CCCXLVI.—*The Reaction between Nitrous Acid and Hydrogen Sulphide.*

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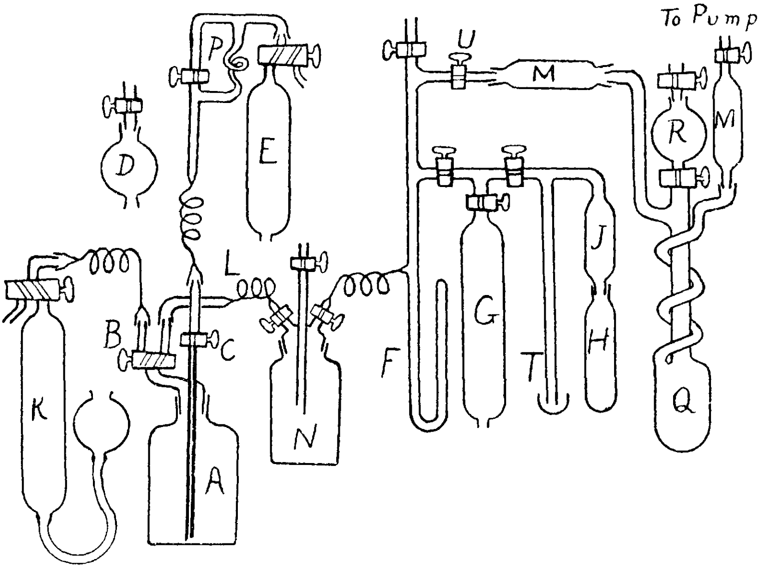
THE precise nature of the products of reaction between nitrous acid and hydrogen sulphide solutions has not been well defined. Divers (J., 1887, **51**, 48) found ammonia and oxides of nitrogen but no hydroxylamine when a mixture of alkali nitrite and sulphide was acidified. By reaction between hydrogen sulphide and the less soluble nitrites (such as that of silver), he obtained some hydroxylamine, an intermediate silver compound being postulated to account for its formation. A simpler explanation of this reaction is now offered.

FIG. 1.



In the course of the present work the concentration of the solutions was found to have a pronounced effect on the nature of the products, and hydroxylamine was formed under certain conditions.

EXPERIMENTAL.

In order to study the effect of very dilute nitrous acid and at the same time to obtain sufficient product for examination, an apparatus (Fig. 1) was constructed to allow of the slow passage of measured volumes of nitric oxide into a vessel containing hydrogen sulphide solution and oxygen. The reaction vessel, *A*, of 450 c.c. capacity, was suspended on a stirrup in a thermostat at 30°, and a rocking motion was imparted to it by means of an arm projecting vertically from the stirrup and connected with a pin on a motor-driven pulley. A ground cap carried a two-way tap, *B*, for exhaustion or for admission of oxygen and hydrogen sulphide. A single-way tap, *C*, on a tube projecting into the vessel served to admit solutions or nitric oxide as required. The tube reached the bottom of the vessel for solutions, but was cut off above the liquid level for admission of nitric oxide. Connexions for transference of gases were made by flexible glass spirals with ground joints. Solutions were admitted to *A* from *D* which fitted to a double grinding on *C*.

One arm of the tap *B* led to a manometer, *F*, and a T-piece connecting with a Toepler pump and a system for generating and storing oxygen. The hard-glass tube, *H*, connected by a ground joint, contained potassium permanganate from which oxygen was generated by heat after exhaustion of the system with the mercury pump. The oxygen passed through a soda–lime tube, *J*, and was collected in the graduated holder, *G*, by displacement of mercury, the first portion generated being rejected through the mercury trap, *T*.

Nitric oxide was prepared by dropping concentrated sodium nitrite solution into a sulphuric acid solution of ferrous sulphate. The gas was passed through concentrated sodium hydroxide solution and then over solid hydroxide before collection in the graduated vessel, *E*. Glass connexions with ground joints were used. The generating apparatus was exhausted through the three-way tap on *E* and filled with nitric oxide several times before the collection of gas. The nitrite solution in the dropping funnel was exhausted to remove dissolved air.

