

## The Interaction between Sulphites and Nitrites.

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The present paper gives an account of a series of experiments, the results of which seem to leave no room for doubt as to the truth of the following propositions respecting the sulphonation of nitrites:—(1) normal sulphites are inactive upon nitrites; (2) pyrosulphites are not active to their whole extent upon nitrites; (3) pyrosulphites are active in their entirety upon nitrous acid or its equivalent of nitric oxide and nitric peroxide (nitrous fumes); and (4) sulphurous acid and nitrous acid or the oxides and water equivalent to them interact of themselves and in such a way that the base of the sulphite, that may be used in place of the sulphurous acid, is needed only to preserve from hydrolysis the products of their interaction. Concerning these assertions we would point out that the first directly contradicts the conclusions drawn by other workers from their experiments; the

*second* is novel like the first, the facts on which it is based having been misunderstood ; the *third* has indeed been already enunciated, but not with intention to limit it to a strict interpretation, and only theoretically, without any experimental treatment of it ; and, lastly, the *fourth* has been also made before and upon the basis of experiment, but experiment quite inadequate to justify it.

The establishment of these propositions, taken along with what we have already published as to the constitution of Fremy's salts will then allow of the further assertion being made, that the interaction of nitrous acid with a pyrosulphite results in their conversion into a two-thirds normal hydroximidosulphate (and water), and that all the other sulphazotised salts are secondary products simply derived. It is thus established that the only interaction between sulphites and nitrites is one of the greatest simplicity, instead of being full of complications, as hitherto believed.

I.—*a. A Normal Sulphite inactive upon a Nitrite.*

Dipotassium or disodium sulphite is quite inactive upon a nitrite. In establishing this fact we have mixed solutions of normal sulphite and nitrite in proportions varying in different experiments, and left them in closely corked flasks, almost full, for days and for weeks. No change has ever happened. When coloured with rosolic acid, a drop of dilute acid would at any time, as at first, discharge the colour. Had any action occurred, alkali hydroxide must have been generated (as to the possibility of which see sect. II. *b.*). A portion of the solution to which had been added a drop of dilute sulphuric acid reacquired the pink colour of the rosolic acid when left to stand for some time

—the minute quantity of pyrosulphite which the acid had produced having slowly interacted with the nitrite, but when that was used up, no more action occurred and, at any time added one drop of dilute acid would again remove the colour of the solution.

No further proof of the activity upon a nitrite of a normal alkali sulphite is wanted, but additional evidence of the fact is readily obtainable. Thus, in the case of the potassium salts, while the action of pyrosulphite upon nitrite shows itself (except in cases of high dilution) by the formation of the insoluble nitrilosulphate, no separation of this salt occurred in the above experiments. Again, barium chloride, added, at any time, to the mixed and to litmus very alkaline solution of normal sulphite and nitrite, precipitated all the sulphur as sulphite (with also a very little sulphate) and left the nitrite in solution, neutral to litmus. Had sulphazotised salts been present, precipitation of the sulphur would have been incomplete, and the mother-liquor would have preserved a strong alkalinity to litmus and when acidified soon have deposited barium sulphate in the cold and at once if boiled.

Fremy, Claus, and Raschig all believed in the activity of dipotassium sulphite upon potassium nitrite, although the last named chemist recognised the value also of the pyrosulphite, as Berglund had done before him. Fremy apparently used sulphite neutral to litmus and took it to be the normal salt, and Claus certainly did so. Since, therefore, they used sulphite which was, for the most part, pyrosulphite, no evidence upon the point in question can be gathered from their work. We would account for Fremy's finding sodium sulphite inactive upon sodium nitrite, otherwise inexplicable, by assuming that the solution of sodium sulphite which he tried happened to contain no pyrosulphite.

Claus's statement that some potassium sulphite neutral to litmus was as active upon nitrite, after he had added potash in 'excess' to it, as it was before only requires us to assume that the excess spoken of was large enough to give the solution a markedly alkaline action upon litmus and yet small enough to leave much pyrosulphite unchanged.

I.—*b. Potassium Hydroxide not a Factor in the Formation of the Sulphazotised Salts.*

That a normal sulphite, potassium or sodium, remains still inactive upon nitrite, when alkali hydroxide is added, was ascertained by leaving the three substances together in solution in a closed flask for some time, as in the experiments where no hydroxide was present, and then precipitating with barium chloride after addition of ammonium chloride, and finding no sulphur compound left in the filtrate. (Ammonium chloride prevents precipitation of hydroximidosulphate, this Journal 7, 48, 69).

On the many occasions we have had to prepare sulphazotised potassium salts by submitting solutions of nitrite and hydroxide to the action of sulphur dioxide, taking care to keep the solution briskly agitated, we found that, even in ice-cold solutions, precipitation of these very sparingly soluble salts only began from the point at which there was no more hydroxide left, and then went on freely until the solution had become neutral to lacmoid paper. In proportion as the hydroxide disappeared, sulphite became abundant, whilst from the time that the replacement of hydroxide by sulphite was complete, the quantity of sulphite steadily decreased as the sulphazotised salts formed, sulphazotised sodium salts being very soluble no preci-

precipitation occurs during their preparation, and with these, therefore we made an experiment to determine quantitatively what happens up to the point when the last portion of hydroxide disappears, a point indicated by rosolic acid losing its pink colour.

