

As was shown by experiment, absolute alcohol could not be used in place of ether or benzene. Its affinity for water is much stronger than that of silicon dioxide, and dehydration began long before the removal of the water mechanically present.

Orthosilicic acid, as obtained above, is an amorphous white powder, perfectly dry to the touch, which may be preserved indefinitely in hermetically closed vessels, but loses its water of hydration steadily on exposure to the air, and especially when in contact with absorbent media.

As examples of this latter property the following analyses were made of (A) samples taken from cakes just dried, and (B) of samples taken from the same cakes, after being pressed for five to ten minutes longer between sheets of filter paper.

No.	Water.	
	A. Per cent.	B. Per cent.
1.....	37.02	37.01
2.....	37.50	37.30
3.....	38.02	34.42
4.....	37.01	36.95
5.....	37.31	33.30
6.....	36.50	36.40
7.....	36.60	36.10
8.....	37.50	36.40

It is probable that in all our experiments a slight loss of water of hydration occurred before the ether or benzene was completely removed by contact with bibulous paper, as the average of the analytical results is slightly below the theoretical figure, 37.5.

The existence of the orthosilicic acid as a definite body may be therefore considered as established.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

LIV.—DERIVATIVES OF BENZENESULPHONIC ACID.

BY T. H. NORTON.

Received August 27, 1897.

IN connection with a general study of the derivatives of benzenesulphonic acid,¹ carried on in this laboratory, the material for the two following notes was collected.

PREPARATION OF BENZENESULPHONIC BROMIDE.

The only recorded method of preparing the substance is that

¹ Norton and Schmidt: *Am. Chem. J.*, 10, 136; Norton and Westenhoff: *Ibid.*, 10, 129.

given by the discoverer, Otto,¹ and consists in warming together bromine and benzenesulphonic acid. As the preparation of the latter compound involves the use of benzenesulphonic chloride, it seemed desirable to devise a shorter and simpler method for obtaining the bromide, as well as to determine some of its constants. In looking over the brief list, as given in Beilstein's Organic Chemistry, of sulphonic bromides thus far known, most of which we owe to Otto, it will be seen that the corresponding sulphonic acid is almost unvariably used. Experiment showed that satisfactory results could be obtained by treating dry sodium benzenesulphonate with phosphorus pentabromide. The latter was employed either in the solid form or dissolved in carbon disulphide. The former method gave the best yield. In either case the perfectly dry sulphonate was well rubbed in a mortar with the pentabromide. Considerable heat was involved. On adding the product to water, the benzenesulphonic bromide, $C_6H_5SO_2Br$, separated out in the form of a heavy liquid, colored red from free bromine. It was well washed with water, and dried in contact with calcium chloride. Several preparations were made, but in no case was the yield over one quarter of the theoretical.

Thus prepared, the bromide is a colorless liquid, frequently with a faint reddish tinge, of an oily appearance, with a sharp penetrating odor. Its specific gravity is 1.693 at 21°. It distils at 140°-141° (uncor.) with slight decomposition.

An analysis by Carius' method gave :

	Found.	Theory.
Bromine.....	35.02	36.20

BENZENESULPHONATES OF THE ALKALINE METALS.

Although two of these salts are used technically, none of them have been subjected to careful analysis or examination.

Sodium Benzenesulphonate, $C_6H_5SO_3Na$. This salt was prepared by adding an aqueous solution of sodium carbonate to an aqueous solution of barium benzenesulphonate until the point was exactly reached, at which no further precipitate was formed. The filtered solution of the sodium benzenesulphonate was evaporated to the point of crystallization. It crystallizes in the form of small, white, anhydrous leaflets. It melts with some decomposi-

¹ Otto: *Ann. Chem.* (Liebig), 341, 373.

tion at about 45° . It is insoluble in ether and benzene, and but slightly soluble in alcohol. It dissolves in 1.75 parts of water at 30° and in 0.8 part of boiling water.

Analysis.—The salt dried to constant weight over sulphuric acid *in vacuo*, lost no weight on heating to 135° .

0.3624 gram of the dried salt gave 0.1423 gram $\text{Na}_2\text{SO}_4 = 0.046$ gram Na = 12.72 per cent.

	Theory.	Found.
Sodium	12.77	12.72

Potassium Benzenesulphonate, $\text{C}_6\text{H}_5\text{SO}_3\text{K}$.—This salt was prepared in the same way as the sodium salt, potassium carbonate being used. It crystallizes ordinarily in long, delicate, colorless needles, with a silky luster, united frequently in radiated clusters. Long flat prisms are obtained by very slow evaporation. The salt is anhydrous and melts at about 408° . It is insoluble in ether and benzene, and nearly insoluble in alcohol. It dissolves in 0.66 part of water at 30° , and in 0.29 part of boiling water.

Analysis.—The salt dried to constant weight over sulphuric acid *in vacuo*, lost no weight on heating to 115° .

0.2567 gram of the dry salt gave 0.1121 gram potassium sulphate = 0.05 gram potassium = 19.58 per cent.

	Theory.	Found.
Potassium.....	19.90	19.58

Ammonium Benzenesulphonate, $\text{C}_6\text{H}_5\text{SO}_3\text{NH}_4$.—This salt was prepared in a manner similar to those above described, ammonium sulphate being used in the precipitation of the barium salt. Crystals are obtained with difficulty on account of the deliquescent nature of the salt. When prepared in a vacuum, over sulphuric acid, they show a radial structure with pearly luster, but are poorly defined. The salt begins to decompose at 236° and melts at 256° . It is soluble in 1.02 parts of cold water and in 0.31 part of boiling water. It dissolves in five and two-tenths parts of cold alcohol and in three and one-tenth parts of boiling alcohol, but is insoluble in ether and benzene.

Analysis.—The salt dried over sulphuric acid *in vacuo*, lost no weight at 105° .

One-half gram of the dry salt gave by the potassium chlorate

method, 0.652 gram barium sulphate, or 0.0895 gram sulphur = 17.87 per cent.

	Theory.	Found.
Sulphur.....	18.28	17.87

Lithium Benzenesulphonate, $C_6H_5SO_3Li$.—This salt was prepared in the same way as the sodium salt, lithium carbonate being used. It crystallizes in stellate groups of delicate, white, anhydrous needles. It melts at a dull red heat. It is soluble in 1.02 parts of water at 30°, and in five-tenths part of boiling water, in one and five-tenths parts of cold alcohol, and in nine-tenths part of boiling alcohol. It is insoluble in ether and benzene.

Analysis.—The salt dried over sulphuric acid *in vacuo*, lost no weight at 105°.

0.3032 gram of the dried salt gave 0.1032 gram lithium sulphate, or 0.013 gram lithium = 4.27 per cent.

	Theory	Found.
Lithium.....	4.26	4.27

I am indebted to H. C. Buell and H. E. Newman for aid in these determinations.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI]

LV.—ON A SOLUBLE COMPOUND OF HYDRASTINE WITH MONOCALCIUM PHOSPHATE.

BY T. H. NORTON AND H. E. NEWMAN.

Received August 27, 1897.

THE following experiments were made in connection with an endeavor to enlarge the number of soluble salts of hydrastine, especial interest attaching to the combination of the alkaloid with a mineral salt of recognized value in medicine.

As is well known, but few salts of hydrastine are readily soluble in water. In our work we made use of monocalcium phosphate, which was carefully purified by prolonged washing with alcohol. A saturated solution of the salt in cold water was prepared by thorough trituration, the phosphate being in excess. On triturating this saturated solution with a large excess of pure hydrastine, a certain amount of the latter would enter into solution, time, as was eventually found, being an important factor.