Hydrogen sulphide was prepared by saturating magnesium hydroxide suspension in water with the gas obtained from ferrous sulphide, exhausting the solution to remove dissolved gases and then displacing the hydrogen sulphide by heat. The gas after passage through phosphoric oxide was condensed by liquid air, the container then being attached to the graduated reservoir, *K*, by a short, mercury-sealed, rubber joint, and the air removed from the container by a Geryk pump through the two-way tap. About one-quarter of the hydrogen sulphide was allowed to boil off through a mercury trap, and the gas was then collected in *K* by mercury displacement, leaving a considerable portion of residual liquid.

In carrying out an experiment, the vessel *A* was given a preliminary exhaustion by a Geryk pump through all the taps to free the barrels from air. The connecting spiral, *L*, was then fitted, and the vessel *A* and the connecting leads to the oxygen reservoir exhausted by the mercury pump; 50 c.c. of water or *N*/20-hydrochloric acid solution, previously freed from air by exhaustion in *D*, were run into *A*. Any trace of dissolved gas was carried over by the flow of water vapour to the phosphoric oxide tubes, *MM*, attached to the mercury pump. The tap *B* was then closed, and the pentoxide tubes allowed to absorb the water vapour in the connecting tubes. A measured volume of hydrogen sulphide was introduced from *K* through a spiral which had been freed from air by several alternate exhaustions and fillings with the gas. Nitrous acid solutions were prepared and introduced by mixing in *D* under paraffin oil (Taylor, Wignall, and Cowley, J., 1927, 1923) measured volumes of *N*/2-sodium nitrite and hydrochloric acid solutions, previously freed from air by exhaustion. For nitric oxide reactions, the tap *U* was closed, and the connecting leads and manometer filled with oxygen from *G*, a measured volume of about 140 c.c. being finally introduced into *A*. A measured volume (about 40 c.c.) of nitric oxide was introduced through *C* from *E* through a spiral connexion attached by the double grinding on *C*, and freed from air in the same manner as the hydrogen sulphide connexion. The capillary spiral, *P*, controlling the rate of flow of nitric oxide, was short-circuited by a tap for exhaustion of the leading tube, this tap being closed before gas flow started. The spiral used required $\frac{1}{2}$ hour for the passage of the 40 c.c. of nitric oxide used for a run. The reaction vessel was kept shaken during the admission of the gas.

Tests with measured volumes of nitric oxide in the absence of hydrogen sulphide, dilute alkali solution being used as absorbent, showed that the nitric oxide was practically all converted to nitrous acid under the experimental conditions (see p. 2642). During an actual experiment, the nitrous acid, being continually removed by reaction with hydrogen sulphide, would not attain appreciable concentration. For determination of the nature of the products with appreciable concentrations of nitrous acid, solutions of this substance were run into the same apparatus in the absence of oxygen.

Analysis of Products of Reaction.—(a) *Gases.* Gaseous products were collected through the mercury pump, and the procedure varied according as nitric oxide or hydrogen sulphide was absent: in most of the runs they were not present together. (1) When nitric oxide was absent, nitrous oxide and excess of hydrogen sulphide were condensed in the receiver, *Q*, by liquid air, nitrogen and oxygen being collected at the pump. Nitrogen was estimated by removal of oxygen with phosphorus or pyrogallol. Hydrogen sulphide in *Q* was absorbed by running in alkali solution previously rendered air-free in *R*, the taps on *MM* being closed until absorption was complete. The nitrous oxide was then collected through the pump, being identified by non-absorption in a small volume of alkaline pyrogallol, the re-kindling of a glowing splint, and combustion with hydrogen. (2) In the experiments with nitrous acid in excess of the hydrogen sulphide, the products were nitric and nitrous oxides. The former was estimated by careful addition of small volumes of pure oxygen over a small volume of alkali solution, the final excess of oxygen being removed by pyrogallol, and the residual nitrous oxide was confirmed by explosion with hydrogen. In the cases described, products remaining in solution could be determined after removal of gaseous products. (3) In reactions with nitrous acid solution and excess of hydrogen sulphide, the gaseous products contained this excess together with nitric and nitrous oxides. Alkali absorption of the hydrogen sulphide was not applicable in this case owing to reaction between the alkali sulphide and nitric oxide, and removal was effected by cupric chloride solution, blank tests having shown that a satisfactory separation was effected (see p. 2642). For solutions with excess of hydrochloric acid, the cupric chloride was added direct to the reaction vessel, a separate run being made for determination of products in solution. For reactions in absence of excess of hydrochloric acid, where residual nitrite was present in solution, the gases were expanded into the exhausted vessel *N* containing cupric chloride solution, the gases remaining after removal of the hydrogen sulphide by shaking being passed to the pump and fresh gas expanded until the reaction vessel was exhausted.