Washed sulphur dioxide was sent in a steady stream into a solution of 11.21 grams real sodium hydroxide and 19.34 grams sodium nitrite in about 198 grams water, kept in active motion and immersed in ice. The sodium compounds were in molecular proportions; more nitrite would not have mattered. In a short time a 10 cc. pipetteful was removed; soon after a second; and not very long after a third one, just when the pink colour of the rosolic acid present had disappeared. The three portions were treated alike. Each was mixed with excess of solutions of ammonium and barium chlorides and the precipitate filtered off, oxidised to sulphate, washed with dilute hydrochloric acid, and weighed as barium sulphate. The ammonium-chloride filtrate was evaporated to dryness, during which operation all the sulphur of the sulphazotised salts was converted to sulphate by the nitrite and ammonium chloride. The soluble salts were washed out with dilute hydrochloric acid, and the barium sulphate collected and weighed. The solution of salts removed from the barium sulphate was concentrated and then heated under pressure for hours, after which it was found to be still clear and therefore free from sulphate, which must have formed by hydrolysis had any sulphazotised salt escaped decomposition during the evaporation with nitrite and ammonium salts.

We give the quantities of sulphur dioxide found in each pipetteful as sulphite and as sulphazotised salts, and also state these quantities as parts per hundred of the total sulphur dioxide which had entered it.

Sulphur dioxide as	1st 10 cc.	2nd 10 cc.	3rd 10 cc.
Sulphite	.0662 grms. = 96.6%	.1204 grms. = 96.5%	.3996 grms. = 91.5%
Sulphazot.	.0023 „ = 3.4%	.0047 „ = 3.5%	.0365 „ = 8.5%

It will be seen that all but 3.5 per cent. of the sulphur dioxide entering the solution in the early stages of the experiment remained in the form of sulphite, and that even up to the time when the last of the hydroxide had been consumed, all but 8.5 per cent. of the total sulphur dioxide was in the state of sulphite. That it must be impossible to prevent all temporary local excess of sulphur dioxide will be at once admitted, as also that it must be difficult in the later stages to keep down this local excess to very narrow limits. Therefore it will seem in the highest degree probable, if not certain, from this experiment that sulphur dioxide, equally with normal sulphite, does not act upon nitrite in presence of alkali hydroxide.

Now Fremy believed that potassium hydroxide helps the formation of sulphazotised salts and endeavoured, accordingly to keep some of it always present when passing sulphur dioxide into a solution of potassium nitrite. This he did by adding it occasionally during the process, and to such an extent that at the end of the operation the mother-liquor of his salts was always not merely alkaline but caustic and destructive to filter paper. Claus did not go so far as to believe that the potash exercised any specific influence upon the action between the sulphur dioxide and the nitrite, but, agreeing with Fremy as to its value in precipitating and preserving the sulphazotised salts, he adopted the precaution to stop passing in sulphur dioxide when the alumina contained in the potassium hydroxide began to precipitate, since this occurs while the solution is still strongly alkaline to litmus. Raschig, in attempting to prepare Fremy's

*sulphazate*, also used precipitation of alumina as the indication to stop the process while yet alkali remained.

Thus, then, it would seem, Fremy, Claus, and Raschig, the last in less degree, have all prepared sulphazotised salts without difficulty, under conditions which we pronounce to be incompatible with their production. To remove this apparent contradiction in results it is sufficient to assume, for one thing, that, in Fremy's way of working, success followed only because, temporarily and locally, the point of saturation of the alkali was reached and exceeded again and again where the gas entered the solution,—a state of things, never avoidable altogether, above all at the time when the potassium hydroxide is nearly exhausted. There is nothing to show that, to check this, he kept his solution well agitated. Secondly, we can assume, with great probability that his solution often lost its alkalinity between the additions of the hydroxide which he made. Working as we believe he actually did, we have found it easy to get results such as his. So far as Claus and Raschig followed Fremy's method, their results are equally open to objection, while it is to be remarked of their alumina indicator that, not only is normal sulphite alkaline to litmus but, as we have found, any aluminium present is precipitated as hydroxide just when the sulphur dioxide has converted all alkali into normal sulphite. They will, therefore in their experiments have preserved none of the alkali unchanged and most probably have generated also some pyrosulphite. There is besides indirect evidence in Claus's work that normal sulphite is either inactive or only very slowly active upon nitrite, for when, having taken no excess of this salt, he stopped the process just after precipitation of alumina, much of this nitrite remained in the solution, while, as we have just pointed out, much normal

sulphite must also have been present. The two salts were, therefore, together in solution unchanged. Raschig, too, found that sulphite and nitrite are inactive upon each other when in presence of potassium hydroxide dissolved in only its own weight of water.

II.—*a. Even Pyrosulphite only active upon a Nitrite till it has become Normal Sulphite.*

Pyrosulphite, neutral to lacmoid paper and containing therefore, neither sulphurous acid nor normal sulphite, freely sulphonates nitrite, but is far from being all consumed in the process, as it has been represented to be by Claus, Berglund, and Raschig. Quantitative experiments have shown us that, when pyrosulphite is left in solution with excess of nitrite in a closed vessel for a considerable time, about one-third of the sulphite remains inactive by becoming converted into the normal salt, separable, as in other cases, from the sulphazotised salts by precipitation with barium chloride in presence of ammonium chloride. From this it follows that 3 mols. pyrosulphite are needed to convert 2 mols. nitrite into hydroximidosulphate (this Journal, 7, 19) and not 2 mols. only, as had been supposed. The third mol. sulphite remains unavoidably in the solution but all the nitrite sulphonated:— $2\text{NaNO}_2 + 3\text{Na}_2\text{S}_2\text{O}_5 + \text{OH}_2 = 2\text{Na}_2\text{HNS}_2\text{O}_7 + 2\text{Na}_2\text{SO}_3$  using less pyrosulphite, some nitrite remains at the end along with normal sulphite. That sodium pyrosulphite is not easily all used up in sulphonating sodium nitrite was observed by Raschig.

