XXXVI.—*On the Production of the Sulphates of the Alcohol-Radicals from the Nitrites by the action of Sulphurous Acid.*

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MR. MILES H. SMITH and myself, whilst working on the reactions of nitric and nitrous ether, observed that nitrite of amyl is very readily attacked by sulphurous acid, even when in aqueous solution, or when combined with ammonia, in the form of acid sulphite of ammonia.

When nitrite of amyl is added to strong aqueous solution of acid sulphite of ammonia, a very violent reaction takes place, gases are evolved, and neutral sulphate of ammonia is precipitated. The liquid product of the reaction is complex, nor do I know any method by which it may be resolved into its proximate constituents. The reaction with strong aqueous sulphurous acid is less violent. Free sulphuric acid is amongst the products, nitric oxide is evolved, and again a complex liquid product is formed.

When sulphurous acid gas is passed into nitrite of amyl it is rapidly absorbed. The nitrite changes in colour from yellow to green, from green to blue; it then begins to effervesce, and at the same time becomes very hot and boils violently. Nitric oxide is evolved in abundance, and a yellow liquid product remains; this liquid cannot be distilled without decomposition; it contains no nitrogen. When an attempt is made to distil it with water, the oily liquid found in the distillate consists principally of amylic alcohol. When the liquid is distilled *per se* it blackens, gives off sulphurous acid, and yields a complex distillate, which contains, amongst other things, valerianate of amyl.

From the above it will be obvious that any attempt to obtain an insight into the nature of the reaction, by an examination of the liquid product, was very unpromising; I therefore determined to attack the subject quantitatively. With this object I determined the nature and amount of the gas evolved by the action of excess of sulphurous acid on a known weight of the nitrite. The result proved that the gas evolved consisted of pure nitric oxide, and that the whole of the nitrogen present in

the nitrite escaped in this form. The details of this and all other determinations mentioned in this paper will be found in an appendix at the end. I also determined the amount of sulphurous acid required to decompose a given quantity of the nitrite. This determination was made by observing the quantity of sulphurous acid which disappeared when an excess of sulphurous acid acted on a known quantity of nitrite. The result proved with sufficient accuracy that one atom of sulphurous acid acted upon two atoms of nitrite of amyl, and liberated two atoms of nitric oxide. Lastly, the alteration of weight which nitrite of amyl undergoes by the reaction was determined. This result confirms the supposition that the reaction consists in the replacement of two atoms of nitric oxide by one of sulphurous acid. The result may, therefore, be formulated as follows :—

The resulting liquid compound had, therefore, the composition of neutral sulphate of amyl.

To prepare it, nitrite of amyl is placed in a retort, the beak of which points upwards, and is adapted to an inverted condenser, so that any liquid which may be volatilized and condensed will return to the retort. To the tubular of the retort a cork and bent tube are adapted, so that the end of the tube dips beneath the surface of the nitrite; pure dry sulphurous acid gas is now passed into the liquid, and the retort gently warmed to start the reaction. If the warming be omitted the sulphurous acid is absorbed for some time, without any reaction occurring, but when the reaction does start it is with almost explosive violence, whereas if the liquid be warmed at first, the reaction starts at once, and proceeds regularly and evenly. When the effervescence which accompanies the reaction has quite ceased, the retort should be heated in a water-bath, the stream of sulphurous acid being still continued; lastly, the stream of sulphurous acid is to be discontinued, and a stream of carbonic acid or hydrogen substituted for it; this serves to expel the excess of sulphurous acid. It is desirable to fill the retort and condenser with carbonic acid before commencing to pass the sulphurous acid; the advantage of this is that the air, the oxygen of which would unite with the nitric oxide and

