

Chemistry. — “*n.α-Sulphobutyric acid and its optically active components*”. By Prof. H. J. BACKER and J. H. DE BOER. (Communicated by Prof. F. M. JAEGER).

(Communicated at the meeting of January 27, 1923).

After it had been shown that α -sulphopropionic acid can be separated into its optically active components¹⁾, we tried to effect this resolution also for norm. α -sulphobutyric acid. At the same time the occasion was taken to study this acid, which has been known already since 1875, but hitherto had not been obtained in a pure crystallised state.

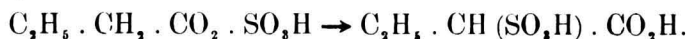
The acid is formed by direct sulphonation of *n.α*-butyric acid or of butyric anhydride²⁾.

Just as in the case of the propionic acid, the sulphonic acid group is attached to the α -carbon atom, as proved by its relation to α -bromobutyric acid, of which the structure is fixed.

HEMILIAN caused the ester of this acid to react with ammonium-sulphite and we have applied this reaction to the free α -bromobutyric acid; in both cases the same sulphobutyric acid was formed as by direct sulphonation.

We also obtained the sulphobutyric acid in a good yield (70 %) from ethylmalonic acid, which by sulphonation loses one molecule of carbon dioxide. Besides, this formation may serve as an argument for the structure, the active hydrogen atom of the ethylmalonic acid having the greatest chance of being substituted by the sulphonic acid group.

As a method of preparation we used the sulphonation of the carefully fractionated *n.* butyric acid with sulphur trioxide. In the cold butyrylsulphuric acid is formed, which on heating passes into sulphobutyric acid:



The acid was separated in the form of its barium salt, which was purified by crystallisation, and from which sulphuric acid liberated again the organic acid.

¹⁾ FRANCHIMONT and BACKER, These Proceedings **17**, 653 (1914); Recueil d. trav. chim. **39**, 751 (1920).

²⁾ HEMILIAN, Ann. d. Chemie **176**, 2 (1875). FRANCHIMONT, Recueil d. trav. chim. **7**, 27 (1888). VAN PESKI, Recueil **40**, 736 (1921).

Sulphobutyric acid was hitherto only known as a viscous liquid. We succeeded in obtaining the acid in the crystallised state by leaving a concentrated pure solution for a long time in vacuo over phosphorus pentoxide.

The α -sulphobutyric acid forms colourless hard crystals. Like sulphoacetic and sulphopropionic acids it contains one molecule of water of crystallisation and is extremely hygroscopic. The melting point, determined by the aid of a formerly described apparatus¹⁾, was found to be 66°.

Since sulphoacetic acid melts at 84—85° and sulphopropionic acid at 100.5°, we have here perhaps the beginning of an alternating series of melting points, as shown by the fatty acids.

From sulphobutyric acid we have prepared some salts with aromatic amines.

The acid sulphobutyrate of aniline forms small glistening crystalline plates with the melting point 175°.

The acid sulphobutyrate of *p*-toluidine, which is separated by ether from its alcoholic solution in the form of an ethergel, may be obtained as a white crystallised substance of the melting point 163°.

The acid salts of *p*-anisidine and *p*-phenetidine were obtained in a crystallised state, but not pure and colourless.

If these sulphobutyrate are heated with an excess of the corresponding amines, the carboxyl group is changed into amide through loss of water, the sulphonic acid group remaining combined with a molecule of the amine.

In this way aniline formed the *butyranilide- α -sulphonic acid salt of aniline*



which crystallises from water in concentrically grouped featherlike needles, occasionally 5 cm. in length, which melt at about 253°—256°.

From the other above mentioned aromatic amines well crystallised amides were also obtained, viz.

butyro-p-toluidide- α -sulphonic acid salt of p-toluidine, m.p. 260—263°,

butyro-p-anisidide- α -sulphonic acid salt of p-anisidine m.p. 242°,

butyro-p-phenetidide- α -sulphonic acid salt of p-phenetidine, m.p. 264—266°.

When heated with aromatic *o*-diamines, sulphobutyric acid, just as sulphopropionic acid, loses two molecules of water and gives derivatives of benzimidazole.

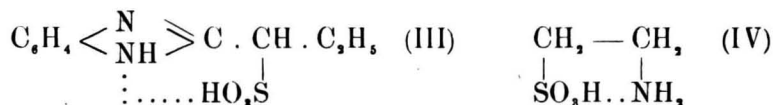
The sulphobutyrate of *o*-phenylenediamine, for instance, formed

¹⁾ Chem. Weekbl. 16, 1564 (1919).

on heating at 180° *benzimidazole-2-propylsulphonic acid* (I), whilst from the sulphobutyrate of 3,4-diaminotoluene was formed in the same way *methylbenzimidazole-2-propylsulphonic acid* (II).



These imidazoles were obtained as white crystalline substances. They are almost insoluble in the common solvents, have a very high melting point, and, notwithstanding the presence of a sulphonic acid group, they do not combine with aromatic amines and they are not hygroscopic. All these properties indicate, that the sulphonic acid group forms an internal salt with the basic function of the imidazole (III) and they completely recall the properties of taurine, for which an analogous structure is assumed (IV).



With strong bases, such as baryta, these imidazolesulphonic acids give well crystallised salts. From the barium salt and copper sulphate a green solution is formed, which, however, decomposes immediately when heated and also when kept for a long time at the ordinary temperature, so that the copper salt could not be separated in a crystallised pure state. It deserves attention, that, in spite of many efforts, also no copper salt of taurine has been obtained.

The resolution of racemic α -sulphobutyric acid was attempted with the aid of strychnine, by reason of previous experience with sulphopropionic acid, and the attempt was successful.

The acid strychnine salt of the d-acid is less soluble than the salt of the l-acid, just as in the case of sulphopropionic acid.

After three or four crystallisations the acid strychnine salt of the d-sulphobutyric acid is entirely free from the other component. It crystallises with two molecules of water in small glistening needles.

On concentration, the first mother liquor slowly gives a crop of the acid strychnine salt of l-sulphobutyric acid, which by repeated crystallisation from alcohol is obtained in a pure state.

Decomposition of the strychnine salts by baryta gives the barium salts of the active acids.

These barium salts crystallise from water in long needles which contain $2\frac{1}{2}$ molecules of water, in contradistinction to the racemic barium salt, which separates in small glistening leaflets with two molecules of water of crystallisation.

The direction of the rotation of the neutral barium salts is, as in the case of sulphopropionic acid, opposite to that of the free acids.

The molecular rotatory power depends on the concentration; on dilution it rises a little. The barium salts, for instance, give in a 2½% solution for sodium light a molecular rotation of 32.2° and in a 5% solution a rotation of 29.9°. In a 2½% solution the presence of 10% of barium chloride lowers the molecular rotation to 29.3°.

This indicates, that the rise of the molecular rotation on dilution may be ascribed to an increasing of the ionisation, a phenomenon, which is perhaps connected with the fact that the sign of rotation of the neutral salts is opposite to that of the free acids.

The molecular rotation of the free salts for sodium light is 7.8°.

The acid salts rotate the plane of polarisation in the same direction and to about the same amount as the free acids.

In this respect also, the behaviour of sulphobutyric acid is therefore analogous to that of sulphopropionic acid.

The investigation is being continued and will be published later in greater detail.

*Groningen. 13 Jan. 1923. Organic Chemical Laboratory of
the University.*
