

force, *shall have the dynamical property by which the optical phenomena of transparent bodies in the magnetic field are explained*; (2) with spiral arrangements of component parts, having axes all ranged parallel to a fixed line, *shall have the axial rotatory property corresponding to that of quartz crystal*; and (3) with spiral arrangements of component groups, having axes totally unarranged, *shall have the isotropic rotatory property possessed by solutions of sugar and tartaric acid, by oil of turpentine, and many other liquids.*

- V. "Researches on the Action of Sulphuric Acid upon the Amides and Nitriles, with Remarks on the Conjugate Sulpho-acids." By GEORGE B. BUCKTON, Esq., F.L.S., F.C.S., and A. W. HOFMANN, Ph.D., F.R.S. Received May 13, 1856.

(Abstract.)

Since we had the honour of addressing the Royal Society upon the subject of the behaviour of acetamide and acetonitrile towards sulphuric acid, we have completed our experiments upon the amides and nitriles, and extended our researches to other groups of bodies. The results of these additional inquiries we now beg to present in the form of a second short summary, the analytical details and the more extended description of the new compounds being given in the complete memoir, which, at the same time, we have the honour of submitting to the Society.

Before proceeding, however, to give an account of our new compounds, it may be desirable to state that several considerations, suggested by the progress of our inquiry, have induced us finally to adopt the name of Disulphometholic acid instead of the provisional term Tetrasulphomethylic acid under which we have described, in our first communication, the new acid generated by the action of sulphuric acid upon acetamide and acetonitrile.

ETHYL-SERIES.

Action of Sulphuric Acid upon Propionitrile.

Considerable difficulty is experienced in preparing this nitrile in a

state of purity. It was finally obtained by acting upon propionamide with anhydrous phosphoric acid.

When three parts by measure of the nitrile are cautiously mixed with two parts of fuming sulphuric acid, and heat is applied, the liquids enter into a sort of ebullition, carbonic acid being copiously evolved; at the same time a portion of propionic acid passes into the receiver, the amount of which may be lessened by raising the temperature only gradually.

At the close of the operation a tenacious mass is found in the retort, which, when dissolved in water and neutralized with carbonate of barium, furnishes two rather soluble but readily crystallizable salts, very difficult to separate one from the other. Their isolation may be conveniently effected, by converting them into the corresponding ammoniacal compounds, by precipitating their solution with carbonate of ammonium.

The filtrate yields two substances, one of which crystallizes, while the other is quite uncrystallizable.

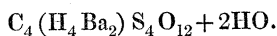
The latter substance, when long digested with carbonate of barium, produces crystals of a barium-salt whose analysis gives numbers leading to the formula

$$\text{C}_6(\text{H}_4\text{Ba}_2)\text{S}_2\text{O}_{10}.$$

This substance is obviously sulphopropionate of barium, the compound next in series to the sulphacetate discovered by M. Melsens.

It is generally deposited from its solution in fine silky crystals, which arrange themselves in spherical groups. They are very stable, and bear a high temperature without decomposition.

The salt associated with the uncrystallizable sulphopropionate of ammonium crystallizes with ease, either in rectangular prisms or in octohedra. Similarly converted into a barium-compound, it was found by analysis to contain at $100^\circ\text{C}.$,



It forms regular six-sided plates, which are moderately soluble in water, but insoluble in alcohol and in ether. It loses two equivalents of water of crystallization between 100° and 170° , but a few degrees above this temperature it is decomposed with blackening, yielding water, sulphurous acid, volatile organic products, and sulphate of barium.

We designate this salt as disulphetholate of barium.

Disulphetholic acid is prepared by precipitating a solution of the barium-salt with sulphuric acid, the excess of which is again removed by digestion with oxide of lead, and subsequent treatment with sulphuretted hydrogen. It is a crystalline and stable compound, very acid to the taste, and very deliquescent. With oxide of lead, or with carbonate of silver, it readily forms the respective salts, both of which are crystalline.

After what has been said with reference to the action of sulphuric acid upon acetamide, it is scarcely necessary to remark that the sulphopropionates and disulphetholates may be prepared with equal, or even greater facility from propionamide. Care, however, should be taken to use the amide in a perfectly dry state, which prevents in great measure the formation of free propionic acid.

PROPYL-SERIES.

Action of Sulphuric Acid upon Butyramide.

Equal parts by volume of melted butyramide and Nordhausen sulphuric acid evolve much heat when mixed together. In the reaction two acids are eliminated, showing that the series bears a strict analogy with the deportment exhibited by the preceding group.

As the ammonia-salts of these acids are wholly uncrystallizable, their separation is almost impossible. The barium-compounds also are scarcely to be obtained of a definite form, so that it is a matter of great difficulty to procure salts of sufficient purity for exact estimation. Recourse was had to fractional precipitation by alcohol.