sulphurous acid, is expelled. The liquid product of the reaction is of a straw-yellow colour, and somewhat syrupy consistence. It may be heated up to about 110° C. without showing any signs of alteration, but if kept for any length of time at a temperature somewhat above this, it begins to blacken, and soon decomposes with an appearance of ebullition. As before stated, it cannot be distilled in any way; it is very readily decomposed by water; if boiled with water for a few hours it is completely resolved into amylic alcohol and sulphuric acid; long standing with water in the cold produces the same result. I do not think it can even be washed without decomposing to a greater or less extent. Boiled with caustic soda it yields amylic alcohol and sulphate of soda. Treated with strong hydriodic acid it yields sulphuretted hydrogen, water, free iodine, and iodide of amyl. Bichromate of potash and sulphuric acid cause it to yield valerianic acid. Its leading characteristic in short is, its extreme readiness to split up into sulphuric acid and amylic alcohol in presence of the elements of water. Its specific gravity is somewhat less than that of water.

Sulphurous acid and nitrite of butyl react upon each other in a manner precisely analogous to that of sulphurous acid and nitrite of amyl, but the resulting product is even more unstable, blackening at the heat of the water-bath. The product has not been examined in detail, but it appears to react in a manner strictly analogous to the corresponding amyl compound.

Nitrite of ethyl and sulphurous acid do not very readily react upon each other, at least at the common temperature. There are numerous practical difficulties, chiefly connected with the extreme volatility of the nitrite, in operating at a higher temperature, and I have not yet had the time or opportunity to overcome them.

The first point which suggests itself in considering the foregoing results is this—are these compounds properly speaking sulphates of alcohol-radicals, or are they only isomeric therewith? The reaction of the amyl compound with water is very different from that ascribed to neutral sulphate of ethyl under similar circumstances, but is strictly analogous to that of neutral sulphate of methyl.

It would obviously be of great interest to compare the sulphate of ethyl obtained from nitrite of ethyl and sulphurous acid with that obtained from ether and anhydrous sulphuric

acid; at any rate it is beyond all doubt that the sulphate of amyl, prepared from the nitrite, does not form any acid analogous to the isethionic acid when it is boiled with water; it splits up entirely into sulphuric acid and amylic alcohol, as a determination in the appendix will fully prove.

The question of the possibility of isomerism among sulphates of alcohol-radicals dependent on differences in linking the constituents together, is one which has now to be considered. I may leave on one side all cases of isomerism dependent on the existence of isomeric organic radicals. Representing our alcohol radical by R then, and assuming sulphur and oxygen to be both diatomic elements, and that there is no difference in the value of the two "bonds," or attaching powers, which they each respectively possess, it will be apparent that two very distinct compounds may exist; in one both the molecules of organic radical are linked to oxygen directly, and by oxygen to sulphur; in the other one of the radicals is attached directly to sulphur, and the other indirectly through the oxygen. They may be formulated as follows; the former would be:—

and the second

It may, I think, be safely predicted, that whatever be the formula of the sulphate of ethyl produced by the action of anhydrous sulphuric acid on ether, the formula of the sulphate of amyl prepared from the nitrite, resembles the first of the above formulæ, that is, the amyl is linked to the sulphur by oxygen, and not directly. In the case of the sulphate of ethyl, I should incline to the opposite belief: for it is difficult to see when ether, itself a perfectly saturated body, unites with a diatomic body, how it can do so without splitting into a peroxide of ethyl, and ethyl.

Now, if peroxide of ethyl and ethyl were to attach themselves to a diatomic body, the one would obviously be directly attached, and the other attached by its oxygen. Now the radical SO_3 is a diatomic radical, and we have no reason whatsoever for supposing that when it unites with other bodies the point of union is alone on the side of the oxygen. With at least equal probability we may assume that it unites both by

its sulphur and by its oxygen. Now let us further assume that the ethyl of the ether goes direct to the sulphur, and the oxide of ethyl to the oxygen, we should then have a body of the second formula—

Now if a body of this kind were acted upon by water, it would naturally split up into isethionic acid and alcohol; it would in fact be no sulphate of ethyl at all, but isethionate of ethyl. It is not, however, necessary to assume that the whole of the ethyl produced by the splitting up of the ether shall go to the sulphur, and the whole of the oxide of ethyl simultaneously produced to the oxygen; they may, and probably do, unite somewhat irregularly. If I may use so materialistic an expression, they may unite just as they happen to come in contact, and in this case we should obtain a mixed body, which would present precisely the reactions ascribed to sulphate of ethyl. This view of the case derives considerable support from the fact already mentioned, that sulphate of methyl resembles the above-described sulphate of amyl in its reactions, and not the sulphate of ethyl, for sulphate of methyl is formed direct from methylic alcohol, that is, from oxide of methyl plus hydrogen; the methyl is therefore, most probably, united to the sulphur by oxygen.

