VI. *On Hyposulphathylic, Hyposulphamethylic, Bisulphithylic and Bisulphimethylic Acids, produced by the action of nitric acid upon the Sulphocyanides and Bisulphides of Ethyl and Methyl, &c.* By SHERIDAN MUSPRATT, PH. D.

The action of nitric acid upon mercaptan and the bisulphide of ethyl has been studied by Löwig, Weidmann, and Kopp, who found that the same acid was produced from the two substances. In the former, an atom of hydrogen was removed and four of oxygen entered into combination; while with the latter the hydrogen remained intact, and four atoms of oxygen were assumed :

Bisulphithylic acid gives crystallizable salts with all the bases which are described in the interesting memoirs* of the above-cited chemists. The action of nitric acid upon the sulphocyanogen compounds of ethyl and methyl has been, up to the present time unknown, and it was possibly this circumstance that induced my much esteemed preceptor and friend, Baron Liebig, to suggest the investigation to me. A careful examination of the subject has led to the discovery of two new acids, which are formed in a very remarkable manner. When a new acid is obtained in the ethyl series, we may, with a degree of certainty, assume the existence of a corresponding one in the methylic class of bodies; and although the latter series is not as yet so extended as the former, still the analogues of all the sulphur and oxygen compounds of the ethyl combinations, will, I am convinced, before long be brought to light, and *vice versa*; and as soon as this is the case, more definite conclusions may be drawn by chemists with regard to the basyles and salt radicals, upon which the whole fabric of chemical theory is at present based.

Preparation of sulphocyanide of ethyl.—It is very difficult to obtain this body in large quantities. The best method of preparing it is by distilling in a retort equal measures of strong solutions of sulphovinate of lime and sulphocyanide of potassium. The capacity of the retort must be twelve times that of the space occupied by the mixture, so as to prevent any of the solution passing over into the receiver, which it is very apt to do, owing to a violent intumescence that occurs at intervals. The decomposition which takes place may be represented by the annexed equation:

Sulphocyanide of ethyl, discovered by Liebig and studied by Cahours,† is an oily and very dense liquid, possessing an odour of garlic. The latter chemist states in his Treatise, that “pretty-concentrated nitric acid dissolves it with the aid of heat; but that upon cooling, it separates again completely.” I cannot imagine how so accurate an investigator as M. Cahours could have made this mistake. Rather strong nitric acid decomposes the sulphocyanides

* Löwig's Organic Chemistry, vol. II. p. 427, and Poggendorff's Ann. der Phys. und Chem. Bd. XLVII. p. 153.

† Ann. der Pharm. 61-2, p. 99.

of ethyl and methyl with great rapidity, affording acids which will be subsequently described.

Process for obtaining hyposulphathylic acid.—About an ounce and a half of sulphocyanide of ethyl and the same quantity of tolerably concentrated nitric acid were introduced into a retort, connected with one of Liebig's condensers. A slight heat was applied to the retort during the whole process. At first the action was very brisk, and attended by the evolution of nitrous fumes, carbonic acid, and nitric oxide. Sulphuric acid was also formed during the operation; the quantity, however, depended upon the concentration of the acid employed. If weak nitric acid is used, traces only of sulphuric acid can be detected in the liquid. The distillate was repeatedly returned to the retort, so that very little loss of oil was sustained. The menstruum, after four or five distillations, was poured into a porcelain basin, and evaporated in a water-bath until the last trace of nitric acid was expelled. A fluid, like oil of vitriol, remained, possessing a slight alliaceous odour. This was diluted with water, in which it readily dissolved, saturated with carbonate of barytes, and filtered to remove the excess of carbonate and any sulphate of barytes. The filtrate, when evaporated very slowly, afforded large crystals of hyposulphathylate of barytes. These crystals were dissolved in water, precipitated by an excess of absolute alcohol, and re-crystallized. The acid may be obtained in a state of purity by precipitating the barytes with sulphuric acid from the aqueous solution of the salt, filtering, digesting the filtrate with carbonate of lead, re-filtering and decomposing the solution containing the lead salt by hydrosulphuric acid. When the sulphide of lead is separated and the filtrate evaporated in a water-bath, the acid is left in a pure state.