Not only hydroximidosulphate but a little nitrilosulphate is formed when a pyrosulphite acts upon a nitrite, but this need

never be enough, with ordinary care, to cause much less than one-third of the sulphite to remain inactive. If excess of pyrosulphite is used the interaction appears to be— $\text{NaNO}_2 + 2\text{Na}_2\text{S}_2\text{O}_5 = \text{Na}_3\text{NS}_3\text{O}_9 + \text{Na}_2\text{SO}_3$ , but we have not made any quantitative determination of the sulphite remaining, the qualitative evidence being sufficient.

The interaction between pyrosulphite and nitrite proceeds at first very rapidly and with great elevation of temperature, but, when the temperature is kept down by cooling, soon slows down, so as to require many hours for its completion. The normal sulphite seems here to inhibit the action of the pyrosulphite, just as does the salt of a weak acid inhibit the action of that acid, an effect now well recognised. This consideration points to the propriety of looking upon the passage of pyrosulphite to normal sulphite as its action as an acid upon the nitrite, and not as the yielding up of half of its sulphurous acid for the sulphonation of the nitrite, the interactions being  $2\text{NaNO}_2 + \text{Na}_2\text{S}_2\text{O}_5 + \text{OH}_2 = 2\text{HNO}_2 + 2\text{Na}_2\text{SO}_3$ , and then  $2\text{HNO}_2 + 2\text{Na}_2\text{S}_2\text{O}_5 = 2\text{Na}_2\text{HNS}_2\text{O}_7$  (see section III *a*).

II.—*b. Alkali not produced in the Sulphonation of a Nitrite.*

One of the most remarkable things, according to Claus, is the production of potassium hydroxide by the formation of Fremy's salts through the agency of a sulphite. He explained this production by the equation— $\text{KNO}_2 + 2\text{K}_2\text{SO}_3 + 2\text{OH}_2 = \text{K}_2\text{HNS}_2\text{O}_7 + 3\text{KHO}$ . Such an equation was also published by Berglund (*Lunds Univ. Årskr.* 1875, 13, 14). Raschig gave the same equation for results obtained by himself and, in order to express

other results, gave also the equation— $\text{NaNO}_2 + 2\text{NaHSO}_3 = \text{Na}_2\text{HNS}_2\text{O}_7 + \text{NaHO}$ . Finding also, and again in agreement with Claus, that dipotassium hydroximidodisulphate does not combine at once or even at all with potassium hydroxide, he argued that this salt cannot have a similar constitution to that of Fremy's 'basic' sulphazotate because potassium hydroxide is produced along with it instead of being combined with it as Fremy's 'basic' sulphazotate.

Now, all this is wrong in fact on the part both of Claus and Raschig, as we have already shown (this Journal 7, 30) or here show in other sections of the present paper, except as to the generation of alkali hydroxide, which we now proceed to deal with. Claus's emphatic statement, supported as it is by Berglund and by Raschig, that potassium hydroxide is formed when a sulphite meets a nitrite in solution, rests upon no other evidence than what we now set down in full, recalling the fact (section I, *a.*) that between the normal sulphite and nitrite there is really no activity of any kind. A solution of sulphite made neutral to litmus and a solution of nitrite of either potassium or sodium become hot and strongly alkaline to litmus when mixed together, and then contain much hydroximidodisulphate and nitrilosulphate, both neutral to litmus, which soon crystallise out if they are the potassium salts. That is all these chemists had as evidence for the production of the hydroxide; let us add to these facts that addition of excess of barium chloride removes all the alkalinity. It follows, since pyrosulphites are a little acid to litmus and normal sulphites are very alkaline to it, that the phenomena depended upon offer no grounds whatever for the belief that alkali hydroxide is produced. Except by the use of lime, baryta, or other base, there is, we believe, only one way by

which potassium hydroxide can be generated from potassium sulphite and that is one made known by us, namely, treatment of the sulphite first with nitric oxide and then with alcohol and water (this Journal, 9, 106).

III.—*a. A Pyrosulphite all active upon Nitrous Acid.*

As remarked at the end of section II. *a.*, a pyrosulphite appears to act as an acid upon the nitrite and then sulphonates the nitrous acid itself, only indirectly, therefore, sulphonating the nitrite of a metal or of ammonium. One third of the pyrosulphite should, accordingly, be replaceable by some other acid, and so it proves to be (section III. *d.*). It is not new to formulate the sulphonation of  $\text{HNO}_2$ , and to speak of 'nitrous acid' as the reacting substance, for (passing over Fremy) Raschig has already done so. But, whereas we would be understood to confine the activity to nitrous acid itself, or its acidic equivalents (sect. III. *d.*), such was not the thought of Raschig, who only wrote H as a general symbol, and 'acid' as a general term, while representing metal nitrites as active by generating alkali hydroxide.

