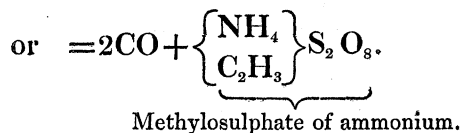
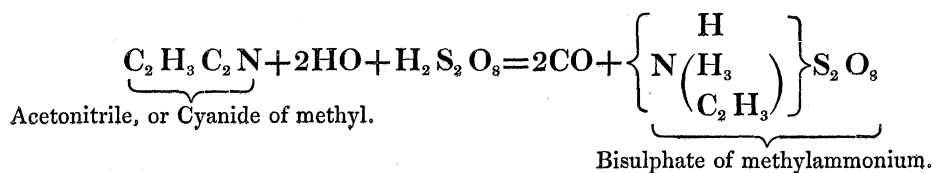
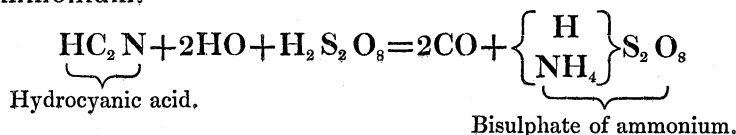


XX. *Researches on the Action of Sulphuric Acid upon the Amides and Nitriles, together with Remarks upon the Conjugate Sulpho-acids.* By GEORGE B. BUCKTON, Esq., F.L.S., F.C.S., and A. W. HOFMANN, LL.D., Ph.D., F.R.S. &c.

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EVER since the experiments of DUMAS, MALAGUTI and LEBLANC on the one hand, and those of KOLBE and FRANKLAND on the other, have established the identity of the hydrocyanic ethers with the nitriles, it has been a favourite problem with chemists to reproduce the alcohols from these bodies, the solution of which would afford a passage from an acid, $C_{n_2} H_{n_2} O_4$, to an alcohol, $C_{n_2-2} H_{n_2} O_2$.

We have been likewise engaged with this question. The deportment of hydrocyanic acid (formonitrile) under the influence of concentrated sulphuric acid, which, as is well known, gives rise to an evolution of carbonic oxide, suggested an examination of the other nitriles in a similar direction. There appeared to be a chance of producing in this manner from a nitrile, the sulphovinic acid of an alcohol containing two equivalents of carbon less than the nitrile. Acetonitrile, for instance, might have been thus converted either into sulphate of methylammonium or into sulphomethylate of ammonium.



Experiment has corroborated neither of these anticipations. This reaction gives rise to the formation of a remarkable conjugate sulpho-acid, which may be considered as the type of a most extensive class of analogous compounds, some isolated terms of which have been met with already in previous investigations.

Before, however, detailing the conditions under which these new bodies are formed, it may not be unacceptable to make a few statements regarding the most efficient

method of procuring the nitrile of the methyl-series in quantity and in a state of purity.

PREPARATION OF ACETONITRILE.

The preparation of cyanide of methyl (acetonitrile), by decomposing sulphomethylate of potassium with cyanide of potassium, is unsatisfactory, both as to quantity and quality of the product obtained. The presence of a minute amount of moisture in the materials employed gives rise to a number of secondary products, the chief of which are, cyanide and carbonate of ammonium, and a gas possessing a highly offensive odour, which imparts to the distillate a smell not at all due to the nitrile itself. By far the most advantageous method of preparing acetonitrile consists in acting upon acetamide with anhydrous phosphoric acid, as proposed by M. DUMAS.

Acetic ether is not immediately soluble in a moderate quantity of aqueous ammonia; but after five or six hours' contact, the layers at first formed disappear, and the liquid becomes homogeneous.

If distillation be now at once commenced, scarcely a trace of acetamide will be obtained. The change, on the other hand, is complete if the mixture be exposed for some hours to a temperature of 120° or 130° C.

We have employed in this operation a wrought-iron cylinder, similar to that used by Dr. FRANKLAND in his researches, which had been constructed for us by Mr. JAMES NASMYTH, who never fails most kindly and liberally to lend the extraordinary resources of his celebrated establishment for scientific purposes. Equal volumes of acetic ether and concentrated ammonia were introduced into the boiler, the brass valve of which was protected from corrosion by a steel screw and leaden washer. After six hours' digestion the acetamide was separated by distillation with the thermometer from the alcohol formed, that part only being reserved as anhydrous which had passed over above 200° . When acetamide is intimately mixed with about an equal volume of anhydrous phosphoric acid in a retort, a powerful action commences immediately, and the nitrile passes over colourless, but contaminated with acetic and hydrocyanic acids. Towards the end of the operation it is necessary to use a strong heat to drive off the last portions. The distillate is now agitated with just sufficient aqueous potash to neutralize the acids, when the nitrile floats on the surface, and may be removed for rectification over a fresh quantity of phosphoric acid, to render it perfectly anhydrous. Pure acetonitrile possesses an ethereal odour, faintly recalling that of cyanogen; its aromatic taste is pungent, but not disagreeable. We observed the boiling-point 77° - 78° , which coincides with that observed by DUMAS. It does not appear to have been previously noticed, that acetonitrile burns with a luminous flame, the edges of which are beautifully tinged with peach-blossom colour. The flame and odour of acetonitrile unmistakeably bespeak the cyanic relations of this compound.

ACTION OF SULPHURIC ACID ON ACETONITRILE.

This body, when mixed with its own volume of fuming sulphuric acid, gives rise to a very energetic reaction, a considerable amount of heat being evolved, which causes much of the nitrile to volatilize and thus escape decomposition. In order to avoid this, the operation is best conducted in a retort surrounded with cold water, when a perfect mixture can be effected, scarcely a change of colour becoming perceptible. On application of heat the mixture powerfully intumescs with copious evolution of a gas which on examination over mercury proves to be carbonic acid, without a trace of carbonic oxide; at the same time strong acetic acid passes into the receiver. If the temperature be kept up by the gas-flame until the effervescence almost entirely ceases, the mass when cold forms a brown, tough and transparent solid, readily soluble in water and in alcohol. The aqueous solution, boiled with an excess of carbonate of barium, is then passed through a hot-water filter, when a magnificent salt is deposited, in the form of brilliant colourless rectangular plates which, when gathered in mass, exhibit a nacreous lustre. This salt is remarkably stable. It loses no weight at 100°C ., but gives off water of crystallization somewhat below 150° . At a temperature of 220° the substance still remains unaltered, but when heated beyond this point, it commences to turn yellow, disengages water, sulphurous acid and carbonic oxide, whilst sulphur sublimes. When strongly heated it becomes incandescent, leaving a residue of sulphate and sulphite of barium. The new salt may be crystallized unchanged from hydrochloric acid, and may be boiled for hours with concentrated nitric acid, without formation of sulphate of barium. It is quite insoluble in alcohol.

ACTION OF SULPHURIC ACID UPON ACETAMIDE.

As acetamide differs from acetonitrile only in containing two additional equivalents of water, this compound, when heated with fuming sulphuric acid, undergoes a perfectly analogous transformation.