APPENDIX.

The nitrite of amyl used in the following investigation was carefully prepared from pure amylic alcohol. It boiled constantly, and I have every reason to believe was perfectly pure.

The determinations of the amount of sulphurous acid absorbed by a given quantity of the nitrite, of the amount of nitric oxide evolved, and of the weight of the resulting liquid, were all made in one and the same operation. Preliminary experiments had been made in which one or other of these points had been roughly ascertained.

I constructed an apparatus represented in the annexed wood-cut. The tube, *b b*, was made of light thin glass. It was expanded into the bulb, *a*, and fitted into the vessel, *h h*, by an india-rubber joint, which, though water-tight, could be readily dismounted. The mouth of it was closed by a tightly-fitting cork, through which passed two narrow glass tubes, the one,

ff, reaching to the bottom of the bulb, the other, *gg*, only passing through the cork. Both tubes were perfectly straight. To use the apparatus, the tube, *bb*, was first detached from *hh*,

APPARATUS employed to determine the amount of NITRIC OXIDE evolved from NITRITE of AMYL by the action of SULPHUROUS ACID, and the amount of sulphurous acid absorbed by the nitrite.

filled with carbonic acid, and, together with the tubes, *ff* and *gg*, was carefully weighed. Next a small quantity of nitrite of amyl was introduced by means of a very fine funnel through *ff*, and the tube *bb*, was weighed again. The difference gave the weight of nitrite of amyl employed. Next the tube was reconnected with *hh*, and *hh* filled with ice and salt. *ff* was now connected by means of an india-rubber tube with *c*, a stout sealed tube drawn off to a very fine point, and containing liquefied sulphurous acid. It had previously been carefully weighed. It also was surrounded by ice and salt. The tube, *gg*, was connected with the delivery-tube which dipped under the surface of a mercury-bath, over which was inverted the cylinder, *d*. *d* had been entirely filled with mercury and inverted into the trough, then water had been let up into it, and, finally, oxygen; so that it was about half-full of the gas, and about

one-half of the remaining space was occupied by water, the other by mercury. Matters being disposed as here described, the point of the sealed tube, *c*, was broken off inside the india-rubber tube, and the ice and salt removed from around it. The liquefied sulphurous acid soon began to vapourize. As soon as this was the case, the bulb, *a*, containing the nitrite was warmed over a spirit lamp. The reaction soon started, and proceeded quite regularly and smoothly to its close; though it was obviously completed long before all the sulphurous acid was evolved. The tube, *b b*, surrounded by ice and salt, proved a most efficient condenser. Of course, the sulphurous acid was in great excess. It therefore swept all the nitric oxide evolved into *d*, where, meeting at once with oxygen and water, it was rapidly converted into nitric acid, the sulphurous acid at the same time being converted into sulphuric acid. More oxygen was from time to time passed into *d*. When the evolution of sulphurous acid from *c* had quite ceased, *c* was removed, together with the little piece of glass broken off in opening it, and both together weighed. The difference between this weight and their weight when full gave the quantity of sulphurous acid employed. Next a stream of carbonic acid was sent through the pipe, *f f*, so as to drive all the gases evolved out of the apparatus and into *d*. The tube, *b b*, was then detached from its connections and weighed. The difference between this weight and its former weight indicated the difference of weight caused in the nitrite by the reaction. Lastly, the mixed nitric acid and sulphuric acid in *d*, were determined by neutralization of one-fourth of the aqueous contents of *d* with carbonate of baryta. Of course nothing but nitrate of baryta remained in the solution. The excess of carbonate of baryta, together with the sulphate of baryta formed, was filtered off and well washed, the washing being added to the filtrate, which latter was evaporated to dryness and the dry residue weighed. In another fourth of the liquid the amount of sulphuric acid was determined by precipitation as sulphate of baryta. Calculating the quantity of sulphurous acid unused from the quantity of sulphate of baryta found, and deducting this from the known weight of the sulphurous acid taken, the difference will represent the sulphurous acid used. From the quantity of nitrate of baryta it is easy to calculate the quantity of nitric oxide evolved. The following are the details of this operation:—