Nor is it new to learn that nitrous acid can be sulphonated. By treating a dissolved sulphite with nitrous acid (nitrous fumes) Fremy did succeed in obtaining sulphazotised salts, but the difficulty of moderating the flow of the gas, and the presence in it of nitrogen peroxide and nitric acid made the operation so inconvenient, he said, that he did not use it in preparing any of the salts he examined, and gave no further attention to it. We have taken up the matter, since untouched and unmentioned, where Fremy left it half a century ago. Our work has been very simple but very effective, and has consisted in subjecting a

solution of pyrosulphite (and of normal sulphite, but of that we treat in sect. III. *b.*) to nitrous fumes which act as nitrous anhydride when of the right composition. The gases were found to be fully absorbed by a concentrated solution of potassium pyrosulphite kept cold in a flask immersed in ice and brine and well agitated. Soon an abundant precipitation began of hydroximidodisulphate mixed with a little nitrilosulphate. While still much pyrosulphite remained, the process was stopped and the mother-liquor at once drained off. In this way we had great success in getting much hydroximidodisulphate and only a little nitrilosulphate, notwithstanding the presence all along of so much pyrosulphite; for, as was pointed out by us long ago, in sufficiently cold solutions sulphonation to nitrilosulphate hardly occurs.

The next five sections (III. *b, c, d, e, f*) treat of various mixtures which, from the acid constitution of one of the components, behave like that of nitrite and pyrosulphite, that is, as if each contained pyrosulphite and nitrous acid.

### III.—*b. Normal Sulphite also all active upon Nitrous Acid.*

Replacing the pyrosulphite used in the last experiment by the normal sulphite, it was found that again but in this case gradually, hydroximidodisulphate precipitated, as well as very little nitrilosulphate. But here potassium nitrite proved to be another product, which by gradually replacing the potassium sulphite in the solution allowed the process to be carried very far towards completion. The reaction is expressed by the equation— $3\text{HNO}_2 + 2\text{K}_2\text{SO}_3 = 2\text{KNO}_2 + \text{OH}_2 + \text{K}_2\text{HNS}_2\text{O}_7$ , from which it is seen that only one-third of the nitrous acid becomes sulphonated, the rest being used up simply as an acid.

This interaction is what, we believe, Raschig must inadvertently have got, when seeking to prepare Pelonze's salt (hyponitrosulphate) by the use of nitric oxide. The conditions are favourable to the production of the nitrito-hydroximidosulphate (this vol., p. 222).

III.—*c. Action of Sulphur Dioxide upon Normal Sulphite and Nitrite.*

It has been shown in this paper (sect. I. *b*) that the hydroximidosulphate which, from the first, accompanies the normal sulphite as joint product of the action of sulphur dioxide upon alkali nitrite and hydroxide, keeps steadily to small proportions to the sulphite until nearly all the hydroxide has been saturated. After that point is passed and when, therefore, sulphur dioxide is meeting a mixture of nitrite and normal sulphite, examination of the solution, by the method already described, shows that, along with a greater production of hydroximidosulphate than before, there is pyrosulphite produced in no insignificant quantity. This remarkable growth in the quantity of pyrosulphite, considered along with the fact (sect. II. *a*) that it is itself active upon nitrite proves that much of the sulphur dioxide goes altogether to the normal sulphite. Only after the greater part of this salt has been acidified to pyrosulphite is the sulphur dioxide active in sulphonating the nitrite, which it then does by combining with it in conjunction with the pyrosulphite, thus:—

$2\text{KNO}_2 + \text{K}_2\text{S}_2\text{O}_5 + 2\text{SO}_2 + \text{OH}_2 = 2\text{K}_2\text{HNS}_2\text{O}_7$ , the hydroximidosulphate being produced in this way with much greater facility than by the pyrosulphite alone because of its production not being accompanied here by the regeneration of normal sulphite

with its inhibitory effect upon sulphonation (sect. II. *a*). In this change it still holds true that it is nitrous acid itself which is sulphonated, the potassium leaving the nitrite to enter the sulphonate radical, and being replaced by hydrogen.

Claus held that there could be no difference between the effect of submitting a nitrite to the action of a sulphite and that of mixing it with a solution of hydroxide and then treating it with sulphur dioxide. The contents of this section and section II. *a* show that essential difference exists between the courses and results of the two procedures.

### III.—*d. Action of Carbon Dioxide and of an Acid Carbonate upon Normal Sulphite and Nitrite.*

As would be expected, the gradual addition of one of the stronger acids to a solution of normal sulphite and nitrite leads to the formation of sulphazotised salts. But even carbon dioxide and the acid carbonates of the alkalis are effective in exciting action in a solution of these salts. Concerning the activity of carbon dioxide there is nothing to add to what was published in our first paper (J. Ch. Soc., 1887, 51, 661), that the gas is very slowly absorbed by the mixed salts in solution though not by either salt alone and at the mean temperature, and that sulphazotised salts are then produced. Normal carbonates of the alkalis are inactive.

It is known that nitrites are not decomposed by carbon dioxide, and also that alkali carbonates are decomposed by pyrosulphites as freely at the mean temperature as by sulphur dioxide itself. Accordingly, we have found that potassium or sodium acid-carbonate dissolved along with excess of normal

potassium or sodium sulphite gives off carbon dioxide to a current of decarbonated air much to the same extent as when dissolved alone in water. But sodium acid-carbonate may be added to an ice-cold solution of sodium pyrosulphite, containing also much normal sulphite, and be only very gradually decomposed with effervescence. Indeed, an ice-cold concentrated solution of normal sodium sulphite will deposit some acid-carbonate when charged with carbon dioxide.