From the comparative facility of its preparation, acetamide offers peculiar advantages for procuring the new substance in large quantity. The chief difficulty which presents itself consists in operating with the right proportions of acid and amide. Distillation of equal volumes of dry acetamide and ordinary Nordhausen acid, for instance, gives scarcely a trace of anything but acetic acid and sulphate of ammonia. The most efficient proportions we found to be two volumes of amide to three volumes of acid. The distillation should be pushed very far, in fact until the product of distillation is accompanied by sulphurous acid. The solution of the solid residue may at once be saturated with carbonate of barium; it will be found, however, more economical to treat the liquid with finely-powdered Carrara marble until the free acid be neutralized, and to reserve the pure carbonate of barium, which is so difficult to wash thoroughly, merely for decomposing the sulphate of ammonium towards the end of the process. The liquid must be boiled with excess of the carbonate until

From these data we calculate for the anhydrous salt the formula



which requires the following numbers:—

	Theory.		Mean of experiments.
1 equiv. of Carbon . . .	6	3·85	3·71
1 equiv. of Hydrogen . . .	1	0·67	0·63
1 equiv. of Barium . . .	68·5	44·05	44·05
2 equivs. of Sulphur. . .	32	20·57	20·83
6 equivs. of Oxygen . . .	48	30·86	30·78
	<hr/>	<hr/>	<hr/>
	155·5	100·00	100·00

Considerations which we shall develop hereafter, especially the production of similar compounds in analogous series, induce us to double this expression, and to represent the new barium-salt by the formula



The salt, as has been stated, retains water of crystallization at 100° C. In determining this water,—

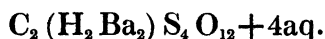
I. 0·8414 grm., dried at 100°, lost 0·0888 grm. at 190° C.

II. 0·5820 grm., dried over sulphuric acid, lost 0·0613 grm. at 210° C.

These results indicate four equivalents of water:

Theory.	Experiment.	
	I.	II.
10·37	10·55	10·53

The formula of the crystallized salt is therefore



We propose for this substance the name *disulphometholate of barium*, and for the acid the term *disulphometholic acid*, without wishing, however, to express by this term any particular view regarding the actual arrangement of the constituent molecules in the substance.

If the formula above given be correct, disulphometholate of barium is the salt of a bibasic acid, the composition of which would be represented by the expression



furnishing salts of the general formula,



and



The barium salt which has been described belongs to the second class.

We have not yet succeeded in preparing any acid salts. Disulphometholate of barium crystallizes unchanged from a hydrochloric acid solution.

0.6216 grm. of salt thus crystallized gave 0.4636 of sulphate of barium.

	Acid salt.	Neutral salt.	Experiment.
Percentage of barium . . .	28.13	44.05	43.85.

Disulphometholic Acid.

To prepare this acid, the barium-salt is precipitated by a small excess of sulphuric acid which is again removed by means of oxide of lead. Hydrosulphuric acid is then passed through the liquid which becomes thus strongly acid. It may be concentrated to a syrup without decomposition, and even carefully heated until white fumes appear. On cooling the liquid thus concentrated under the receiver of the air-pump, a crystalline mass of fine radiated needles is produced, exceedingly soluble in water and very deliquescent. They have a pure acid taste, with somewhat the flavour of tartaric acid. The attraction of this acid for water is so great, that we have failed in obtaining it in a solid condition by evaporation over sulphuric acid.

It is not changed by boiling with nitric acid, and chlorine gas passed through the aqueous solution does not liberate sulphuric acid.

The corresponding salts are readily obtained by digesting the oxides or the carbonates of the various metals with solutions of the acid. The barium-salt is immediately precipitated by adding chloride of barium to this solution. The salts are all soluble in water, but insoluble in alcohol.

Disulphometholate of Silver

crystallizes either in tufts of flat needles, or in broad tables of considerable size. It is produced when the aqueous solution of the acid is neutralized with carbonate or oxide of silver. We had hoped to obtain crystals of sufficient regularity for measurement of the angles; but although they may be easily produced of sufficient size, the edges are mostly rounded and imperfect.

It bears a temperature of 150° C. without decomposition, but blackens and froths when strongly heated, yielding sulphur, sulphurous acid, and metallic silver. It is insoluble in absolute alcohol, but may be crystallized from spirits of wine.

I. 0.8066 grm. at 120°, by ignition, gave 0.4470 grm. of silver.

II. 0.6045 grm. at 120°, by ignition, gave 0.3345 grm. of silver.

III. 1.0151 grm. at 120°, burnt with chromate of lead, gave 0.1110 grm. of carbonic acid and 0.0534 grm. of water.

	Percentage composition.		
	I.	II.	III.
Silver	55.49	55.33	—
Carbon. . . .	—	—	2.97
Hydrogen. . . .	—	—	0.58

leading to the formula



	Theory.		Mean of experiments.
2 equivs. of Carbon . . .	12	3·07	2·97
2 equivs. of Hydrogen . . .	2	0·51	0·58
2 equivs. of Silver	216	55·37	55·41
4 equivs. of Sulphur	64	16·41	—
12 equivs. of Oxygen	96	24·64	—
	<hr/>	<hr/>	
	390	100·00	

Disulphometholate of Ammonium.

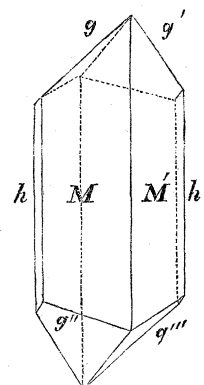
The formation of this substance has been already described. It is sparingly soluble in cold, but very soluble in hot water; from which it is again deposited in colourless crystals, often an inch in length. They are anhydrous, decrepitate when heated, and bear a temperature of 190° without being changed.

Through the kindness of Mr. CHARLES BROOKE we are enabled to give the following angular measurements:—

$$\text{MM}' \quad 97^\circ 45'.$$

$$\text{M}h \quad 131^\circ 15'.$$

$$\text{M}g \quad 92^\circ 50'.$$



The form belongs to the oblique prismatic system, which is in fact nothing more than a hemihedral form of the right prismatic system.

When submitted to analysis this salt gave the following results:—

I. 0·7692 grm. at 190°, ignited with chromate of lead, gave 0·1501 grm. of carbonic acid and 0·3623 grm. of water;

II. 0·5135 grm. at 150°, ignited with chlorate of potassium, gave 1·1425 grm. of sulphate of barium;

III. 0·4508 grm. at 170°, ignited with soda-lime, gave 0·9440 grm. of chloroplatinate of ammonium;

IV. 0·5735 grm. at 170°, ignited with soda-lime, gave 1·1770 grm. of chloroplatinate of ammonium;

these numbers correspond to the formula



	Theory.		Mean of experiments.
2 equivs. of Carbon	12	5·71	5·32
10 equivs. of Hydrogen	10	4·76	5·22
4 equivs. of Sulphur	64	30·47	30·55
2 equivs. of Nitrogen	28	13·33	12·98*
12 equivs. of Oxygen	96	45·73	45·93
	<hr/>	<hr/>	<hr/>
	210	100·00	100·00

Disulphometholate of Potassium

is most readily obtained by adding the crystallized barium-salt by degrees to a boiling solution of carbonate of potassium, avoiding an excess of the former. After filtration, the new substance separates easily from excess of alkali in fine shining needles or brilliant grains, according to the rapid or slow precipitation from its solution. It is not very soluble in cold water, one part requiring fourteen parts of water at 22° C. for solution.