(b) *Dissolved products.* In the reaction solutions, sulphur was determined by collection on a Gooch crucible and drying at 95° (tests having shown that loss during drying did not exceed 0·5 mg.), and sulphur trioxide by barium sulphate precipitation. Sometimes colloidal sulphur passed through the Gooch crucible and was carried down by the barium sulphate; in this case, loss of sulphur by volatilisation was prevented by suspending a beaker of cold water in the mouth of the precipitation beaker, and sulphur and sulphate were determined by drying followed by ignition. Ammonia was determined by distillation into standard acid. In certain cases the nitrogen products collected did not correspond with the quantity of nitric oxide taken. Examination of these solutions (see p. 2637) showed the presence of hydroxylamine, and this was determined by titration with $N/100$-iodine solution in an aliquot portion of the filtrate from the barium sulphate precipitation in experiments where excess of hydrochloric acid was present, the acid solution being boiled again to ensure absence of traces of hydrogen sulphide.

The iodine solution was standardised by means of a standard solution of recrystallised hydroxylamine hydrochloride.

For determination of hydroxylamine and sulphur products in the absence of excess of hydrochloric acid, in which case ammonium nitrite and sulphide were present in the solution, the combined hydrogen sulphide was removed by adding sodium bicarbonate and passing a rapid stream of carbon dioxide for several hours. Sulphur was filtered off, the hydroxylamine determined in a portion of the filtrate, and sulphate in the residue after acidification. Blank tests with known quantities of material showed that this procedure gave satisfactory results.

Tests showed that very nearly one-third of the hydroxylamine was converted into ammonia during alkali distillation for ammonia estimation. This is allowed for in calculating the quantity of ammonia existing in solution.

Small amounts of nitric acid formed were estimated colorimetrically by comparison with a standard sodium nitrate solution, the brucine reaction being used. Nitrite was determined by reduction with Devarda's alloy after distillation of the ammonia, allowance being made for the small amount of nitrate.

Results are shown in Tables I and II, where volumes of gases are reduced to N.T.P., the reactions having been carried out at 30°. In each case reactions were carried out in aqueous solution (the calculated quantity of hydrochloric acid being added to the sodium nitrite when nitrous acid solutions were being prepared), and repeated with a solution of *N*/20-hydrochloric acid in the reaction vessel. The columns headed " S as SO_3 " show the actual quantities of sulphur present as trioxide. In Table II, for comparison with Table I the quantities of nitric oxide that would produce the nitrous acid used if entirely converted into it are shown. On account of the less extensive reduction, it was necessary to take larger amounts of nitrous acid than correspond to the 40 c.c. of nitric oxide of Table I, but the yields have been calculated to 40 c.c. and are shown together with the actual amounts of reacting substances. In Expts. 13—16, where an excess of nitrous acid was taken, the amount consumed by reaction was calculated from the amounts of nitrogen products. If the amount of sulphur products equivalent to the nitrogen products other than nitric oxide is calculated, the residual sulphur corresponds fairly closely with the amount of nitric oxide recovered, showing that very little has been produced by direct decomposition of nitrous acid. Table I contains results for reactions with considerable hydrogen sulphide and very little nitrous acid; the opposite condition of excess of nitrous acid in quantity and low hydrogen sulphide concentration is shown in Table II

TABLE I.