It is, therefore, not surprising that sodium or potassium acid-carbonate has a very marked action upon mixed normal sulphite and nitrite. When the three salts are left together in solution in a closed vessel for a day or two, much sulphazotised salt is formed, so that after carbonate and excess of sulphite have been precipitated by baryta and barium chloride in presence of ammonium chloride, the filtrate from the precipitate when boiled with acid gives much barium sulphate and reduces cupric hydroxide freely. The interaction of the salts may be expressed by the equation— $\text{KNO}_2 + 2\text{K}_2\text{SO}_3 + 3\text{KHCO}_3 = \text{K}_2\text{HNS}_2\text{O}_7 + 3\text{K}_2\text{CO}_3 + \text{OH}_2$ , but since the two-thirds normal hydroximid sulphate is to a small extent converted by normal carbonate into a more nearly normal salt and acid-carbonate (this Journal, 7, 32), the change expressed by the above equation cannot proceed to completion.

### III.—e. *Action of Sulphur Dioxide upon Normal Carbonate and Nitrite.*

When sulphur dioxide is added to two mols. nitrite and one mol. normal carbonate until the solution becomes acid to lacmoid paper, the only products are hydroximid sulphate and carbon dioxide. This was long ago pointed out by us, and also that

sulphite and acid carbonate are intermediate products, the latter of which separates for a time from concentrated solutions. We have made further experiments to ascertain the effect of the first portions of the sulphur dioxide in producing hydroximidosulphate, which, where alkali hydroxide is used, we have shown to be insignificant.

These experiments were carried out in the same way as those for testing the effect when sodium hydroxide is employed (I. *b*) but with the modification of making two pipettings each time instead of one, and of weighing both instead of merely measuring them, then in the one we determined the sodium, as sulphate and used the result for calculating what fraction of the original solution the other quantity was in which we determined sulphite and sulphonates. We thus made ourselves independent of the change of volume during the reaction caused by loss of carbon dioxide and gain of sulphur dioxide. We found in this way, admitting of no refined accuracy, that at a later sampling the solution contained at most, as much as  $3\frac{1}{2}$  per cent. less sodium than at an earlier sampling, a difference however hardly large enough to need attention.

The flask for receiving the portion for the sodium determination was previously weighed empty but that for the other portion was weighed containing some concentrated solution of sodium hydroxide, placed there to arrest all action in the pipetteful dropped into it. In the first portion could be seen, by its changes on standing, how necessary the sodium hydroxide was for fixing the composition of the solution at the time it was sampled; sometimes acid carbonate was deposited by it, sometimes hardly at all; sometimes the precipitated acid carbonate slowly disappeared sometimes not. The solution used contained

1 part of sodium nitrite in 4.64 parts of water, besides the calculated quantity of anhydrous sodium carbonate.

The results of the experiments showed that hydroximid sulphate was largely produced from the beginning, in proportion to the sulphite also formed. Thus, in one experiment, when 25 per cent. of the sulphur dioxide required for complete sulphonation had been passed in, 55.3 per cent. of it had become sulphonate, the rest (44.7 per cent.) sulphite. When 53.6 per cent. of the sulphur dioxide required had been used, 74.9 per cent. of it had become sulphonate and 25.1 per cent. sulphite. In another closely comparable experiment, when 33.7 per cent. sulphur dioxide of that required had been absorbed, 62.7 per cent. of it had become sulphonate and the rest sulphite; when 44.4 per cent. of the whole had been used, 72.75 per cent. of it had become sulphonate; and when 62.2 per cent. of the whole had been used, 81.5 per cent. of it had become sulphonate. That is to say, as for the last statement, when 20.2 grams of sodium nitrite (with carbonate) had received 37.5 grams sulphur dioxide, 23.3 grams of this had become sulphonate and 14.2 grams had become sulphite.

Uniform results are here, however, as when hydroxide is started with, only obtained by uniform working, of which the following experiment is a good example. A solution of sodium nitrite and carbonate was divided approximately into one-fifths and four-fifths, and both portions were treated, as nearly as could be, alike, their unequal quantities making the only difference. The smaller portion when it had received 20 per cent. of the full amount of sulphur dioxide was found to contain 61.8 per cent. of it in form of sulphonate, 38.2 per cent. of it as sulphite. The larger portion, having received 25 per cent. of the amount necessary for

its full sulphonation, was found to have only 53.3 per cent. of it as sulphonate and 44.7 per cent. of it as sulphite, as already given; had we stopped here at 20 per cent. sulphur dioxide, as we did with the smaller portion, the difference would have been more striking still. The difference observed was due to the smaller portion having, in relation to its quantity, received sulphur dioxide four times more rapidly than the larger portion had, the stream of sulphur dioxide having been steady and closely alike in the two cases. The result was that local saturation was less checked by the agitation of the flask in this case than when the much larger portion of solution was under treatment.

The lack of uniformity in the results here described, does not affect in the least the evidence they afford that the sulphonation of nitrite in presence of carbonate differs greatly in its course from that it runs in presence of alkali hydroxide.

Respecting the formation and destruction of sulphite in the process, this salt was observed to be produced rapidly until in quantity it had become equivalent to about one-eighth of the sulphur dioxide needed for sulphonation of all the nitrite. Then, for a time, its quantity remains nearly steady, all sulphur dioxide entering the solution during that time becoming sulphonate. Finally, it steadily lessens in quantity as more sulphur dioxide is added, and disappears just at the end of the sulphonation. The more rapidly the sulphur dioxide is blown in at first, the less of it becomes sulphite, and the more sulphonates, as already stated above.