Properties of the acid.—When the acid is fused with potash and the residue treated with sulphuric or muriatic acid, large quantities of sulphurous acid are evolved. It withstands a very high temperature before suffering decomposition; fumes of sulphuric acid first escape, and then sulphurous acid is eliminated. The taste of the acid is most disagreeable and acrid, and of this the salts, all of which are soluble, also partake. The acid is miscible with water and alcohol in all proportions, and is very persistent.

Hyposulphathylate of barytes.—This salt is so very soluble in water, that it can only be obtained in fine rhombohedral prisms by allowing a concentrated solution to evaporate slowly. It is also very soluble in spirits of wine and ether, but insoluble in alcohol, which throws it down in beautiful satiny crystals. It parts with its water at 212°. The dried crystals, when heated with soda-lime, gave no

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indications of ammonia; fused with potassium and tested with iron solutions, the absence of nitrogen was fully proved; and this is the most remarkable feature with regard to the acid. In what form was the nitrogen of the sulphocyanide of ethyl eliminated? Not as ammonia, for no trace of this alkali could be detected. It must have passed off in the form of nitric oxide or nitrous acid. No instance of similar decomposition has hitherto been observed, *i. e.* an acid containing *no nitrogen* has never yet been produced by the action of one nitrogenous body upon another.

- I. 0·4140 grms. of the salt dried at 212° and burned with chromate of lead afforded: 0·2090 grms. carbonic acid and 0·1200 grms. of water.
 II. 0·4763 grms. of the salt gave: 0·2300 grms. carbonic acid, and 0·1310 grms. of water.
 I. 0·2560 grms. of the salt gave: 0·1665 grms. sulphate of barytes = 0·1093 grms. barytes.
 0·4190 grms. of the salt treated with potash and nitre gave: 0·5495 grms. sulphate of barytes = 0·0753 grms. sulphur.
 II. 0·4160 grms. of the salt gave: 0·2750 sulphate of barytes = 0·1800 grms. barytes.
 0·2340 grms. of the salt gave: 0·3000 grms. sulphate of barytes = 0·0411 grms. sulphur.

Centesimally represented:

			Theory.	Experiment.		
				I.	II.	Mean.
4 eq. Carbon . .	24·00	13·52	13·76	13·16	13·46	
5 „ Hydrogen . .	5·00	2·81	3·21	3·05	3·13	
2 „ Sulphur . .	32·00	18·01	17·99	17·56	17·77	
5 „ Oxygen . .	40·00	22·54	22·35	22·97	22·66	
1 „ Barytes . .	76·60	43·13	42·69	43·26	42·98	
	177·60	100·00	100·00	100·00	100·00	

The following formulæ agree very well with the above results:

or,

The decomposition that takes place when nitric acid acts upon sulphocyanide of ethyl may therefore be represented by the annexed equation:

yield :

0.7270 grm. salt, dried at 212° , gave : 0.0365 grm. water, which is equivalent to :

		Theory.	Exp ^t .
1 eq. hyposulphathylate of barytes	177.60	95.16	
1 „ water	9.00	4.84	5.02
	<u>186.60</u>	<u>100.00</u>	

Formula : $\text{BaO}, \text{C}_4 \text{H}_5 \text{S}_2 \text{O}_5 + \text{aq.}$

The barytes salt, when heated in a tube, blackens and gives off fumes possessing a most stifling smell.

Hyposulphathylate of lead.—This salt crystallizes from a hot, concentrated solution in beautiful colourless plates, which are extremely soluble in water, spirits, and alcohol. They intumesce when heated, and the residue contains sulphide of lead.