Nitric Oxide–Oxygen–Hydrogen Sulphide.

(Hydrogen sulphide in excess; 225 c.c. in each case.)

Quantities of product calculated to 40 c.c. of NO.

	Expt. No.	NH_3.	NH_2OH.	N_2O.	N_2.	Free S, mg.	S as SO_3, mg.	Equivalent S, mg.	Calculated S, mg.	Oxygen used, c.c.
		Equivalent to c.c. of NO.								
HCl solution.	†1	26	9·6	0·4	1·0	146	0·3	147	147	11
	2	25	10	0·4	2·0	142	0·2	143	138	13
	3	27·5	10	0·4	0·6	150	0·1	150	155	11·5
	4	25·5	10	0·6	1·0	146	0·5	148	148	10·4
Aqueous solution.	‡*5	36		0·4	3					
	*6	34		0·4	1·5					15
	*7	34		0·4	2·5					16
	8		2·2			145	2·0	153	158	
	9		2·2			144	3·0	156	158	
Aqueous solution acidified after reaction.	10	28·5	1·7	4·1	4·6	160	2·0	168	143	16
	11	30·5	1·3	5·0	5·2	155	4·0	170	154	19
	12	27·4	2·5	4·5	6·5	153	3·0	165	145	20

* In Expts. 5—7 the quantities of product are for 40 c.c. of nitric oxide exclusive of that converted into nitrite, the amounts of which were equivalent to 21 c.c. of NO in Expt. 5, 22 c.c. in Expt. 6, and 21·5 c.c. in Expt. 7.

† HNO_3 equivalent to 0·5 c.c. NO was produced in this experiment.

‡ HNO_3 equivalent to 0·7 c.c. NO was produced in this experiment.

TABLE II.

Nitrous Acid and Hydrogen Sulphide.

		Expt. No.	NO equivalent of HNO_2 taken.	NH_3.	NH_2OH.	N_2O.	N_2.	NO.	Free S, mg.	S as SO_3, mg.	H_2S taken, c.c.
				Quantities of product calculated for nitrous acid equivalent to 40 c.c. of NO.							
				Equivalent to c.c. of NO.							
Excess HNO_2.	HCl soln.	13	224	0·2		5	1	35	15	5	58
		14	224	0·2		4·5	1	34	14	5	58
	Aqueous soln.	15	224	0·15		5	1	34	17	4·5	62
		16	224	0·15		4·1	1·5	33	17	4·0	64
Excess H_2S.	HCl soln.	17	112	6·5	0·4				43	2·7	350
		18	112	7	0·3				43	3·2	350
		19	112			10	1·5	21·5			350
		20	112			10·5	1·5	21·5			350
	Aqueous soln.	†*21	112	8	0·8	10	1·0	25	49	1·2	350
		*22	112	7·5	0·9	10·4	0·6	26·5	46	1·3	350

* In Expts. 21 and 22 the quantities of product are for the equivalent of 40 c.c. of nitric oxide exclusive of that remaining as nitrite, the approximate amounts of which were equivalent to 4 c.c. of NO in each case.

† In Expt. 21, nitric acid was produced equivalent to 0·1 c.c. of NO.

(Expts. 13—16), where the hydrogen sulphide was admitted over the water in the reaction vessel and the nitrous acid solution run in beneath the water, reaction being completed by subsequent shaking with consequent solution and oxidation of the hydrogen sulphide. Expts. 17—22 of Table II represent an intermediate condition, the hydrogen sulphide being in excess but the nitrous acid being present in quantity. In this case, the water in the reaction vessel was nearly saturated with hydrogen sulphide by admitting gas and shaking until the pressure was nearly atmospheric before addition of the nitrous acid.