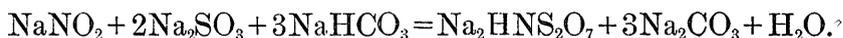
One other striking thing observed in these experiments was the great variability of the point at which acid carbonate first precipitated, as well as the variability of its quantity. With quick working acid carbonate precipitated much earlier and in

much larger quantity than in slow working, proportionately, that is, to the fraction the solution had received of the quantity of sulphur dioxide needed for complete sulphonation of the nitrite. Thus, while, with quick working, acid carbonate separated in abundance when 20 per cent. of all sulphur dioxide had been absorbed, it only precipitated, and then much less copiously, when 44 per cent. of all sulphur dioxide had been supplied relatively more slowly to the solution. In another experiment it showed itself only when 53 per cent. of the sulphur dioxide had been added. The main condition, therefore, for early precipitation of acid carbonate is rapid addition of the sulphur dioxide at first,—the same condition as favours growth of sulphonates at the expense of sulphite.

Now for the discussion of the results. It becomes highly probable from a consideration of these results, together with what we know of the several substances concerned, that the first action or tendency to act of sulphur dioxide when it enters the solution is to convert carbonate into normal sulphite and acid carbonate, and to leave the nitrite untouched, and that this action remains prominent so long as much normal carbonate is undecomposed. Though this cannot be shown experimentally, it is certain that this action does take place, for its products present themselves freely, products which could not be derived from the sulphonation of the nitrite. Both normal sulphite and acid carbonate are active along with sulphur dioxide in sulphonating nitrite.

In accordance with what is stated in III. *d.* the normal sulphite and acid carbonate together slowly disappear of themselves from the solution when addition of more sulphur dioxide

is stopped, owing to sulphonation of the nitrite and reconversion of acid carbonate to normal carbonate—



such a mode of sulphonation will therefore be also in operation when the entrance of more sulphur dioxide has not been arrested, but it is very slow in presence of normal carbonate and may be disregarded as a factor in the process of sulphonating when sulphur dioxide is also at work. Here we would insert that only to simplify discussion do we speak of normal sulphite and carbon dioxide, or even acid carbonate, being together unchanged; these substances, as previously stated, act on each other to a large extent in ice-cold solutions, and in our work we met with precipitated acid-carbonate at times when it could only be there in consequence of carbonic acid withholding sodium from pyrosulphite.

That in the earlier stages of the process, when much carbonate is present, the normal sulphite plays a very small part in the sulphonation not only follows from the observation of its rapid increase in quantity at first but is also shown by its then nearly constant quantity for a long time though sulphur dioxide is still entering the solution and forming sulphonates. Only later, as the carbonate gets consumed, does the sulphite become an important factor in the sulphonation by freely becoming pyrosulphite, for then its quantity rapidly falls.

The part played by sulphite in the early stages being thus insignificant, we have to seek in the carbonates the source of the early considerable sulphonation of the nitrite. It would be unreasonable to assume, with acid carbonate present, that the normal carbonate takes part in sulphonation; equally so to assume that it remains inactive to sulphur dioxide. We are therefore compelled to recognise that sulphonation goes on only after conver-

tion of all carbonate *locally* present to acid carbonate and sulphite has been effected. Then the reaction that ensues is—



When all normal carbonate in the solution has been acidified by the carbon dioxide, the sulphite becomes as active as the acid carbonate and neither salt gets consumed before the other.

While it seems certain that first the sulphur dioxide converts the normal carbonate into normal sulphite and acid carbonate, and only then produces hydroximidosulphate by acting on the nitrite along with acid carbonate in the earlier stages and on both this and normal sulphite collaterally in the later stages, the experimental results show that local saturation must take place largely where the sulphur dioxide enters the solution, since so much sulphonate is produced along with the sulphite. In consequence of the activity of acid carbonate, local saturation becomes twice as difficult to prevent as when hydroxide is used in place of carbonate.

If in order to impede local saturation we slacken the rate of passage of the sulphur dioxide into the solution, we meet with a good amount of success. Thus, it was shown by the results of experiments already given, that the slower rate gave proportionately less sulphonate and more sulphite. But the effect of slowness in passing in the gas has its limit, in consequence of the continuous though slow interaction which takes place between nitrite, normal sulphite, and acid carbonate whereby sulphite disappears to give place to sulphonate. It follows that too slow as well as too rapid an addition of sulphur dioxide is unfavourable to the accumulation of sulphite, rather than of sulphonate, in the solution, and that a medium rate of supply is best for raising the proportion of sulphite.

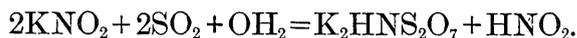
There remains to be explained the great variability in the commencement of precipitation of the acid carbonate. This takes place the sooner the faster the sulphur dioxide is blown into the solution. When it occurs in the earlier stages of the process, it is, therefore, accompanied by greater predominance than usual of production of hydroximidosulphate over production of sulphite. It does not however depend upon this, for while sulphur dioxide liberates a molecule of carbon dioxide in changing carbonate into sulphite, four mols. of it are needed to liberate one mol. of carbon dioxide in changing carbonate and nitrite into hydroximidosulphate.