0.2790 grm. of dried salt gave : 0.2000 grm. sulphate of lead = 0.1472 grm. ox. lead, corresponding to :

		Theory.	Exp ^t .
1 eq. hyposulphathylic acid . .	101.00	47.41	
1 „ oxide of lead	112.00	52.59	52.76
	<u>213.00</u>		

The preceding results agree with the formula :

0.6110 grm. dried over sulphuric acid, and heated at 212° , gave : 0.0250 grm. water, corresponding to :

		Theory.	Exp ^t .
1 eq. hyposulphathylate of lead	213.00	95.98	
1 „ water	9.00	4.02	4.09
	<u>222.00</u>	<u>100.00</u>	

Formula : $\text{PbO}, \text{C}_2 \text{H}_5 \text{S}_2 \text{O}_5, + \text{aq.}$

Hyposulphathylate of copper.—It is very difficult to obtain this salt in well-defined crystals, on account of its great solubility in water and spirits. When the crystals are heated in a tube, they intumesce, and as soon as they blacken, vapours are evolved, possessing a most disagreeable odour.

0.2020 grm. of this salt dried over sulphuric acid, yielded : 0.0970 grm. carbonic acid, and 0.0880 grm. water.

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0·6170 grm. of the salt gave: 0·1338 grm. oxide of copper, which, centesimally represented, is equivalent to :

		Theory.	Expt.
4 eq. Carbon	24·00	12·90	13·11
10 „ Hydrogen	10·00	5·37	4·84
2 „ Sulphur	32·00	17·20	
10 „ Oxygen	80·00	43·03	
1 „ Oxide of copper . . .	40·00	21·50	21·68
	<u>186·00</u>	<u>100·00</u>	

The annexed formula agrees with the above numerical results :

I thought it would be very interesting, if by acting upon the sulphocyanide of ethyl with chlorate of potash, the same acid as the one just described could be produced. When sulphocyanide of ethyl is gradually added to a mixture of chlorate of potash and hydrochloric acid, a very violent action takes place, which is sometimes so brisk as to inflame the volatile products. As soon as the oil had entirely disappeared, the liquid was placed in a water-bath and evaporated to dryness, in order to get rid of the excess of hydrochloric acid. The residue was then treated with absolute alcohol, in which medium the chloride of potassium and any sulphate of potash are insoluble. When this solution was filtered and the filtrate evaporated on a water-bath, an oily acid was left, which was saturated with carbonate of barytes, and the whole again filtered. The solution that passed through, gave beautiful silky crystals, with absolute alcohol, possessing all the appearance of the hyposulphathylate of baryta. There was not enough of the salt for a combustion ; I consequently only made a determination of the barytes :

0·1060 grm. of salt, dried at 212° , gave: 0·0685 grm. of sulphate of barytes = 0·0450 grm. barytes.

The above result affords 42,45 per cent of barytes, and the formula

requires 43·13 per cent. I have, therefore, no doubt, that the acid is the same as that produced by the action of nitric acid upon the sulphocyanide of ethyl. One equivalent of sulphocyanide of ethyl, three equivalents of chlorate of potash, and seven equivalents of hydrochloric acid, contain the elements of one equivalent of hyposulphathylic acid, two equivalents of carbonic acid, one equivalent of nitric oxide, three equivalents of chloride of potassium, seven equivalents of water, and seven equivalents of free chlorine.

The sulphocyanide of ethyl is readily acted upon by chlorine gas.

When a stream of the gas is passed through it for some time, large quantities of chloride of cyanogen are formed, and there subsides a heavy yellow oil, which disappears when repeatedly washed. I have not further investigated this reaction. When a cold alcoholic solution of potash is mixed with sulphocyanide of ethyl, and the mixture is allowed to stand for some days in a corked vessel, decomposition takes place. The liquid becomes blood-red, and acquires a most singular odour; but there are no indications of the presence of ammonia. The results of the above decompositions will be embraced in a treatise on the action of chlorine, bromine, potash, &c., upon the sulphocyanides of ethyl and methyl.