For the identification of hydroxylamine, the material was prepared in greater quantity by passing rapid streams of oxygen and hydrogen sulphide and a slow stream of nitric oxide through several hundred c.c. of *N*/5-hydrochloric acid solution in a bottle carried on a shaker. After several hours, when the solution had become nearly neutral, the sulphur was filtered off, and the solution evaporated to dryness with sufficient barium chloride to precipitate all the sulphuric acid. The residue was extracted with absolute alcohol, the extract evaporated, the crude residue extracted with alcohol–ether, and the solvent again removed. The resulting white solid reduced iodine solution and Fehling solution (Found : Cl, by $AgNO_3$ titration, 52·4. Calc. for NH_2OH,HCl, 51·1; for NH_4Cl, 66·4%); 0·014 g. required 58 c.c. of iodine solution, 29 c.c. of which were equivalent to 10 c.c. of *M*/100-hydroxylamine solution (Calc. for NH_2OH,HCl, 58·4 c.c.).

Discussion.

Considering first the nitrogen products, it will be seen from Table II that when the nitrous acid is in excess and the hydrogen sulphide concentration relatively small (Expts. 13—16) very small amounts of hydrogenated nitrogen compounds are formed (the very small quantities of ammonia were determined by Nessler solution), nitric oxide and smaller amounts of nitrous oxide being the principal reduction products. When the hydrogen sulphide is in excess, however, and the nitrous acid concentration is very small (Table I) the reduction is almost entirely to hydrogenated products, ammonia and hydroxylamine in acid solution, and chiefly ammonia with a smaller proportion of hydroxylamine in aqueous solution.

In the presence of excess of oxygen, nitric oxide would be reconverted into nitrous acid, and a catalytic effect would be apparent from a greater quantity of sulphur products and greater oxygen consumption; but it can be shown from Expts. 1—4, 8, and 9 that there has been no such catalytic effect. In the tables, the quantities of sulphur found as trioxide have been multiplied by 4 to give the quantity of free sulphur that would have been produced by a corresponding amount of oxidation, and the equivalent quantity of free sulphur added to the actually determined free sulphur is given in the column " Equivalent S." The column " Calculated S " shows the amount of sulphur corresponding to the oxidation equivalent of the various nitrogen products collected. As the calculated and the equivalent sulphur correspond, reduction to the nitrogen products found must have been direct without intervening formation of nitric oxide. The quantities of oxygen consumed in Expts. 1—4 are also very close to the 10 c.c. required for direct formation of nitrous acid from 40 c.c. of nitric oxide, further re-formation of which would consume more oxygen. The greater quantity of oxygen consumed in Expts. 6 and 7 is discussed later.

The most noteworthy product is the hydroxylamine, which is destroyed by reaction with nitrous acid. Its formation and stability during reduction of very dilute nitrous acid solution are probably due to the fact that each molecule of the acid is reduced by the excess of hydrogen sulphide before it has opportunity to react with hydroxylamine. The production of the compound by Divers (*loc. cit.*) may be similarly explained, for the effect of hydrogen sulphide on a slightly soluble salt in suspension would be to produce a small concentration of nitrous acid which would be continually removed by the hydrogen sulphide.

When the addition of nitric oxide is effected in the absence of hydrochloric acid, there is still only a very small yield of gaseous products, but ammonia is the principal reduction product, the quantity of hydroxylamine being smaller than in acid solution; but, as shown in Expts. 5—7, a proportion of the nitrous acid has formed ammonium nitrite which has not had time to react with the hydrogen sulphide—it will be shown later that this reaction is very slow (p. 2639).

The result of acidifying the solutions containing nitrite is shown in Expts. 10—12 (Table I), where hydrochloric acid was added after addition of nitric oxide. The calculated quantity of sulphur is smaller than the sulphur found, whilst the oxygen consumption is greater than in Expts. 6 and 7, where no acid was added after reaction. Evidently, the nitrous acid set free on addition of hydrochloric acid had sufficient concentration to form some nitric oxide and thus, to a small extent, to act catalytically. The relatively considerable amounts of nitrogen and nitrous oxide must also have been produced during the reaction after acidification, very little being obtained in Expts. 5—7.

Considering next the sulphur products, it will be seen that, except in the case where nitrous acid is present in quantity and in excess, the hydrogen sulphide concentration being small (Expts. 13—16), the greater proportion of the hydrogen sulphide is oxidised to sulphur with a relatively small amount of sulphur trioxide. Expts. 17—22 show that, even when nitrous acid solution of appreciable concentration is added to a fairly concentrated hydrogen sulphide solution, the sulphur predominates.