An explanation is suggested by a consideration of the fact that when working the process at a moderate rate, the first crystallisation of acid carbonate takes place long after the point at which the solution must contain the maximum of the salt, at least potentially, the point, that is, when half the carbonate has become either sulphonate or sulphite. When it does occur the quantity of it in solution has become much less. Only where crystallisation is started early by a very rapid addition of sulphur dioxide, does the acid carbonate continue to separate out in much such quantity as it could do at the stage of the process reached. The cause in one word is supersaturation. The acid carbonate, it would seem, is slow to begin to precipitate from the solution while that is not charged with carbon dioxide. At a medium rate of working this only happens in the later stages, any normal carbonate and even much normal sulphite present keeping down the quantity of carbon dioxide, but by a rapid rate of working local saturation occurs and the acidified portion of the solution then crystallises. Once crystallisation has been started, it proceeds unchecked. In slower working when crystallisation only begins

late in the process, the amount of salt separating is small, and generally depends then for its existence upon its power to resist the action of acid sulphite in ice-cold solutions. The solution when, potentially at least, it is richest in acid carbonate, was found by us to crystallise soon, if left to stand in closed vessel, although sulphonation which is destructive of acid carbonate was slowly going on in it.

### III.—*f. Primary Action of Sulphur Dioxide upon a Nitrite.*

Solution of sulphur dioxide added to that of potassium or sodium nitrite produces a sulphate and either nitric or nitrous oxide, according as one or other of the interacting substances is in excess. That is the ordinary well-known result, but there are two ways of limiting the extent of the action so as to get either hydroximidosulphate and nitrous acid or the undoubted products of their transformation. By these ways, the interaction of sulphur dioxide and a nitrite is shown to be—



The more important way to thus limit the action is by an experiment first tried by Claus (*Ber.*, 1871, 4, 508; see preceding paper) which consists in adding an alcoholic solution of sulphur dioxide to excess of potassium nitrite in strong aqueous solution. For this experiment gives, as we have ascertained, potassium nitrito-hydroximidosulphate which precipitates and ethyl nitrite which boils off by the heat of the reaction:—



By becoming ethyl nitrite the nitrous acid is rendered inactive on the hydroximidosulphate, which is thus saved from oxidation.

The other way of tracing the earlier action of sulphur dioxide

upon a nitrite was found out by Raschig, when trying to prove another point (sect. IV. *a.*). He added the nitrite to excess of sulphur dioxide, both being in very dilute and well cooled solution, evaporated down and neutralised the solution with chalk, and again evaporated the filtered solution. After much potassium sulphate had crystallised out, potassium amidosulphate was finally obtained, as proof that hydroximidosulphate had been formed at an earlier stage. Our own experiments have yielded us an earlier product of the degradation of this compound.

At the time when Raschig published his observation, we published (*J. Ch. Soc.*, 1887, 51, 659) one of ours, that silver nitrite and mercurous nitrite, when decomposed by sulphur dioxide solution, yield a substance answering to the copper test for hydroxylamine. This we now know to be hydroxyamidosulphuric acid, but at the time we took it to be hydroxylamine itself. We have also found that, after adding a dilute solution of sodium nitrite to excess of a cooled solution of sulphur dioxide and then blowing out of the solution the residual sulphur dioxide by a current of air, enough hydroxyamidosulphate (hydrolysed hydroximidosulphate) is present to be easily identified by the copper test for it. A hydroxyamidosulphate is distinguishable from hydroxylamine in applying this test by finding that the mother-liquor of the cuprous oxide (which need not be filtered off) gives sulphurous acid when acidified (this *Journal* III, 225).

Though less successful than Claus's experiment, Raschig's method is serviceable for showing that the alcohol used in that, plays only a secondary part. While excess of nitrite is successfully used in that experiment, the sulphur dioxide must be in excess in Raschig's method. To understand this, it has only to

be remembered, firstly, that nitrous acid would oxidise hydroximidodisulphate at once, and secondly that sulphurous acid sulphonates the hydroximidodisulphate slowly enough to allow a little of it being secured in a hydrolysed state.

IV.—*a. Sulphonation of Nitrous Acid by Sulphurous Acid.*

Fremy believed that certain of his sulphazotised salts are formed in the first action of sulphurous acid upon nitrous acid. From this belief Claus strongly dissented, holding that the presence of a base (as salt) was essential to the production of these acids. Raschig considered that his experiment of treating potassium nitrite with sulphur dioxide in excess (sect. III. *f.*) proved the correctness of Fremy's belief; but that cannot be admitted since potassium is present in this experiment playing the part of base. It is, however, quite practicable to establish Fremy's belief and that no base whatever is necessary to bring about the formation of sulphazotised acids.

When a solution of sulphur dioxide, better ice-cold, is treated with a relatively small quantity of nitrous fumes passed on to its surface while it is being well agitated in a flask, and is then deprived of remaining sulphur dioxide by a rapid current of air, or even by quick boiling, it will give a good reaction for hydroxyamidodisulphuric acid with the copper test. A little deviation in the composition of the nitrous gas from that of nitrous anhydride is not of importance. If the object is only to get amidodisulphuric acid, the solution of sulphur dioxide is left to stand for a day after it has received the nitrous acid without expelling what is left of the sulphur dioxide. If it is then evaporated on the water-bath and further concentrated in the

vacuum-desiccator, the amidosulphuric acid will crystallise out from the sulphuric acid with which it is accompanied (this Journal, 9, 230). We have purified the acid by recrystallisation, and have hydrolysed it at  $150^{\circ}$ , by means of hydrochloric acid, into acid ammonium sulphate; we have also completely volatilised the acid by heat thus proving the absence of base accidentally derived.

Nitrosyl sulphate dropped into much excess of cooled solution of sulphur dioxide also yields the hydroxyamid sulphate reaction with copper sulphate and potassium hydroxide.