Before commencing the corresponding reactions in the methyl series, I prepared Löwig's acid from the bisulphide of ethyl. The combustion of its copper salt dried at 212° , afforded me the following results :

0·3765 grm. salt, burned with chromate of lead, gave : 0·2000 grm. carbonic acid, and 0·1730 grm. water, numbers agreeing perfectly with Löwig's formula :

as may be seen from the annexed centesimal table :

		Theory.	Löwig and Weidmann.	Muspratt.
4 eq. Carbon	. . . 24·00	14·20	14·78	14·48
9 „ Hydrogen	. . . 9·00	5·33	5·65	5·10
8 „ Oxygen	. . . 64·00	37·94	36·47	
2 „ Sulphur	. . . 32·00	18·93	19·82	
1 „ Oxide of copper	. 40·00	23·60	23·28	
		169·00	100·00	100·00

Thus we possess two more sulphur acids belonging to the ethyl series; the one, that of Löwig, obtained from the bisulphide of ethyl, and the other, by the action of nitric acid upon the sulphocyanide of ethyl. Is it not probable that the series may be still more extended, and that compounds may be produced, corresponding with the whole sulphur series of acids? *i. e.* by acting upon the higher sulphides of ethyl with oxidizing agents. In the following formulæ the known ethyl and sulphur acids are represented collaterally with those that are required to complete the series.

Ethyl series.		Sulphur series.	
Sulphathylic acid	$\text{C}_4 \text{H}_5 \text{S} \text{O}_3$	Sulphuric acid	$\text{S} \text{O}_3$
Hyposulphathylic acid	$\text{C}_2 \text{H}_5 \text{S}_2 \text{O}_2$	Hyposulphurous acid	$\text{S}_2 \text{O}_2$

Ethyl series.			Sulphur series.		
Bisulphithylic acid	$C_4 H_5 S_2 O_2$		Bisulphurous acid		$S_2 O_4 ?$
Hyposulphathylic acid	$C_2 H_5 S_2 O_5$		Hyposulphuric acid		$S_2 O_5$
Tritrionathylic acid	$C_2 H_5 S_3 O_5 ?$		Tritrionic acid		$S_3 O_5$
Tetratrionathylic acid	$C_2 H_5 S_4 O_5 ?$		Tetratrionic acid		$S_4 O_5$
Pentatrionathylic acid	$C_2 H_5 S_5 O_5 ?$		Pentatrionic acid		$S_5 O_5$

Preparation of sulphocyanide of methyl.—This body is prepared in a similar manner to the ethyl compound. I distilled together equal quantities of strong solutions of sulphate of methyl and lime and sulphocyanide of potassium. The same precautions were observed as those described under sulphocyanide of ethyl. Sulphocyanide of methyl is a heavy oil, possessing a disagreeable alliaceous smell. It is very readily decomposed by strong nitric acid, yielding an analogous compound to the hyposulphathylic acid. The acid possesses no smell, and is not easily decomposed by heat.

Hyposulphamethylate of baryta.—The same course was followed for procuring this salt as with its analogue. It is very soluble in water, but is precipitated from that solvent in fine needles by spirits of wine and alcohol.

0.3640 grm. of the salt dried at 212° , and burned with chromate of lead, gave: 0.0965 grm. carbonic acid, and 0.0500 grm. water.

0.3385 grm. of the salt gave: 0.5200 grm. sulphate of barytes = 0.071 grm. sulphur.

0.2430 grm. of the salt gave: 0.0730 grm. sulphate of barytes = 0.1136 grm. barytes.

Centesimally represented:

		Theory.	Exp ^t .
2 eqs. Carbon . . .	12.00	7.34	7.23
3 „ Hydrogen . . .	3.00	1.24	1.58
2 „ Sulphur . . .	32.00	19.56	19.80
5 „ Oxygen . . .	40.00	25.04	24.65
1 „ Baryta . . .	76.60	46.82	46.74
	<hr/> 163.60	<hr/> 100.00	<hr/> 100.00

The preceding numerical results agree perfectly with the formula:

Hyposulphamethylate of barytes behaves like its analogue when heated in a test-tube; water first passes off, and is followed by sulphuric and sulphurous acid fumes.

0.5325 grm. salt, dried over sulphuric acid and heated at 212° for two days, gave: 0.0278 grm water, corresponding to:

		Theory.	Exp ^t .
1 eq. Hyposulphamethylate of barytes	163·60	94·78	
1 „ Water	9·00	5·22	5·25
	<hr/> 172·60	<hr/> 100·00	

Formula : $\text{BaO}, \text{C}_2 \text{H}_3 \text{S}_2 \text{O}_5 + \text{aq.}$

Hyposulphamethylate of lead.—This salt crystallizes in fine rhombic prisms from an aqueous solution. When heated, it gives off water with intumescence.