In the hope of obtaining further information as to the nature of the processes involved, the reaction between hydrogen sulphide and ammonium nitrite was investigated. In Table IIIA is shown the result of passing hydrogen sulphide continuously through an approximately *N*/20-solution of ammonium nitrite (prepared from silver nitrite and ammonium chloride). There was gradual reduction of nitrite, chiefly, but not completely, to ammonia, about 50% being reduced in 24 hours. The sulphur produced was partly precipitated and partly dissolved as yellow polysulphide. The slow reaction when compared with the extremely rapid oxidation with free nitrous acid suggests that the free acid produced in the present case by hydrolysis is the active agent, and not the nitrite ion which is now present in quantity. The solutions saturated with hydrogen sulphide had a very feebly acid reaction, which diminished as the ammonium sulphide increased; p_H values determined by a comparator with phenol-red are shown. In order to study the effect of sulphide-ion concentration, the experiment was repeated with addition of sufficient ammonium sulphide to make the solution *N*/6 with regard to ammonia. The result of passing a continuous stream of hydrogen sulphide through this mixture is shown in Table IIIB. The reaction, at first slower than in the absence of excess of sulphide, accelerated considerably after a few hours. The sulphur produced dissolved, forming a yellow polysulphide solution.

TABLE III.

Hydrogen Sulphide and *N*/20-Ammonium Nitrite.

(25 C.c. samples.)

A. Nitrite + H_2S.

Time (hrs.)	0.	$\frac{1}{3}$.	3.	6.	9.	12.	27.	32.
C.c. of *N*/10-HCl for NH_3 ...	12·2	12·5	13	13·7	14	14·3		16
C.c. of *N*/10-HCl for HNO_2	12·0	11·5	10·9	10	9·4	8·9	6·1	5·5
p_H			6·0			6·3		6·6

B. Nitrite + H_2S + *N*/6-NH_4HS.

	(1)					(2)		
Time (hrs.)	0.	$3\frac{1}{4}$.	6.	8.	11.	0.	$1\frac{1}{2}$.	$3\frac{1}{2}$.
C.c. of *N*/10-HCl for HNO_2	12	11·5	8·5	5	2·3	12	11·8	11·3

C. Nitrite + H_2S + *N*/6-Polysulphide.

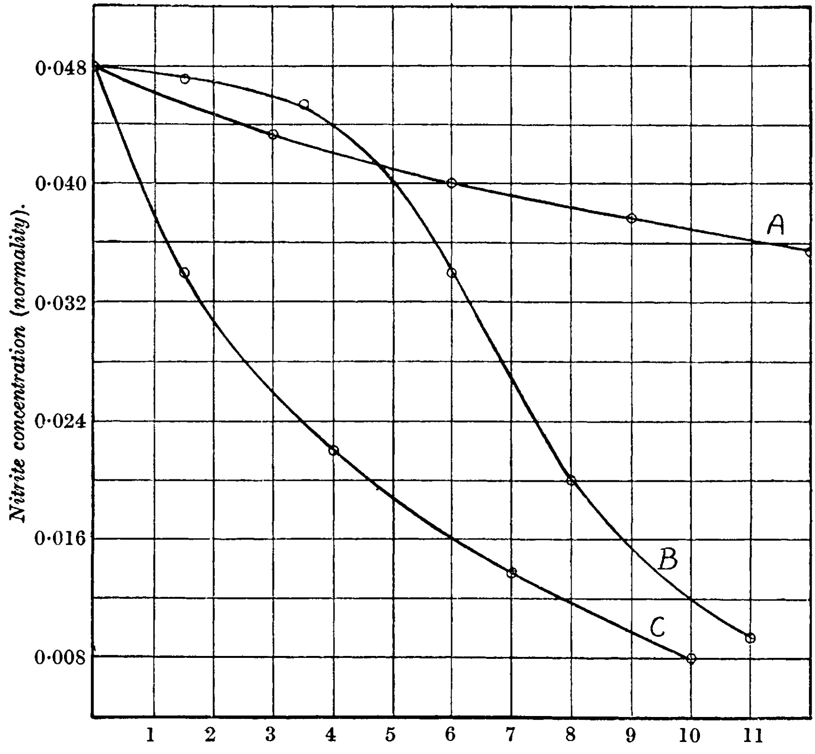
Time (hrs.)	0.	$1\frac{1}{2}$.	4.	7.	10.
C.c. of *N*/10-HCl for HNO_2 ...	12	8·5	5·5	3·4	2·0