Disulphometholate of Zinc.

When metallic zinc is heated with an aqueous solution of the acid, hydrogen gas is liberated, and on concentration a syrup is formed which crystallizes with great difficulty. Alcohol does not precipitate this salt from its solution.

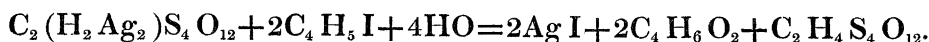
Disulphometholate of Lead

forms small square nacreous plates not unlike those of the barium-compound. It is very soluble in water.

Disulphometholate of Copper

is produced by careful precipitation of the barium-salt by sulphate of copper. It yields radiated needles or small prisms of a green colour. They are insoluble in absolute alcohol, but soluble in spirits of wine.

We have not succeeded in preparing the ethers of this acid. We anticipated that they would be formed by bringing together iodide of ethyl and disulphometholate of silver. A strong solution of the silver-salt reacts at once on the iodide without application of heat. Iodide of silver is precipitated, but the ether which is formed splits immediately into disulphometholic acid and alcohol, according to the equation



* The mean of nitrogen in Experiments III. and IV., viz. 13·11 and 12·85. They were made with specimens of different preparations.

EXAMINATION OF THE MOTHER-LIQUOR OF DISULPHOMETHOLATE OF AMMONIUM.

Sulphacetate of Ammonium and Sulphacetate of Barium.

It has been already noticed that another salt is present in the mother-liquid obtained during the purification of disulphometholate of ammonium. To procure this substance in a state of purity the mother-liquid was concentrated, and the crystals of the disulphometholate removed from the thick syrup as completely as possible.

After a moderate addition of cold water the liquid was mixed with an excess of chloride of barium, and the whole allowed to stand for five or six minutes, when it was filtered, and the filtrate set apart for twenty-four hours. At the expiration of this time a copious granular precipitate had formed which was well washed with cold water and then recrystallized from boiling water, in which, when once deposited, it proved to be very little soluble.

This substance differs both in its crystalline form and in its reactions from the disulphometholate. When strongly heated, it turns black and burns away like tinder. The residuary mass, moistened with hydrochloric acid, evolves according to the time of ignition, hydrosulphuric and sulphurous acid.

By analysis, 0.6266 grm., dried at 220°, gave 0.5287 of sulphate of barium.

The percentage of barium resulting from this experiment agrees well with the amount required by the formula of sulphacetate of barium. We append the theoretical and experimental percentages:—

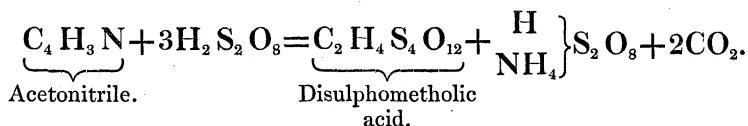
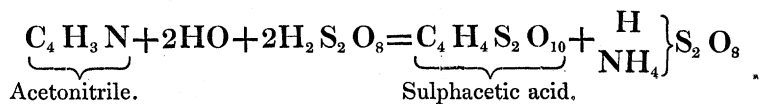
Formula.	Barium calculated.	Barium found.
$C_4(H_2Ba_2)S_2O_{10}$	49.81	49.60
Sulphacetate of barium.		

The quantity of sulphacetate of ammonium produced, mainly depends upon the degree of heat maintained during the reaction of sulphuric acid upon acetamide or acetonitrilè. If the mixture be made gradually and cooled after each addition of acid, the elimination of carbonic acid may be entirely prevented, and the chief product is then sulphacetic acid. On the other hand, if the heat be urged as far as is practicable, disulphometholic acid takes the place of the sulphacetic, carbonic acid being evolved at the same time.

Two phases may therefore be traced in the reaction. In the first, nascent acetic acid simply combines with the elements of two equivalents of anhydrous sulphuric acid. In the second phase the acetic molecule undergoes a more thorough transformation, splitting, as it does, into carbonic acid and marsh-gas, the latter of which combines with the elements of four equivalents of anhydrous sulphuric acid.

The new acid may also be regarded as sulphacetic acid, which, losing carbonic acid, has assimilated an equal number of equivalents of anhydrous sulphuric acid.

The two stages in the action of sulphuric acid on acetonitrile may be represented by the following equations:—



Acetamide containing but two equivalents of water more than acetonitrile, the production of sulphacetic acid and disulphometholic acid from this substance is intelligible by means of the same equations.

The action then of bases and of acids upon acetic acid presents a remarkable analogy. Under the influence of both agents, we may assume, it splits into marsh-gas and carbonic acid; in the first case, it is the carbonic acid which is fixed by the alkali, whilst in the latter the marsh-gas remains in combination with the acid.

The possibility of assuming the existence of marsh-gas in disulphometholic acid, suggested the idea of endeavouring to combine marsh-gas directly with sulphuric acid. The dry gas obtained by the distillation of acetate of soda with potash-lime was passed into a receiver charged for this purpose with anhydrous sulphuric acid, but we could not detect any combination of the two bodies, either at ordinary temperature or when the receiver was heated to 100° C. The sulphuric acid, after treatment with water and carbonate of barium, furnished no soluble salt whatever.

Although we have thus been unable to convert marsh-gas into disulphometholic acid, we have found that this acid may be readily transformed into marsh-gas. When heated with hydrate of baryta the salts of the acid yield marsh-gas, together with sulphate and sulphite of barium. A method is thus indicated by which probably all the hydrocarbons, $\text{C}_{n2-2}\text{H}_{n2}$, may be prepared from the corresponding sulpho-acids*.

The simplicity of relation which exists between sulphacetic and disulphometholic acid, left no doubt in our mind regarding the convertibility of the former into the latter. We have established this fact moreover experimentally. Sulphacetic acid, prepared by the action of anhydrous sulphuric acid upon glacial acetic acid, furnished without difficulty disulphometholic acid, when again treated with sulphuric acid. A similar observation had in fact been made already by M. MELSENS. This chemist, in his researches upon the sulphacetates, appears in some sort to have anticipated the existence of the disulphometholates. He remarks that he once found in the mother-liquor obtained from the preparation of sulphacetate of silver, a crystalline salt the composition of which he represents by the formula



* We are unable to corroborate M. AIMÉE's remarks, that marsh-gas is decomposed by sulphuric acid into water, carbon, and sulphurous acid. The acid remains colourless, and the gas after the process exhibits its usual properties unmodified.

It is evident that this was nothing but the disulphometholate of silver, but M. MELSENS does not appear to have investigated the subject further, or to have connected the appearance of this salt with the evolution of carbonic acid gas, which he likewise found among the secondary products of the action of sulphuric acid upon acetic acid.

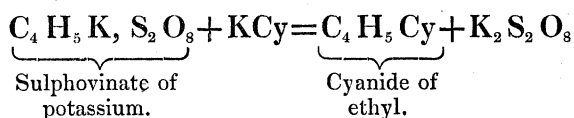
The chemical character of disulphometholic acid is so marked, and the reaction which produces it so simple and definite, that there could be no doubt regarding the existence of numerous corresponding terms in homologous and even in analogous series of substances. In fact disulphometholic acid may be considered as the type of a very numerous class of bodies of similar composition, some of which are actually known, while a great many remain to be discovered.