Nitrite employed.....	5.44	grms.
SO ₂ taken.....	3.894	„
Residue in A after operation.....	5.521	„
Nitrate of baryta yielded by one-fourth of the aqueous contents of <i>d</i>	1.495	„
Sulphate of baryta from ditto	2.216	„

From these numbers the following amounts of sulphurous acid consumed and nitric oxide liberated may be calculated. They are given in per cents. of the nitrite taken :—

NO found.	SO ₂ used.	Residue, supposed sulphate of amyl.
25.27	26.82	101.49 per cent.

Now, if the reaction proceeded according to the equation on page 416, it would have required the following percentages :—

NO required.	SO ₂ required.	Sulphate of amyl required.
25.64	27.35	101.71

It will be observed that the quantities both of nitric oxide found, and of sulphurous acid used, are slightly smaller than those required by theory. This would obviously be the case if a small quantity of the nitrite were volatilized with the escaping gases, and, despite every precaution, a very minute quantity of the nitrite would be sure to escape in this manner. Even not taking this fact into account, the accordance between the observed and calculated numbers is as close as that furnished by any of the common methods of analysis, and is at the same time very far indeed from corresponding with any other interpretation of the reaction.

A determination of the amount of sulphuric acid liberated by digesting the sulphate of amyl with water was made. The sulphate was sealed up with about fifty times its own volume of water in a capacious glass tube; the lower part of the tube was heated by a boiling saturated salt-bath for about six hours. It was then opened, its contents transferred to a flask, rinsed out, and the rinsings also put into the flask, and the whole boiled for a few minutes to expel the amylic alcohol. It was then precipitated with chloride of barium, and the sulphate of baryta so obtained weighed.

Sulphate of amyl taken.	1.143	gram.
Sulphate of baryta found	1.1113	„

This indicates that the liquid has yielded 40.06 per cent. of SO_4 . Sulphate of amyl should contain 40.34. It is therefore obvious that no part of the sulphate can have been converted into compounds analogous to isethionic acid.

NOTE appended Nov. 29th, in consequence of some doubts being expressed at the Chemical Society when the paper was read, as to the accuracy of the method of estimation adopted.

The method of estimating nitric oxide and sulphurous acid mentioned in the text, was experimentally investigated before being employed. The points investigated were, whether the presence of mercury interfered with the estimation; whether the presence of sulphurous acid interfered; and whether the process gave trustworthy and constant results. The result was to prove that if care were taken always to keep a large excess of oxygen and a large volume of water present throughout the whole of the process, neither the presence of sulphurous acid, nor that of mercury interfered in any way. If but little water is present the process is not trustworthy as far as concerns the nitric oxide, but the sulphurous acid determination may still be depended upon. It is necessary that the water employed should be a little above the ordinary atmospheric temperature, and that sufficient time be allowed to complete the reaction. It is desirable to let the apparatus stand in a warm room over night before completing the determination. This is not the place for a detailed account of trial experiments; I will therefore only say that I have operated on known quantities of nitric oxide under the circumstances indicated, and have arrived at the conclusion that the method described in the text may be implicitly relied on to yield results not more than $2\frac{1}{2}$ per cent. from the truth. The error is always in deficit, and seldom reaches 2 per cent. The nitric oxide was obtained in measured quantities by acting on known weights of nitrate of potash with excess of an acid solution of proto-sulphate of iron.