The first salt which was deposited formed minute grains, which adhered strongly to the sides of the glass vessel containing the solution. It gave a percentage of barium which unmistakably indicated the formula

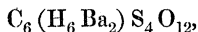


which is that of sulphobutyrate of barium.

This substance in its reactions closely resembles (with the exception of its greater solubility in water) the corresponding body of the ethyl-series. It burns like tinder, with evolution of sulphurous acid, and leaves a residue of sulphite and sulphate of barium. The aqueous solution presents a gummy mass on evaporation.

A further addition of alcohol to the mother-liquor of the sulphobutyrate of barium throws down a flocculent precipitate, which is

very soluble in water. It was purified by repeated and partial precipitation with alcohol. This substance, when dried at a temperature of 165°C ., furnished upon analysis numbers agreeing with the expression



which is that of disulphopropiolate of barium.

PHENYL-SERIES.

Action of Sulphuric Acid upon Benzonitrile.

From the results obtained in the study of the methyl-, ethyl-, and propyl-series, we may fairly infer that all the homologues of other groups will exhibit a similar deportment.

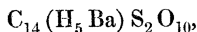
It appeared, however, desirable to extend our researches to a class of bodies which are analogous (not homologous) to the preceding series.

Sulphuric acid appears to act with much less energy upon benzonitrile or cyanide of phenyl than upon the foregoing nitriles. No evolution of gas is observed until the mixture of the two substances is strongly heated, and then so much sulphurous acid is formed from charring of the cyanide that its presence is almost entirely masked.

The digestion was continued for two hours, after which the dark residue was treated in the usual manner for the soluble barium-salts. That first obtained consisted of sulphobenzoate of barium. For identification, both the neutral and acid compounds were prepared, the respective formulæ of which,



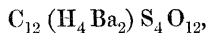
and



were corroborated by analysis.

An examination of the mother-liquor proved, as we had anticipated, the presence of a more soluble salt. By rapid evaporation it appears as an amorphous mass, but a drop allowed to dry spontaneously on the stage plate of the microscope exhibits it in the form of minute shuttle-shaped crystals.

The formula of this body, deduced from a sulphur- and barium-determination, is



which characterizes it as disulphobenzolate of barium.

The question naturally suggested itself, whether the same acid could not be prepared directly from the hydrocarbon benzol.

Mitscherlich has already described an acid (the sulphobenzolic) in which one equivalent of that hydrocarbon is associated with one equivalent of bibasic sulphuric acid. We have proved by experiment that sulphobenzolic acid takes up the elements of an additional equivalent when it is submitted to the prolonged action of Nordhausen sulphuric acid, and that, in fact, the union of these two bodies presents the most ready method of procuring disulphobenzolic acid in a state of purity.

The preceding researches establish in two different groups of bodies the existence of a series of bibasic acids containing four equivalents of sulphur, and which, irrespectively of any special view regarding their molecular arrangement, may be represented as formed by the association of the hydrocarbon (corresponding to marsh-gas) of the various groups with four equivalents of anhydrous sulphuric acid,—

Disulphometholic acid $C_2 H_4 4SO_3$.

Disulphetholic acid $C_4 H_6 4SO_3$.

Disulphopropiolic acid $C_6 H_8 4SO_3$.

Disulphobenzolic acid $C_{12} H_6 4SO_3$.

An acid of analogous composition exists in the naphthalin-series, disulphonaphtholic acid, $C_{20} H_8 4SO_3$, which was discovered by Berzelius, and subsequently studied by Laurent. Many of these substances may be actually obtained directly from the hydrocarbons by the action of sulphuric acid.

On the other hand, chemists are well acquainted with the deportment of olefiant gas under the influence of anhydrous sulphuric acid. The crystalline compound discovered by Magnus, and described by him under the name of sulphate of carbyl, whatever its constitution may be, can be considered as a direct combination of olefiant gas, with four equivalents of anhydrous sulphuric acid,—

Sulphate of carbyl $C_4 H_4 4SO_3$.

It can scarcely be doubted that all the other hydrocarbons, $C_{n2} H_{n2}$, propylene, butylene, amylene, &c., will furnish homologous substances.

Sulphate of carbyl, when submitted to the action of water, assimi-

lates two equivalents, and is converted into a bibasic acid (ethionic), $C_4H_4 4SO_3 + 2HO = C_4H_6O_2 4SO_3$, which accordingly may be viewed as an association of alcohol with four equivalents of anhydrous sulphuric acid. Terms analogous to ethionic acid are sure to be found when the study of the homologues of sulphate of carbyl shall be taken up by chemists.

