XXIX.—*Conversion of Pelouze's Nitrosulphates into Hyponitrites and Sulphites.*

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In the first year of this century, Davy obtained indications of the existence of a potash salt of nitrous oxide or, in other words, of a potassium hyponitrite. Long afterwards, but still fifty years ago, Pelouze found these indications to be due to the formation of a potassium salt of nitrogen, sulphur, and oxygen—potassium nitrosulphate. It is now our fortune to be able to show that Davy, no less than Pelouze, was essentially right, inasmuch as we have succeeded in proving that Pelouze's salt is a hyponitrite compound—the *potassium hyponitrososulphate* or, more simply, *nitrososulphate.**

Conceiving that nitrososulphates would have a constitution allied to that of a sulphate or thiosulphate, instead of the strange one given to them in which the nitric oxide stands as two additions to the radicles already carried by the sulphur of the sulphites, we have put our view to experimental test. The result of this has been that the current opinion as to the nature of these salts can no longer, we think, be upheld, unless it rests on other grounds than that of the want of a better.

The formation of a nitrososulphate is like that of a thiosulphate, with nitric oxide substituted for sulphur; and now we have found that, just as a thiosulphate when treated with sodium becomes sulphite again and sulphide, so a nitrososulphate becomes sulphite again and hyponitrite. We are therefore justified in expressing nitrososulphates and their decomposition in the following manner:—

$$(SO_3K).(N_2O_2).K + 2Na = (SO_3K)Na + Na(N_2O_2)K.$$

The experiment was carried out by treating pure potassium nitrososulphate in a concentrated solution of potassium hydroxide with sodium amalgam for many hours. This caused no sensible rise in temperature, very little evolution of gas, and a very slow decomposition of the salt. The potassium hydroxide, as it is known to do, protected the sodium from the action of the water, although it was also the means of greatly impeding the reduction of the nitrososulphate, because of the slight solubility of this salt in a strong solution of

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* The latter slight modification of the old name, already in partial use, seems sufficient for all purposes. The salt might perhaps be called *sulphuric hyponitrite;* but it cannot, without confusion, be styled, as it has been, a *sulphonate*, since it contains metal outside the group SO_3K.

alkali. The hydroxide, however, could not have been dispensed with, as it was needed in order to preserve the hyponitrite when formed, and thus secure the presence of this in quantity. Together with the sulphite and hyponitrite, some hydroxylamine and a very little ammonia were generated. The hydroxylamine very soon ceased to increase in amount, probably in consequence of its being decomposed continuously by the strong alkali and yielding the ammonia.

When the action of the sodium was completed, the liquid was found to give a series of strikingly varied reactions with a solution of silver nitrate. At first there was a black precipitate of suboxide of silver produced by the hydroxylamine; then, this having been removed, brown precipitates of silver oxide appeared, dissolving in their mother-liquor on agitation; next came a bright yellow precipitate of silver hyponitrite; after this, silver oxide again, now no longer dissolving on shaking; and, lastly, a white precipitate of silver sulphite. The nature of the yellow and white precipitates was fully verified by appropriate tests.

The behaviour of the hyponitrite in this precipitation was exceptional, in that its silver salt took so long to appear. Some experiments with silver hyponitrite and potassium sulphite showed us the reason of this. Silver hyponitrite dissolves freely, like other silver salts, in potassium sulphite solution, and if silver nitrate is added to this solution when saturated, silver hyponitrite is reprecipitated before silver sulphite begins to come down. The following equations show what takes place :—

$$\begin{aligned}
&(1.)\ (AgNO)_2 + 2K_2SO_3 = (KNO)_2 + 2AgKSO_3\\
&(2.)\ (KNO)_2 + 2AgNO_3 = (AgNO)_2 + 2KNO_3\\
&(3.)\ AgKSO_3 + AgNO_3 = Ag_2SO_3 + KNO_3.
\end{aligned}$$

The hydroxylamine which here, as always, accompanies the hyponitrite at its formation, may be represented as coming from the hyponitrite or the nitrososulphate by a process of hydrogenisation :—

$$(SO_3K).(N_2O_2).K + 6Na + 6OH_2 = (SO_3K)Na + 2H_2NOH + KOH + 5NaOH.$$

The nitrososulphate which we used for our experiments was both analysed and tested qualitatively. On decomposing a quantity of it weighing 1·4222 gram by slightly acidifying its solution with hydrochloric acid, evaporating, igniting, moistening with sulphuric acid, and again igniting (in order to transform a little chloride produced during the evaporation with hydrochloric acid), a quantity of potassium sulphate was obtained corresponding with 79·27 per cent. Calculation indicates 79·82 per cent. The salt analysed was only air-dried and was slightly damp. Some of it left in a desiccator for 16 hours lost weight and gave 79·91 per cent. sulphate; as thus prepared, although dry, it contained a little sulphate, which it did not when only air-dried. Further exposure of the dry salt in the desiccator caused no further loss in weight.

In connection with the decompositions of the nitrososulphates described in this paper, it is material to note some points in the properties of these salts. A solution of nitrososulphate, free from either sulphite or nitrite, does not affect an acidified solution of permanganate. Our preparation was certainly free from both these salts when used. When heated moist, nitrososulphate gives off nitrous oxide, as Davy observed, and becomes sulphate with no trace of sulphite. When heated dry, it changes to nitric oxide and sulphite again, as observed by Pelouze.

The attempts we have made to reconvert hyponitrite and sulphite to nitrososulphate by the use of iodine, in imitation of Spring's reactions, have been failures hitherto.