We have ourselves traced the formation of the homologues and analogues of disulphometholic acid in several higher series of bodies, but we have been satisfied in establishing the existence of these substances, without entering into a detailed study of their properties.

ETHYL-SERIES.

Preparation of Propionitrile.

The formation of cyanide of ethyl (propionitrile) by means of cyanide and sulphovinate of potassium, has all the disadvantages above enumerated in the case of cyanide of methyl. A large quantity of an inflammable gas of a highly offensive odour is disengaged, the annoyance of which may be avoided by conducting the gas from the receiver of the liquid into the cylinder of a wire gauze burner, in the air-flame of which it is perfectly consumed. In the preparation of cyanide of ethyl by means of cyanide and sulphovinate of potassium, through the intervention of unavoidable moisture, a variety of different reactions appear to proceed side by side. Together with the formation of cyanide of ethyl,



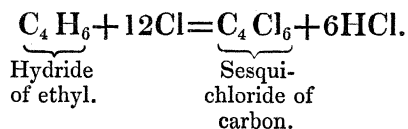
considerable quantities of carbonate of ammonium are produced, whilst an inflammable gas is largely generated, which is nothing but hydride of ethyl. This gas is not absorbed by bromine; it therefore cannot contain any ethylene. It combines with chlorine, forming a gaseous compound, burning with a green-edged flame. This is probably the substance obtained by Drs. KOLBE and FRANKLAND when treating ethyl with chlorine gas, isomeric with chloride of ethyl, C₄H₅Cl. When in contact with excess of chlorine it yields an oily substance, and a crystalline body having the properties and composition of sesquichloride of carbon.

An analysis of the substance gave the following numbers:—

0.1130 grm. gave 0.4100 chloride of silver.

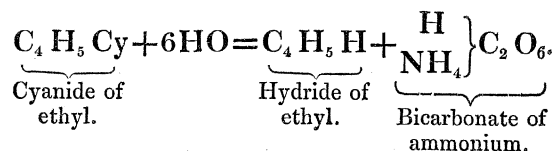
	Theory.	Experiment.
Chlorine in C ₂ Cl ₃	89.87	89.73

It is from this fact chiefly that we infer the identity of the inflammable gas generated in the preparation of propionitrile with hydride of ethyl,



The oily liquid observed obviously consisted of the intermediate substitution-terms.

These substances are evidently secondary products of the decomposition of cyanide of ethyl,



Cyanide of ammonium is likewise invariably present, prussic acid being generated by the action of water upon the cyanide of potassium, while alcohol is reproduced to a very considerable extent. Lastly, this process gives rise to a most remarkable body with a most insupportable prussic smell, the formation of which we have traced in a great variety of reactions. We have not completed the study of this compound.

The method finally adopted for obtaining propionitrile in sufficient quantity for us to experiment upon was that recommended by Dr. WILLIAMSON, viz. the digestion of cyanide of potassium with iodide of ethyl in four volumes of alcohol as a vehicle. The presence of so much alcohol, from which the cyanide cannot be separated by rectification, on account of the similarity of their boiling-points, is an evil which unfortunately involves a series of tedious processes, namely, conversion of the nitrile into propionate of potassium, by the action of caustic potassa, separation of the alcohol by distillation, preparation of propionic ether, transformation of the latter into propionamide by the action of ammonia under pressure, action of phosphoric acid upon propionamide to form the nitrile, and ultimately dehydration of the nitrile by means of anhydrous phosphoric acid.

In preparing disulphetholic acid we have almost invariably employed propionamide, on account of its easier preparation. We have however established by experiment that propionitrile exhibits with sulphuric acid exactly the same deportment as propionamide. To effect the transformation of the propionamide with success, it is necessary to employ this substance in a perfectly anhydrous condition. Unless this point be properly attended to, sulphuric acid produces principally sulphate of ammonium and propionic acid; for this purpose the amide should be heated in a retort, and that portion only collected which passes over above the temperature of 210° C. Below this point the amide retains sufficient water to prevent perfect crystallization.

On mixing equal volumes of melted amide and fuming sulphuric acid, very considerable heat is disengaged; the temperature must be regularly maintained until carbonic acid ceases to be evolved and propionic acid no longer distils over. Some

experiments are necessary in order to fix the quantity of acid required for the conversion of the propionamide, since commercial Nordhausen acid varies considerably in composition. If too much acid be employed, the mixture is often perfectly carbonized, whilst too little acid gives rise to the formation of either sulphopropionic or propionic acid.

If care be taken to regulate the heat so as just to keep up the liberation of carbonic acid, the amount of disulphetholic acid may be considerably increased.

The solid residue in the retort, when cold, is dissolved in water, and treated, as in the case of disulphometholic acid, first with carbonate of barium and subsequently with carbonate of ammonium. On evaporation the liquid thus obtained furnishes two salts, one of which is quite uncrystallizable, and must be separated from the other by washing with weak spirit. A crystalline substance remains on the filter, which, after two or three crystallizations from hot water, is the pure

Disulphetholate of Ammonium.

When deposited from an aqueous solution, this salt forms regular cubic crystals or square prisms, perfectly colourless. It is insoluble in alcohol and in ether. In its general behaviour this substance differs but little from the corresponding salt of the methyl-series, the principal feature of difference being a greater solubility and its leaving a carbonaceous residue when strongly heated.

Disulphetholate of Barium

crystallizes with regularity in six-sided plates, which generally arrange themselves from centres. It is easily formed by heating a solution of the ammonium-salt with hydrate of baryta until every trace of ammonia is expelled, and then passing a current of carbonic acid through the solution to remove the excess of baryta. It is very soluble in water, and stable at a temperature of 180°, but blackens when strongly heated in close vessels, empyreumatic vapours being at the same time given off. The black residue burns with a sulphur-flame.

Disulphetholate of barium is insoluble in concentrated nitric acid, which does not decompose it. It crystallizes from the dilute acid without apparent change.

After fusion with chlorate of potassium and carbonate of sodium, the filtrate contains sulphates in solution, proving that there is more sulphur present than is required for saturating the barium of the compound. By this method the disulphetholates can be distinguished from the sulphopropionates presently to be described.

0.4490 grm., at 170° C., gave 0.3266 grm. of sulphate of barium ;

0.5045 grm., fused with chlorate of potassium, gave 0.7229 grm. of sulphate of barium ;

which numbers accord with the formula



	Theory.		Experiment.
4 equivs. of Carbon . . .	24	7·38	—
4 equivs. of Hydrogen . . .	4	1·23	—
2 equivs. of Barium . . .	137	42·15	42·36
4 equivs. of Sulphur . . .	64	19·69	19·68
12 equivs. of Oxygen . . .	96	29·55	—
	<hr/> 325	<hr/> 100·00	

For the determination of the water of crystallization, 0·5790 grm., dried at 100°, were heated to 220° C., when they lost 0·0347 grm. Two equivalents of water require 5·24; found, 5·99. It is probable that there is a partial decomposition of the salt at this high temperature.