The production of disulpho-compounds of perfectly similar composition, from substances belonging to such different groups of bodies, as the hydrocarbons homologous and analogous to marsh-gas, ethylene and alcohol, suggested the possibility that the substances in question might be but individual examples illustrating a far more general mode of formation. It became, in fact, probable that all organic bodies capable of uniting with the elements of two equivalents of anhydrous sulphuric acid might, under favourable circumstances, be induced to assimilate two additional equivalents of anhydrous sulphuric acid, and thus furnish other terms belonging to the class of disulpho-compounds.

The only additional class of compounds to which we have as yet successfully extended our labours, is the group of organic bases.

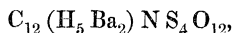
Action of Sulphuric Acid upon Aniline.

The first product which sulphuric acid forms with aniline is simply the sulphate of the base.

A further addition of acid, assisted by heat, dissolves the sulphate, and after a sufficiently long digestion, the whole is converted into sulphanilic acid. If too high a temperature be employed, the acid becomes very dark in colour; and indeed there is a limit beyond which carbon is rapidly deposited, accompanied by the evolution of abundance of sulphuric acid.

The process of converting sulphanilic acid into the disulpho-compound is rather tedious. It may, however, be effected without fail, by treating for several hours the perfectly dry crystalline acid, mixed with strong Nordhausen acid, to the consistence of a paste. The heat should not exceed that at which sulphurous acid just commences to be evolved. We employed an air-bath heated from 160° to 170° C., and the digestion was continued until a portion removed by a glass rod showed no trace of crystallization when cooled or moistened with water.

Treatment with carbonate of barium yielded in this manner a very soluble salt, which furnished a brittle gum when evaporated. The new substance was precipitated from its solution by alcohol and dried at 200° C. A determination of the barium and the sulphur led to the expression



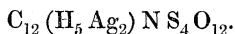
which is the formula of disulphanilate of barium.

This salt is readily attacked by concentrated nitric acid with oxidation of the sulphur. It blackens when strongly heated on platinum foil, and yields sulphurous acid without inflaming, a deportment in which it differs from sulphanilate of barium, which burns with a bright flame. When heated in close vessels it forms a crystalline sublimate, which consists of sulphite of aniline.

Disulphanilic acid is prepared by decomposing the lead-salt with hydrosulphuric acid. It is very soluble in water, and crystallizes with difficulty. It may be precipitated from a strong aqueous solution by alcohol in the form of white grains. The precipitation is assisted by the addition of a little ether. It has a very rough and acid taste.

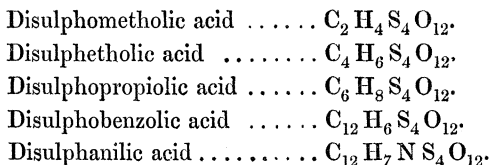
We have also prepared the silver-salt by saturating the acid with carbonate of silver. The most ready method of obtaining it in a solid state is by precipitation with alcohol and ether. The aqueous solution, by concentration, deposits a black powder which makes it very difficult to obtain the crystals colourless.

The formula of disulphanilate of silver is



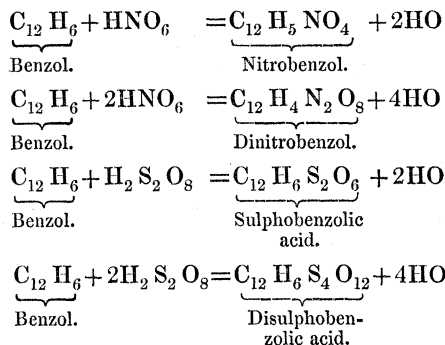
The potassa-salt is crystalline. It forms small grains or minute needles, which are insoluble in alcohol.

The researches detailed in the preceding paragraphs may serve to characterize more fully a class of compounds of which only a few terms, isolated and scattered in widely different groups, had been previously observed. The only disulpho-acids hitherto known, are Berzelius's and Laurent's disulphonaphthalic acid, Magnus's ethionic (disulphethylic) acid, and lastly, dithiobenzic acid, recently discovered by M. Kilkenkamp. To these we now add five new acids, belonging to several of the most important series of compounds:—



Our experiments point out, moreover, the universal occurrence, and the general mode of formation of these substances. All organic molecules, particularly in the nascent state, appear to be capable of assimilating the elements of either two or four equivalents of anhydrous acid.

The formation of the two groups of acids which are thus produced presents a great analogy with the production of the nitro-substitutes generated under the influence of nitric acid. All these compounds are generated with the elimination of water. In the action of nitric and sulphuric acid upon benzol, for instance, we have,



The analogy of these reactions is obvious.

The action of nitric acid upon organic bodies is by no means limited to the production of nitro-compounds corresponding to nitrobenzol and dinitrobenzol; frequently additional substitutes are formed with elimination of six, eight, and in a few isolated cases, even of ten equivalents of water. It is possible that analogous sulpho-compounds may exist. Hitherto, however, no substances have been observed in which the assimilation of sulphuric acid has gone further than in the disulpho-acids.