Table IIIc shows the result of adding ammonium sulphide and sulphur, forming polysulphide, at the commencement of reaction. It will be seen that the reaction is rapid from the beginning. The results shown in Table III are plotted in Fig. 2.

N/6-Ammonium sulphide solution saturated with hydrogen sulphide has a slightly alkaline reaction, p_H 7·2—7·3 by comparator, and the polysulphide solution has a value of the same order. The very slow reaction with considerable ammonium hydrosulphide in solution is probably due to diminished nitrous acid concentration owing to smaller hydrogen-ion concentration. The increased rate when sulphur is formed or added in sufficient quantity may be ascribed to the influence of polysulphide ion. Although Küster (*Z. anorg. Chem.*, 1905, **44**, 431) has shown by *E.M.F.* measurements that these ions have a smaller reduction tendency than the sulphide

FIG. 2.

A = *Nitrite.* B = *Nitrite + sulphide.* C = *Nitrite + polysulphide.*



Hydrogen sulphide and ammonium nitrite.

ion, he has also found (*ibid.*, **43**, 53) that, as the proportion of sulphur increases, the hydrolysis of sodium polysulphide diminishes, thus indicating greater strength for the acid. In the solutions now under consideration, which were saturated with hydrogen sulphide, the principal constituents would be NH_4HS and NH_4HS_x, and the principal ions $NH_4^{\cdot}$ and HS' in one case, and NH_4 and HS_x' in the other. The polysulphide will be less hydrolysed and more dissociated, and the HS_x' ion will be present in greater quantity than the HS' ion in the absence of sulphur; thus a considerable increase in concentration of the reducing ion will be caused by the presence of sulphur dissolved as polysulphide. This in turn may lead to more rapid reaction.

The last experiments thus afford some evidence that the reaction between hydrogen sulphide and nitrous acid is between the undissociated acid and the sulphide ion. It may be suggested that the primary reactions are of simple type, and that nitric and nitrous oxides and nitrogen are secondary products. With appreciable concentration of nitrous acid, the reactions

$$(1)\ 3HNO_2 + S'' \longrightarrow 3HNO + SO_3 (+ 3H_2O)$$

and

$$(2)\ HNO_2 + S'' \longrightarrow HNO + S\ (+ H_2O)$$

may be expected. The proportions in which reactions (1) and (2) occur would largely depend on the relative concentrations of the reacting substances. Reaction of the hyponitrous acid with more nitrous acid would yield nitric oxide. Direct decomposition of hyponitrous acid has been shown to yield nitrous oxide and nitrogen (Divers, J., 1889, **55**, 112). The nitric oxide and some of the nitrogen and nitrous oxide found in various experiments may thus be accounted for, a portion of the nitrous oxide and nitrogen probably being formed as secondary products of reaction (3) (below). With smaller concentration of nitrous acid and considerable hydrogen sulphide concentration, reactions

$$(3)\ HNO_2 + 2S'' \longrightarrow NH_2OH + (H_2O) + 2S$$

and

$$(4)\ HNO_2 + 3S'' \longrightarrow NH_3 + (2H_2O) + 3S$$

may be expected, with the possibility of more nitrous oxide and perhaps nitrogen being formed by reaction between nitrous acid and hydroxylamine.