As has been already stated, the disulphethylates may also be prepared from propionitrile. For this purpose three parts of the propionitrile are distilled with two parts of fuming sulphuric acid. As the action is very energetic, the mixing should be effected by degrees in a moderate-sized retort. A barium-salt was prepared the properties of which agreed in every respect with those of the compound prepared from propionamide.

Disulphetholic Acid

is obtained by decomposing the lead-salt by hydrosulphuric acid. By concentration it forms a thick syrup, which ultimately solidifies into a crystalline mass. By heat it decomposes with deposition of charcoal and production of white fumes.

Disulphetholate of Silver

may be obtained by a process similar to that employed in the case of the disulphometholate. It is crystalline. When dry, it bears a considerable heat without change. The solution blackens on ebullition.

Disulphetholate of Lead

is very soluble in water. When evaporated over sulphuric acid, the salt yields fine prisms or minute quadrangular laminæ. When hastily evaporated it produces a tough gummy mass.

Sulphopropionic Acid.

As might have been anticipated from the results obtained in the methyl-series, disulphetholic acid is by no means the sole product of the action of sulphuric acid upon propionamide and propionitrile. The formation of this acid is preceded by that of another acid richer in carbon and poorer in sulphur, in one word, by that of sulphopropionic acid. The uncrystallizable ammonium-salt, already mentioned, is in fact the sulphopropionate of ammonium. Absolute alcohol throws it down from its solution as a thick treacly mass, with an appearance very unprepossessing to the

analyst. The dilute aqueous solution was therefore boiled with carbonate of barium until entirely decomposed, and the filtered liquid concentrated in a beaker. At a particular point of the evaporation, a quantity of *sulphopropionate of barium* appeared in small cubic grains, which caused so much "bumping" as to make it necessary to evaporate upon the water-bath.

If the concentration be arrested before the deposition of these grains, and the liquid be set aside for twenty-four hours, it yields a plentiful crop of beautiful silky crystals, arranged in spherical groups.

After another crystallization from hot water, in which the substance is moderately soluble, this salt is sufficiently pure. For analysis it was dried at 170°.

0.3636 grm. of substance gave 0.2940 grm. of sulphate of barium.

0.4960 grm. of substance gave 0.2138 grm. of carbonic acid and 0.0672 water.

The results of this analysis agree with the formula of sulphopropionate of barium,



	Theory.		Experiment.
6 equivs. of Carbon . . .	36	12.45	11.75
4 equivs. of Hydrogen . . .	4	1.38	1.49
2 equivs. of Barium . . .	137	47.40	47.52
2 equivs. of Sulphur . . .	32	11.07	—
10 equivs. of Oxygen . . .	80	27.70	—
	<hr/>	<hr/>	
	289	100.00	

PROPYL-SERIES.

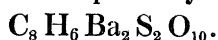
From what has been already said, but few words are necessary on the preparation of disulphopropiolic and sulphobutyric acid. It may, however, be stated, that butyramide boils at 216°, and passes over at that temperature in drops which crystallize beautifully. It has the characteristic sweet taste of the other amides of the series, and, like them, it fumes slightly in the air when gently heated.

Three parts of butyramide produce with two parts of fuming sulphuric acid a horny mass, which, after removal of the sulphuric acid and saturation with ammonia, yields a syrup wholly uncrystallizable. The ammonium-salts were converted into barium-salts, which also possess but feeble powers of crystallization.

M. REDTENBACHER has already pointed out how much the solubility in water of the barium-salts of the acids $C_{n2} H_{n2} O_4$ augments as the value of the coefficient n progressively increases. A similar increase of solubility is observed with the barium-salts of the series of conjugated acids which form the subject of this paper. The contrast between the almost insoluble disulphometholate and the very soluble disulphopropiolate of barium is very marked.

From the extreme solubility of these salts, great difficulty was experienced in separating them completely one from the other. The method adopted was that of partial precipitation by alcohol. To solutions moderately concentrated and cold, sufficient absolute alcohol was added to produce a cloud, permanent when rapidly stirred. On allowing the liquid to stand for an hour, a quantity of a granular substance attached itself to the glass vessel, which, after solution in water and reprecipitation, was dried and decomposed by sulphuric acid.

0.2336 grm. at 160° gave 0.1800 grm. of sulphate of barium, which corresponds to the formula for sulphobutyrate of barium,



The percentage required is—

	Theory.		Found.
8 equivs. of Carbon . . .	48	15.84	—
6 equivs. of Hydrogen . .	6	1.98	—
2 equivs. of Barium . . .	137	45.21	45.29
2 equivs. of Sulphur . . .	32	10.56	—
10 equivs. of Oxygen . . .	80	26.41	—
	<hr/>	<hr/>	
	303	100.00	

We have not been able to procure the disulphopropiolate of barium in a state of purity. The alcoholic liquid which remains after deposition of the sulphobutyrate contains a considerable quantity of the salt, but so mixed, that we were unable more than proximately to isolate it. By continuing the process of fractional precipitation, and drying, and by analysing the different samples, the quantity of barium present in the successive specimens was found to decrease. In three consecutive analyses we arrived at the following percentages:—

43.4, 42.9, 41.7.

The formula



requires the following values:

	Theory.		Found.
6 equivs. of Carbon . . .	36	10.61	—
6 equivs. of Hydrogen . .	6	1.77	—
2 equivs. of Barium . . .	137	40.41	41.7
4 equivs. of Sulphur . . .	64	18.87	—
12 equivs. of Oxygen . . .	96	28.34	—
	<hr/>	<hr/>	
	339	100.00	

This salt is not so wholly uncrystallizable as the sulphobutyrate. By slow evaporation it furnishes very minute crystals, which under the microscope show themselves as thin pearly plates. They appear best when slowly thrown down by alcohol from the solution.

BUTYL-SERIES.

Our experiments in this series have been entirely qualitative. We have been satisfied to establish experimentally the analogy of the reactions. These reactions, however, become less and less definite, and, owing to the still greater solubility of the new products, their separation is attended with difficulties almost insurmountable.

The researches detailed in the preceding pages are quite sufficient to establish the general character of the action of sulphuric acid upon the amides and nitriles. Nevertheless, since these experiments exclusively refer to the derivatives of several homologous terms of the series of fatty acids, it appeared desirable to extend the investigation to a nitrile of the analogous group of aromatic acids. No substance appeared to be more appropriate for such an examination than benzonitrile, or cyanide of phenyl.

PHENYL-SERIES.

Preparation of Benzonitrile.

M. FEHLING originally obtained benzonitrile by subjecting benzoate of ammonium to repeated dry distillations, when the four equivalents of water gradually separated. The process is however objectionable, on account of the necessity of repeatedly returning by hand the sublimed salt to the volatilizing vessel. We hoped to have found a more convenient method, in submitting the same salt to the dehydrating action of chloride of zinc; but on rectifying the distillate, we obtained only one-third of the product in the form of benzonitrile, the remaining portion being benzole. The safest, but somewhat lengthened, process for procuring benzonitrile, consists in dehydrating benzamide with anhydrous phosphoric acid, the former body having been produced by the action of carbonate of ammonium upon chloride of benzoyl, as recommended by M. GERHARDT.

ACTION OF SULPHURIC ACID UPON BENZONITRILE.

