CXIII.—*Economical Preparation of Hydroxylamine Sulphate.*

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IN 1887, Raschig made known that hydroxylamine can be got from a nitrite by sulphonation followed by hydrolysis, and took out patents for its manufacture in this way. As to what extent these patents may have since been worked, and with what success, we have no information; but we cannot believe that this process has been advantageously carried out, unless the directions he gave have been greatly modified. The one we are about to describe is very productive and economical for the preparation of hydroxylamine sulphate, a non-deliquescent salt readily forming large crystals, and soluble in three-quarters of its weight of water at 20°.

Commercial sodium nitrite of 95 per cent. nitrite does not contain more than 1 per cent. of objectionable matters, such as chloride and nitrate, and is, therefore, pure enough. A concentrated solution of this salt (2 mols.), and of sodium carbonate (1 mol.), pretty closely adjusted in these proportions, is treated with sulphur dioxide until just acid, while it is kept well agitated at 2—3° below zero by immersion in ice and brine; at this temperature, the conversion of the nitrite into oximidosulphonate appears to be perfect. When gently warmed with a few drops of sulphuric acid, the oximidosulphonate rapidly hydrolyses, with marked rise of temperature, into oxyamidosulphonate and sodium hydrogen sulphate. The solution of these salts is kept at 90—95° for two days, by the end of which time all the oxyamidosulphonate will have hydrolysed into hydroxylamine sulphate and sodium hydrogen sulphate; the quantity of ammonium salt produced is so small that it can only be detected in the very last mother liquor of crystallisation, using platinic chloride (potassium hydroxide being an unsuitable reagent in presence of hydroxylamine). At 80—85°, five days are necessary, but then practically no ammonia is formed; at 70°, three weeks, at least, are necessary; whilst at the common temperature much oxyamidosulphonic acid remains unchanged after several months, even when much sulphuric acid has been added. On the other hand, the solution kept boiling needs only seven or eight hours usually to deprive it of all sulphonate, bu the effect of the boiling on the hydroxylamine is disastrous, destroying at least one-third of it, by converting it (through amidosulphonic acid?) into ammonia, and wasting another third as a practically inseparable mixture of its sulphate with ammonium sulphate.

To make sure that all sulphonate has been hydrolysed, it is well to add barium chloride in excess to a little of the solution, filter and boil the filtrate with potassium chlorate, to convert any sulphonate into sulphate. When the change is complete, the solution is neutralised with sodium carbonate, using methyl-orange as indicator, and evaporated until it weighs only $10\frac{1}{2}$—11 times as much as the sodium nitrite taken; if now left to cool where its temperature will fall to 0°, or below, nearly all the sodium sulphate will crystallise out, and the mother liquor, on being evaporated sufficiently, and allowed to cool to the common temperature, yields much hydroxylamine sulphate, the mother liquor from which, very slightly diluted and cooled below 0°, gives again a little sodium sulphate, and can then be worked for more hydroxylamine sulphate, as before.

The crude hydroxylamine sulphate weighs about 9 parts for every 10 parts of sodium nitrite taken. It needs to be recrystallised, but the mother liquors can be closely worked up. On the other hand, the sodium sulphate recrystallised, or even washed with ice-water, will give up 1 part more of hydroxylamine sulphate; so that sodium nitrite will yield, on the small scale, nearly its own weight of pure hydroxylamine sulphate. No doubt, on the large scale, the theoretical yield of 118·84 per cent. could be more nearly approached.

Potassium nitrite is not well fitted for the preparation of hydroxylamine, because of the difficulty experienced in closely separating the hydroxylamine sulphate from that of potassium. After several recrystallisations, the hydroxylamine salt still contains 1·8 per cent. of potassium sulphate. The addition of aluminium sulphate is not an improvement, for then the hydroxylamine sulphate, separated as far as practicable from the potassium alum, leaves behind, on ignition, 5·7 per cent. of residue.

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