#### IV.—*b. Influence of the Base of the Nitrite or Sulphite.*

Although Fremy held that sulphurous and nitrous acids combine together, he did not believe that the resulting sulphazotised acids could be obtained in this way, because of their inability to exist in absence of a base. Moreover, he considered that a strong base is influential in bringing about the formation of these acids, even though he had had no success with such a base as sodium. The only hydroximidosulphates he could prepare, indeed, were those of potassium, but from ammonium nitrite he got the nitrilosulphate, and also obtained evidence that calcium, strontium, and barium nitrites are convertible into amidated sulphates.

We have just shown (sect. IV. *a.*) that the interaction of sulphurous and nitrous acids does not require the presence of any base at all for the actual production of sulphazotised acids, although such presence is essential to preserve unchanged the first product of the interaction. To serve this purpose some bases will doubtless be inferior to others, and those which do

not freely form soluble pyrosulphites are difficult to work with. Otherwise, the nature of the base seems to be a matter of indifference. Since the time of our early publications on the subject, we have extended our experiments to several other nitrites than those of sodium, mercurous, and silver, with the results we now record.

*Ammonium salts.*—Ammonium nitrite solution was prepared by triturating silver nitrite with its equivalent of ammonium chloride dissolved in about five times its weight of water, and filtering off silver chloride over the pump. To this solution, after it had been cooled in ice, was added a little less than its equivalent of ammonia-water which had just before been converted to sulphite by passing sulphur dioxide into it. More sulphur dioxide was then passed into the mixture until it reddened lacmoid-paper. In this way the ammonium nitrite was almost all sulphonated, without any evolution of gas having occurred till just at the last, when slight nitrous fumes appeared. Some of the solution was hydrolysed and tested then with copper sulphate and potassium hydroxide; it was thus shown to have contained abundance of ammonium hydroximidosulphate. Another portion of the solution not hydrolysed gave a large precipitation of dipotassium hydroximidosulphate on addition of potassium chloride.

*Barium salts.*—Some barium hydroxide was converted into sulphite by putting it in water and passing in sulphur dioxide; the barium sulphite was then, for the most part, brought into solution by passing in more sulphur dioxide. The product was added gradually to a solution of a little more than its equivalent of barium nitrite, which had been purchased of excellent quality.

Having neglected to cool our solutions we had reason to fear that our experiment was a failure; for along with very much precipitation there was a somewhat large evolution of nitrous gases. But for our purpose we had been amply successful. The solution was only faintly acid to litmus and remained so for hours. Both it and the precipitate contained large quantities of barium hydroximosulphate. The precipitate also contained sulphite and sulphate, the latter being the complement to the nitrous fumes produced. The hydroximosulphate was extracted from the precipitate by a solution of ammonium chloride.

*Calcium salts.*—A solution of calcium nitrate, free from magnesium, sodium, potassium, and other ordinary impurities, was heated with well-washed spongy lead until nitrogen oxides and ammonia began to form. The filtered, very alkaline, solution was freed from lead by hydrogen sulphide not used in excess, Calcium hydroxide was then removed by carbon dioxide. (it was interesting to find that, contrary to assertion, carbon dioxide cannot be used to precipitate lead in presence of calcium salt, since calcium precipitates before lead.) A solution of calcium sulphite in sulphurous acid was prepared just before use, in the same way as the barium salt had been, except that carefully prepared calcium carbonate took the place of barium hydroxide. With the calcium nitrite somewhat in excess of the calcium sulphite, the solution of the latter was gradually poured into the former, both solutions having ice floating in them at the time. No gas was given off and only a moderate quantity of precipitate was formed, which consisted of sulphite. The filtrate was neutral and contained the full quantity of hydroximosulphate expected.

*Zinc salts.*—Zinc nitrite solution was prepared by precipita-

ting zinc sulphate with barium nitrite and filtering. Zinc sulphite in solution in sulphurous acid was made from zinc oxide in water and sulphur dioxide. The two solutions, suitably proportioned and with ice floating in them were mixed. No gas came off, zinc sulphite precipitated, and the solution proved to contain zinc hydroximidosulphate present in it in large quantity.

*Mercurous salts and silver salts.*—Experiments, already referred to in sect. III. *f.* of this paper, sufficiently establish that mercurous and silver nitrites are readily sulphonated. It is now evident that the sulphonation of nitrites is a general reaction, essentially independent of the nature of the base, which only effects the preservation of the products. It is not the salts which are sulphonated but nitrous acid itself.

V.—*What Nitrous Acid becomes when Sulphonated.*

In the paper preceding this it has been established that neither the abundant experimental work of other chemists and ourselves nor theoretical considerations afford any support to the view that the double sulphonation of nitrous acid into a hydroximidosulphate occurs in two stages, or that a monosulphonated nitrous acid,  $\text{ON}\cdot\text{SO}_3\text{H}$  or  $(\text{HO})_2\text{N}\cdot\text{SO}_3\text{H}$ , must be the first product of its change. In the present communication it is shown that the acidity necessary for the sulphonation of a nitrite points clearly to the fact that it is in every case the acid itself, and not its salts, which is directly sulphonated. We are, therefore, in the position to affirm that the fundamental action in the formation of all Fremy's sulphazotised salts is the interaction between actual nitrous acid and a pyrosulphite, in which they unite always to form the one substance, the two-thirds normal hydrox-

imid sulphate corresponding to the pyrosulphite acting—  
 $\text{HONO} + (\text{SO}_2\text{K}) \cdot \text{SO}_3\text{K} = \text{HON}(\text{SO}_3\text{K})_2$ . The origin of all the other salts out of this salt has been traced, partly by others and partly by ourselves, and need not be gone over again here.