Sulphuric acid and benzonitrile mix with liberation of far less heat than is observable in the cases previously recounted. No gas is disengaged until the temperature is very considerably raised, when a portion of benzoic acid sublimes in the neck of the retort and carbon is deposited, while sulphurous acid is simultaneously disengaged. The action was continued for some time after the appearance of sulphurous acid, for the purpose of decomposing the sulphobenzoic acid which analogy would lead us to expect among the products of the reaction. On cooling, a semi-transparent hard mass of glassy fracture remained in the retort. The usual treatment with carbonate of barium evolved ammonia, showing the presence of a salt of that base.

Sulphobenzoate of Barium.

As the filtrate was very dark-coloured, the barium-salt was again decomposed by sulphuric acid, and then boiled with excess of oxide of lead, filtered and treated by hydrosulphuric acid. The sulphide of lead was found to carry down with it almost the whole of the colouring matter. The acid liquid was then saturated with carbonate of barium, a portion evaporated nearly to dryness and treated with hydrochloric acid, when a salt crystallized out from the mother-liquor, which, after washing with water, was again crystallized until free from hydrochloric acid.

Dried at 200°, it gave a percentage of barium which coincided with that required by the acid sulphobenzoate of barium analysed by MITSCHERLICH and FEHLING.

0.4092 grm. gave 0.1768 grm. of sulphate of barium.

Formula.	Theory.	Experiment.
$C_{14}(H_5Ba)S_2O_{10}$	25.41	25.39

Acid sulphobenzoate of barium.

It was therefore obvious that the disulphosalt, if present, was the most soluble, and to be found in the filtrate.

The remaining portion of the neutral solution of the barium-salt was therefore dissolved in water, and about one-half of the solid matter precipitated by alcohol, filtered off and recrystallized.

0.3634 grm., at 190°, gave 0.2510 grm. of sulphate of barium, the percentage of barium in which corresponds to the neutral sulphobenzoate of barium,

Formula.	Theory.	Experiment.
$C_{14}(H_4Ba_2)S_2O_{10}$	40.65	40.58

Neutral sulphobenzoate of barium.

Disulphobenzolate of Barium.

It remained, therefore, to examine the salt last thrown down by alcohol, which, after being purified again by precipitation, gave analytical numbers characterizing the new salt, although still in a state of admixture with sulphobenzoate of barium.

0.4910 grm., at 170°, gave 0.3170 grm. of sulphate of barium, which percentage approximates to that of the salt suggested by theory.

Formula.	Theory.	Experiment.
$C_{12}(H_4Ba_2)S_4O_{12}$	36.72	37.70

This analysis could leave no doubt regarding the nature of the substance analysed, yet it was desirable, if possible, to prepare the new compound in a state of purity; and the question presented itself, whether it could not be more directly formed from sulphobenzolic acid, $C_{12}H_6S_2O_6$, which is so easily obtained by the action of sulphuric acid upon benzol. Success in its preparation by this means was of consider-

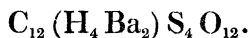
able interest, since in this case it would become highly probable that all the new bodies hitherto described in this memoir might be prepared, from the analogues of sulphobenzolic acid in their respective groups, by a simple assimilation of the elements of sulphuric acid. The method in question is in reality by far the best adapted for procuring the new acid in a state of purity. Sulphobenzolic acid obtained from the lead- or copper-salt is evaporated on the sand bath until the evolution of white fumes proves that the greater part of the water has been volatilized. It is advisable to heat the solution until a slight brown coloration indicates incipient decomposition. The acid is then introduced into a dry retort, together with an equal volume of strong Nordhausen acid, and the whole maintained at the boiling-point for two hours. The liquid is then reduced by evaporation nearly to the original bulk of the sulphobenzolic acid employed. The new acid in this stage has a very dark colour which cannot be removed by boiling with charcoal. Treatment, however, with an excess of oxide of lead, and decomposition of the filtrate by hydrosulphuric acid, furnishes a liquid which is perfectly colourless.

When this liquid is saturated with carbonate of barium and evaporated, an apparently amorphous mass is produced, which, however, under the microscope is distinctly crystalline, showing minute shuttle-shaped forms generally densely grouped together. This salt is very stable. Strongly heated, however, on platinum foil, it burns with evolution of sulphurous acid.

0.3930 grm., at 195°, gave 0.2436 grm. of sulphate of barium ;

0.3046 grm., ignited with chlorate of potassium, gave 0.3850 grm. of sulphate of barium,

leading to the formula of disulphobenzolate of barium,



	Theory.		Experiment.
12 equivs. of Carbon . . .	72	19.30	—
4 equivs. of Hydrogen . . .	4	1.07	—
2 equivs. of Barium . . .	137	36.72	36.43
4 equivs. of Sulphur . . .	64	17.16	17.35
12 equivs. of Oxygen . . .	96	25.75	—
	373	100.00	

For comparison, we subjoin the corresponding number for sulphobenzolate of barium,



Barium	30.38
Sulphur	14.19

The preceding researches establish in two different groups of bodies the existence of a series of bibasic acids, containing 4 equivalents of sulphur, and which, irrespect-

ively of any special view regarding their molecular arrangement, may be represented as formed by the association of the hydrocarbons (corresponding to marsh-gas) of the various groups with 4 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:—

Disulphonaphthalic acid	$C_{20} H_8 4SO_3$
---------------------------------	--------------------

which was discovered by BERZELIUS and subsequently studied by LAURENT.

Many of these substances may actually be produced 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,



It can scarcely be doubted that all the other hydrocarbons of the series $C_{2n} H_{2n}$, propylene, butylene, amylene, &c., will furnish homologous substances.

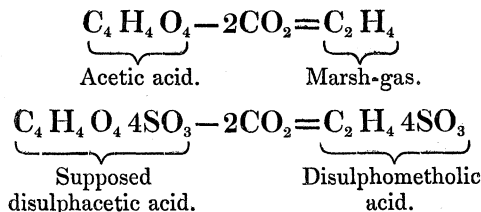
Sulphate of carbyl, when submitted to the action of water, assimilates two equivalents, and is converted into a bibasic acid (ethionic), $C_4 H_4 4SO_3 + 2HO = C_4 H_6 O_2 4SO_3$, which accordingly may be viewed as an association of alcohol with four equivalents of anhydrous sulphuric acid. Terms analogous 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, as ethylene, and as alcohol, suggested the possibility that the substances observed might be but individual examples of 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 terms belonging to the class of disulpho-compounds.

The hope of arriving at a more general interpretation of our observations induced us to institute some further inquiries, the result of which we will briefly append.

The first question which naturally suggested itself, was the examination of the deportment of the sulpho-acids derived from acetic, propionic, butyric, benzoic acid, &c., under the influence of an excess of sulphuric acid. To take acetic acid as an illustration, Is sulphacetic acid, $C_4 H_4 S_2 O_{10} = C_4 H_4 O_4 2SO_3$, capable of combining

with two additional equivalents of sulphuric acid in order to furnish the compound $C_4H_4S_4O_{16} = C_4H_4O_4 \cdot 4SO_3$? The experiments hitherto detailed contain no evidence against this assumption. It appeared to us extremely probable that sulphacetic acid, when submitted to the action of sulphuric acid, is converted into disulphacetic acid, which, losing carbonic acid, produces disulphometholic acid, the department of disulphacetic under the influence of heat being closely analogous with that of acetic acid,



We have endeavoured to decide this question by experiment; but on account of the greater stability of the benzoic molecule, we have preferred to trace the intermediate acid in the benzoyl-series.

