$3KClO = KClO_3 + 2KCl,$$
$$2H_3PO_2 = H_3PO_4 + PH_3.$$

When chlorine is passed into a hot concentrated solution of potassium hydroxide, the hypochlorite which may be taken to be potentially formed at once passes into compounds which are stable under the existing conditions. Hypophosphorous acid, again, is only stable at a low temperature; on being heated it gives rise to phosphoric acid and phosphine. In these two instances the oxidation does not stop short at the intermediate stage of chlorite or phosphite.

One remarkable feature is the behaviour of sulphuric acid, which invariably ensures a larger yield of nitrous oxide. It is evident that the presence of mineral acids has a specific directive influence in determining the course which the reaction follows.

As regards mercurous hyponitrite, the mechanism of the reaction is substantially the same as with its silver analogue. It is noteworthy, however, that the decomposition of this salt by means of sulphuric and nitric acids is never complete. In other words, silver hyponitrite is decomposed with equal readiness by both the oxygen and haloid acids, but the mercurous salt only by the latter.

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* "Sondern Salpetersäure (durch Oxydation der Salpetrigen Säure entstanden)," *loc. cit.*, 333.

† Thum has shown that an aqueous solution of hyponitrous acid is directly oxidised to nitric acid by means of potassium permanganate. The three instances cited above are, however, those of autoxidation and reduction.