

as ozone, for upon ignition of the salt a gas was evolved which liberated iodine from potassium iodide. Hence, there is no doubt whatever that pertungstate of sodium was formed, and although the isolation of this substance was not accomplished, the preparation of the compound by this method is of great importance, as it shows an additional analogy to exist between tungsten and sulphur, the second member of this group.

While pursuing this work, a modification of this process suggested itself as an admirable means of preparing meta- or paratungstate of potassium or sodium. The only change necessary for the accomplishment of this result appears to be the elimination of the acid, and the use of a graduated beaker for the outer vessel. A definite quantity of the normal salt is introduced into the bulb. The diaphragm prevents the contamination of the outer liquid with sodium tungstate, as it was found that it did not permeate the membrane. Definite portions of the solution of the alkali may be removed from time to time, and titrated with normal acid until the requisite amount of alkali has been separated. The ozone present may be removed by heating from 200° to 400°. The crystals are dissolved and transformed into barium meta- or paratungstate by the addition of barium chloride.

The accuracy of this theory will be determined in the near future. From a theoretical standpoint, it appears to be better suited for the preparation of the salts mentioned than the methods now employed.

[CONTRIBUTIONS FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 37.]

OBSERVATIONS ON DERIVATIVES OF ACONITIC ACID.

BY D. C. HANNA AND EDGAR F. SMITH.

Received January 5, 1899.

I. ACTION OF PHOSPHORUS TRISULPHIDE UPON ACONITIC ACID.

A CONITIC acid was prepared by the method of Hentschel.¹ One hundred and sixty-eight grams of it were then converted into the sodium salt, and portions of forty grams of this salt and eighty grams of phosphorus sulphide were intimately

¹ *J. prakt. Chem.* [2], 35, 205.

mixed and heated in a distilling bulb. The vapors which were evolved, were conducted into water. This aqueous solution had an odor resembling that of naphthalene. Sodium hydroxide was mixed with it and steam was then conducted through the solution. Small quantities of a rather heavy oil passed over with the aqueous vapor. It was extracted from the water with ether. The ethereal solution was dehydrated with calcium chloride. The oil remaining after distilling off the ether weighed 0.2980 gram. Its alcoholic solution was mixed with an alcoholic solution of picric acid, when crystals separated which were identical with those of the picric acid derivative of thiophene, obtained by V. Meyer.¹

As the preceding method did not yield the thiophene in very great abundance we mixed and distilled ninety grams of aconitic acid with 180 grams of phosphorus sulphide. The resulting vapors, as before, were conducted into water. A gentle heat was sufficient to start the reaction, which then proceeded with considerable violence. Much hydrogen sulphide was liberated. The distillate was again mixed with sodium hydroxide and steam was conducted through it. An oil passed over and was removed from the water with ether. It proved to be thiophene and weighed 0.6975 gram. This is practically about the same yield of thiophene as was obtained by V. Meyer on distilling citric acid with phosphorus sulphide. Our product boiled at 225°, while Meyer records the boiling-point of the purest thiophene, made from citric acid at 224°-226°.

The second method seems on the whole preferable to the first method. Two grams of our thiophene were dissolved in a little absolute alcohol, and to this solution were added two and five-tenths grams of picric acid in alcoholic solution. The characteristic yellow-colored picric acid derivative immediately crystallized out. The dried compound melted at 133°. It has the formula $C_6H_4S_2 \cdot C_6H_3O(NO_2)_3$. Portions of it were analyzed.

1. 0.2078 gram of the yellow crystals was oxidized with concentrated nitric acid. The sulphur, weighed as barium sulphate, equaled 0.0359 gram = 17.28 per cent. sulphur, instead of 17.34 per cent. sulphur.

¹ Die Thiophen Gruppe, p. 250.

2. A nitrogen determination was made by the Kjeldahl method.

0.1972 gram substance gave 0.0221 gram of nitrogen = 11.20 per cent. nitrogen instead of 11.38 per cent. nitrogen required. The picric acid derivative gave a dark purple-red color with a warm solution of isatine.

II. ACTION OF PHOSPHORUS TRICHLORIDE UPON A CITRIC ACID ESTER.

Conen¹ allowed phosphorus trichloride to act upon triethyl citric ester and obtained, as he thought, triethyl aconitic ester. In the last edition of Beilstein's "Organic Chemistry", Vol. I, p. 817, in the description of triethyl citric ester the following statement occurs: "damit identisch (?) ist das Produkt aus Citronensäuretriaethyl Ester und PCl_3 bei 100° ."

We prepared pure triethyl citric ester, boiling at 270° (295 mm.), and heated eleven grams of it in a sealed tube with four grams of phosphorus trichloride. The temperature of a water-bath was employed in heating the mixture. On opening the tube its contents were transferred to a distilling bulb and subjected to distillation under 295 mm. pressure. The fraction passing over at 252° was collected and redistilled. The boiling-point remained constant. The product was a heavy, colorless oil. It boiled at 274° - 275° at the ordinary pressure, while triethyl citric ester under similar conditions boiled at 294° .

This oily liquid was taken up with water and boiled with barium hydrate. The excess of barium was removed with carbon dioxide and the filtrate concentrated. A hard glue-like mass, consisting of plates, separated. In every respect this salt was identical with barium aconitate. The acid liberated from it separated in forms like these of aconitic acid, and agreed with the latter in all of its physical properties. It dissolved very readily in anhydrous ether, thus proving that citric acid was absent as the latter is insoluble in this solvent. The evidence here presented supports the view that phosphorus trichloride converts triethyl citric ester at 100° into triethyl aconitic ester.

UNIVERSITY OF PENNSYLVANIA.

¹ *Ber. d. chem. Ges.*, 12, 1655.