Sulphobenzoic acid, obtained from the acid barium-salt, was evaporated to dryness and heated until it attained the point of quiet fusion. When cold, the acid was coarsely powdered, and mixed with rather more than its own bulk of crystallized sulphuric acid.

It was then heated in a water-bath to a temperature below that at which gases are disengaged. This appeared to be just below $85^\circ C$. The substances were kept in contact at this temperature for eight hours. Finally, the mixture was subjected to the heat of boiling water for two hours longer; after which it was treated in the usual way for obtaining the soluble barium-salt.

The salt thus obtained in no manner differed, either in appearance, reaction, or composition, from sulphobenzoate of barium.

0.3838 grm. of salt, dried at $165^\circ C$., gave 0.2630 grm. of sulphate of barium, corresponding to 40.28 per cent. of barium.

For comparison, we append the barium-percentages required for the salts of the two acids, and the amounts found by experiment.

Formula.	Theory.	Formula.	Theory.	Experiment.
$C_{14}(H_4Ba_2)S_2O_{10}$	40.65	$C_{14}(H_4Ba_2)S_4O_{16}$	32.85	40.28
Sulphobenzoate of barium.		Hypothetical acid.		

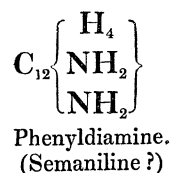
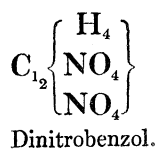
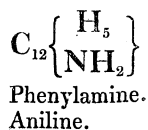
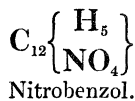
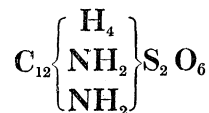
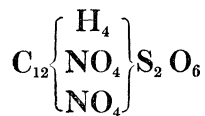
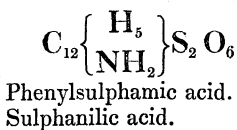
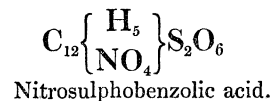
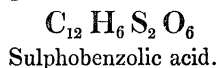
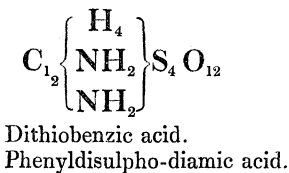
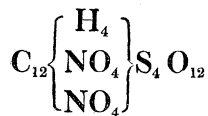
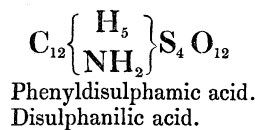
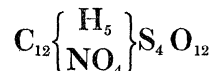
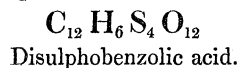
Though the above experiments have failed to realize our hopes of producing disulphobenzoic acid, they by no means disprove the existence of this body, and the possibility of producing it under more favourable circumstances. We insist upon this point, on account of the success which has attended our endeavours to trace the existence of disulpho-acids in a perfectly different group of bodies.

We are indebted to M. GERHARDT for the knowledge of a conjugated sulpho-acid, containing an organic base in the place of hydrocarbons, alcohols, acids, &c., which

are present in the usual sulpho-acids. Sulphanilic acid, $C_{12}H_7NS_2O_6$, may be viewed as formed by the association of one equivalent of aniline and two equivalents of anhydrous sulphuric acid.

We were curious to ascertain whether this acid, by assimilating once more the elements of anhydrous sulphuric acid, was capable of becoming disulphanilic acid, $C_{12}H_7NS_4O_{12}$.

The existence of disulphobenzolic acid, $C_{12}H_6S_4O_{12}$, the barium-salt of which we have described in the preceding pages, together with the formation of an interesting acid lately obtained by M. KILKENKAMP* in the reaction of sulphite of ammonium on dinitrobenzol, appeared to leave no doubt regarding the existence of a disulphanilic acid. In fact, M. KILKENKAMP's dithiobenzic acid, $C_{12}H_8N_2S_4O_{12}$, is most intimately connected with the acid we were in search of, as is obvious by a glance at the following Table, in which we have placed a number of known substances in juxtaposition with bodies, ideal at present, but the existence of which can no longer be doubted.

Hydrocarbons and substitutes.*Sulpho-acids and substitutes.**Disulpho-acids and substitutes.*

The preceding synopsis, whilst it fixes, we believe, the correct position of dithiobenzic acid in the benzol-series, exhibits at the same time its close relation to the disulphanilic acid which we endeavoured to produce, and the formation of which, it may at once be stated, succeeded without much difficulty.

* Annalen der Chemie und Pharmacie, Neue Reihe, B. xix. S. 86.

ACTION OF SULPHURIC ACID UPON ANILINE.

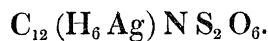
In order to prepare disulphanilic acid, two parts of strong sulphuric acid were mixed with one part of aniline, when heat was freely evolved, sulphate of aniline being thrown down at the same time. On further application of heat the salt redissolved, and as the liquid reached the boiling-point it became very dark in colour, sulphurous acid being freely evolved.

In our first experiment the mixture was kept in full ebullition for ten minutes, and then poured into water after it had partially cooled. A confusedly crystalline mass was produced which was well washed with cold water (in which it is not very soluble), and afterwards recrystallized from hot water.

Sulphanilate of Silver.

A portion of this acid was digested with carbonate of silver. The crystalline silver-salt, obtained by evaporating the solution at a low temperature, was dried at 120° and ignited.

0·3524 gram. gave 0·1360 gram. of reduced silver, which coincides with the theoretical percentage of sulphanilate of silver,

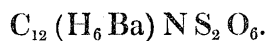


	Theory.	Experiment.
Silver . . .	38·57	38·58

Sulphanilate of Barium.

A barium-salt, prepared in the usual way and submitted to analysis by precipitation by sulphuric acid, gave perfectly analogous results.

0·4250 gram., at 160°, gave 0·2060 gram. sulphate of barium, corresponding to the formula



	Theory.	Experiment.
Barium . . .	28·48	28·40

These experiments proved that the acid produced was nothing but M. GERHARDT's well-known sulphanilic acid, the reaction not having gone far enough for the production of the second acid. The treatment with sulphuric acid was therefore resumed. Finely powdered and dry sulphanilic acid, mixed with strong fuming acid to the consistency of a thin paste, was heated in an air-bath to a temperature just approaching that at which sulphurous acid is generated, to 160° and 170° C. This digestion was continued until a portion taken on a glass rod did not solidify on cooling, or give any solid matter when dissolved in a small quantity of water, which happened after the lapse of seven hours, when the mass had the consistency of treacle.

It was dissolved in cold water, and separated from a black, almost insoluble matter, which appeared to be somewhat crystalline.

Disulphanilate of Barium.

After saturating with carbonate of barium the liquid was evaporated to dryness, by which treatment a further separation of the black substance was effected, and the barium-salt was much improved in colour.