In the present work the slow addition of nitric oxide to the system would produce an exceedingly small concentration of nitrous acid which would not increase, owing to reaction with hydrogen sulphide, and secondary reactions with nitrous acid would not be expected to occur to any extent. Reactions (3) and (4) appear to have proceeded together in Expts. 1—4 in the presence of excess of hydrochloric acid, whilst in absence of acid (Expts. 5—9) reaction (4) predominates. Two causes may be suggested to account for this variation : (1) A reduced free nitrous acid concentration owing to nitrite formation and reduction of hydrogen ion through the presence of hydrolysed ammonium sulphide—it does not seem likely, however, that variation in an already very small concentration of a substance taking a unimolecular part in a reaction would appreciably alter the nature of the reaction in the presence of considerable excess of the second reactant. (2) Variation of sulphide-ion concentration is probably of greater importance; this concentration, very small in hydrochloric acid solution, will be much greater in presence of ammonium sulphide, thus favouring reaction (4).

In Table II there is no definite difference between the products in Expts. 15 and 16 with only nitrous acid, and those in Expts. 13 and 14 with excess of hydrochloric acid. This is to be expected on account of the considerable amount of sulphuric acid produced. Small variations between products in Expts. 17—20 and Expts. 21 and 22 with excess of hydrogen sulphide may be due to variation in acidity, as only small amounts of sulphuric acid were produced. Considerable variation is not to be expected, as the solutions would in all cases remain acid until most of the nitrous acid was destroyed.

A blank test with hydrogen sulphide, oxygen, and an amount of ammonia equal to that present as sulphide at the end of reaction, yielded in the absence of nitric oxide about 4 mg. of free sulphur and 0·3 mg. as trioxide in $\frac{1}{2}$ hour. As the average ammonia concentration during a run would be much less than the maximum, the amount of sulphur formed by direct oxidation in Expts. 10—12 would be very small. The greater oxygen consumption in Expts. 6 and 7 than in Expts. 1—4 may be due to this small direct oxidation.

The following are results of some other blank tests.

(1) Absorption by copper chloride of hydrogen sulphide from mixture with nitric oxide :

100 c.c. of H_2S + 38 c.c. of NO taken; 37·5 c.c. of NO recovered.

(2) Absorption by alkali solution of nitric oxide (41 c.c.) from mixture with oxygen (10 c.c.) :

$KMnO_4$: required 36·9 c.c.; calculated 36·7 c.c.

(3) Estimation of nitrite in ammonium nitrite solution containing polysulphide : 25 C.c. of *N*/20-ammonium nitrite solution were added to concentrated alkali and the ammonia was distilled off. The nitrite was then reduced by Devarda's alloy and the resulting ammonia required 12·0 c.c. of *N*/10-HCl. The process was then repeated with a fresh sample containing the amount of polysulphide used in the experiments of Table IIIc, and 11·9 c.c. of acid were

required. There has evidently been no appreciable reduction of nitrite in the strongly alkaline solution during the time required for preliminary distillation of the ammonia.

(4) In view of the fact that hydroxylamine is known to act as an oxidising agent under certain conditions, the possibility of its reacting with hydrogen sulphide in presence of ammonium sulphide and sulphur was tested under various conditions. It was found that no measurable loss of hydroxylamine occurred in dilute solutions in an hour.

Summary.

The products of reaction of nitrous acid solution with hydrogen sulphide vary with relative concentrations. With appreciable concentration of nitrous acid, the reduction products are chiefly nitric and nitrous oxides; with small concentrations of nitrous acid, they are ammonia and hydroxylamine, the proportions of which vary according to the concentration of sulphide ion in solution.

A series of simple reactions is proposed, nitric and nitrous oxides being regarded as products of hyponitrous acid formed primarily.

The proportion of sulphur trioxide to free sulphur is small even with fairly concentrated nitrous acid solutions unless the hydrogen sulphide concentration is small.

Hydrogen sulphide reacts slowly with ammonium nitrite, converting it into ammonia. The rate of reaction is diminished by addition of ammonium sulphide and increased by addition of polysulphide. A suggested explanation is based on the fact that the polysulphide ion is known to be more acidic than the sulphide ion and would thus furnish a greater concentration of reducing ions in solution.

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