If the barium-salt be redissolved and the solution evaporated on the water-bath, a horny substance is formed, which on cooling splits by cracks in all directions; but if the evaporation be completed under the receiver of an air-pump, a mass of microscopic crystals appear, insoluble in alcohol and in ether.

In preparing the new barium-salt, we have found it convenient to precipitate the liquid gradually by alcohol, and to reject, as retaining generally traces of sulphanilate, the precipitate first formed. Under all circumstances it is very difficult entirely to remove all colouring matter from the solutions of this salt, which is usually of a pale rose colour.

0·4679 grm., at 200°, gave 0·2810 grm. of sulphate of barium;

0·3620 grm., at 190°, gave 0·4310 grm. of sulphate of barium,

which numbers agree well with the formula of disulphanilate of barium,

	Theory.		Experiment.
12 equivs. of Carbon	72	18·58	—
5 equivs. of Hydrogen	5	1·28	—
2 equivs. of Barium	137	35·30	35·30
1 equiv. of Nitrogen	14	3·60	—
4 equivs. of Sulphur	64	16·49	16·32
12 equivs. of Oxygen	96	24·75	—
	388	100·00	

Disulphanilate of barium blackens without inflaming when heated on foil, in which respect it differs from the sulphanilate, which burns with a bright but smoky flame. Heated in close vessels it furnishes a vapour, which sublimes in beautiful crystals, probably of sulphite of aniline, obtained under similar circumstances from sulphanilic acid.

Disulphanilate of barium is attacked by concentrated nitric acid and gives a yellow liquid, which furnishes on evaporation crystals of a very bitter taste; sulphate of barium is formed at the same time.

Disulphanilic Acid

is easily produced from a lead-salt. This substance possesses a very acid and pungent taste; it crystallizes with great difficulty, but is insoluble, in alcohol which precipi-

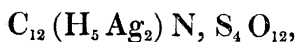
tates strong solutions in white grains. This precipitation is assisted by the addition of a little ether. We have not analysed this body, but we have examined in addition,

Disulphanilate of Silver.

The liquid formed by neutralizing a concentrated solution of the acid with carbonate of silver is precipitated cold by the addition of a mixture of equal volumes of alcohol and ether. The salt subsides in colourless crystalline grains; the deposition is much facilitated by rapidly stirring the contents of the beaker with a glass rod. Disulphanilate of silver crystallizes by spontaneous evaporation of the aqueous solution in small laminæ which blacken and deposit a black powder when boiled with water.

0.4687 grm., dried at 120°, gave 0.2134 grm. of silver.

The formula,



requires

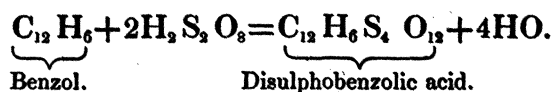
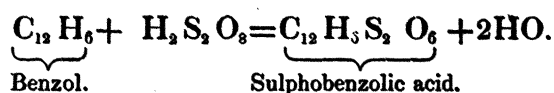
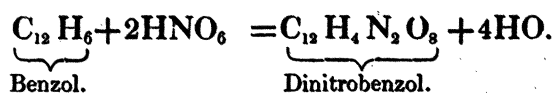
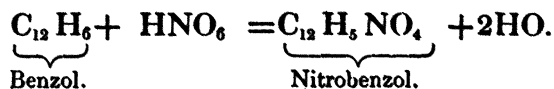
	Theory.		Experiment.
12 equivs. of Carbon . . .	72	15.40	—
5 equivs. of Hydrogen . . .	5	1.07	—
2 equivs. of Silver . . .	216	46.25	45.53*
1 equiv. of Nitrogen . . .	14	2.99	—
4 equivs. of Sulphur . . .	64	13.70	—
12 equivs. of Oxygen . . .	96	20.59	—
	<hr style="width: 100%;"/>	<hr style="width: 100%;"/>	
	467	100.00	

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 very different groups, had been previously observed. The only disulpho-acids hitherto known, were BERZELIUS and LAURENT'S disulphonaphthalic acid and MAGNUS'S ethionic (disulphethylic) acid, and lastly, dithiobenzic (phenyl-disulphodiamic) acid, recently discovered by M. KILKENKAMP. To these this memoir adds five new acids belonging to several of the most important series of compounds.

- Disulphometholic acid . . . C₂ H₄ S₄ O₁₂.
- Disulphetholic acid . . . C₄ H₆ S₄ O₁₂.
- Disulphopropiolic acid . . . C₆ H₈ S₄ O₁₂.
- Disulphobenzolic acid . . . C₁₂ H₆ S₄ O₁₂.
- Disulphanilic acid . . . C₁₂ H₇ N S₄ O₁₂.

* Although this number is rather low, it marks the composition of the salt sufficiently well, since the acid from which it was formed was known to contain traces of sulphanilic acid; for comparison we append the percentage of silver in sulphanilate of silver, which is 38.57.

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 elimination of water. In the action of nitric acid 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 bodies are formed with elimination of 6, 8, and in a few isolated cases, even of 10 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.

APPENDIX.

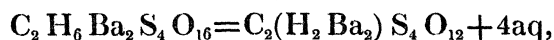
During the prosecution of the researches detailed in the preceding paper, our attention was repeatedly called to the substance which M. LIEBIG has described under the name of *methionic acid*, and which he obtained in the reaction of anhydrous sulphuric acid upon dry ether at low temperatures*. The properties of the barium-salt of this most remarkable acid very closely agree with those which we observed in studying disulphometholate of barium, although both appeared different in composition. We were repeatedly inclined to admit and to doubt the identity of the two substances. We have now arrived at the conclusion, that methionic and disulphometholic acid are actually *identical*.

* LIEBIG, *Annalen der Chemie und Pharm.* xiii. 32; xxv. 39. *Ann. de Chimie et de Phys.* i. 59. 182. WETHERELL, *Ann. der Chemie und Pharm.* lxvi. 122.

The formula adopted by M. LIEBIG for the barium-salt is



If we double this formula we arrive at the expression



which represents disulphometholate of barium with 4 equivalents of water of crystallization. Our experiments have actually proved that this salt contains indeed 4 equivalents of water, and that this water is retained at 100° C., the temperature at which M. LIEBIG dried his salt before submitting it to analysis.

More recently M. REDTENBACHER and M. WETHERELL have investigated the same barium-salt, but neither of them appears to have remarked the fact, that this salt loses water between 100° and 200°. M. REDTENBACHER analysed a salt which M. LIEBIG had prepared himself. M. WETHERELL examined a salt which he obtained as a secondary product in his researches on sulphate of ethyl.

Although we have no longer any doubt regarding the identity of methionic acid and disulphometholic acid, we should have liked to offer a direct experimental proof of our opinion by an analysis of the barium-salt obtained either by M. LIEBIG's or M. WETHERELL's process. We have therefore repeatedly endeavoured to prepare the methionate of barium both by M. LIEBIG's and M. WETHERELL's method. By following exactly the plan described by these chemists, we have actually succeeded in obtaining a salt possessing all the characters of disulphometholate of barium. Unfortunately, although we worked upon rather a large scale, we did not succeed in obtaining by either of these processes a quantity of barium-salt sufficient for analysis. In both processes the salt is the product of a secondary reaction.

May 9th, 1856.