0·5745 grm. of the crystals gave : 0·0245 grm. water.

0·1755 grm. of the crystals gave : 0·1250 grm. sulphate of lead = 0·0921 grm. oxide of lead.

The composition in 100 parts is, therefore :

		Theory.	Exp ^t .
1 eq. Hyposulphamethylic acid	87·00	41·84	
1 „ Oxide of lead	112·00	53·84	53·39
1 „ Water	9·00	4·32	4·27
	<hr/> 208·00	<hr/> 100·00	

These numbers correspond with the formula :

Hyposulphamethylate of copper.—This salt is obtained in very fine crystals, by slowly evaporating the aqueous solution. It is remarkably soluble.

0·2514 grm. of the salt dried over sulphuric acid and burnt with chromate of lead gave : 0·0640 grm. carbonic acid, and 0·1130 grm. water, which numbers correspond with :

		Theory.	Exp ^t .
2 eq. Carbon	12·00	6·98	6·94
8 „ Hydrogen	8·00	4·65	4·99
2 „ Sulphur	32·00	18·60	
10 „ Oxygen	80·00	46·41	
1 „ Oxide of copper . . .	40·00	23·25	
	<hr/> 172·00	<hr/> 100·00	

This salt also agrees in composition with its analogue; the two being represented by the annexed formulæ :

Previously to concluding my investigations on this subject, I wished to ascertain the composition of the acid resulting from the bisulphide of methyl, which has not hitherto been given. Cahours

states* that tolerably concentrated nitric acid acts briskly upon the bisulphide of methyl, affording sulphuric acid collaterally with a peculiar acid, which yields crystals with potash, barytes, &c. In the preparation of the acid, I proceeded in the manner previously described. I remarked on evaporating the decomposed solution in the water-bath, that the fumes passing off were most stifling, and productive of lachrymation. The smell is similar to that of horse-radish, but much more disagreeable and pungent.

Bisulphimethylate of lead.—This salt crystallizes in fine rhombic prisms. When heated, penetrating vapours are expelled, accompanied by some water.

0.6960 grm. of the salt dried over sulphuric acid, gave: 0.1498 grm. carbonic acid, and 0.1265 water.

0.4040 grm. of the salt gave: 0.2980 grm. sulphate of lead = 0.2195 grm. oxide of lead.

Calculated per cent :

		Theory.	Exp ^t .
2 eq. Carbon	. . . 12.00	6.00	5.87
4 „ Hydrogen	. . . 4.00	2.00	2.01
2 „ Sulphur	. . . 32.00	16.00	
5 „ Oxygen	. . . 40.00	20.00	
1 „ Oxide of lead	. . 112.00	56.00	54.33
	<u>200.00</u>	<u>100.00</u>	

The annexed formula may be deduced from the above :

Here then we possess another instance of the remarkable similarity which exists between the ethyl and methyl series of compounds; for the above acid is the analogue of the bisulphithylic.

Before closing this memoir, I shall place some of the salts of the four acids in a tabular form, with the view of displaying the striking similarity existing between the two series :

Bisulphithylate of baryta	$\text{C}_4 \text{H}_5 \text{S}_2 \text{O}_4, \text{BaO} + \text{aq.}$
Bisulphithylate of lead	$\text{C}_4 \text{H}_5 \text{S}_2 \text{O}_4, \text{PbO} + \text{aq.}$
Bisulphithylate of copper	$\text{C}_4 \text{H}_5 \text{S}_2 \text{O}_4, \text{CuO} + 5 \text{aq.}$
Hypsulphathylate of baryta	$\text{C}_4 \text{H}_5 \text{S}_2 \text{O}_5, \text{BaO} + \text{aq.}$
Hypsulphathylate of lead	$\text{C}_4 \text{H}_5 \text{S}_2 \text{O}_5, \text{PbO} + \text{aq.}$
Hypsulphathylate of copper	$\text{C}_4 \text{H}_5 \text{S}_2 \text{O}_5, \text{CuO} + 5 \text{aq.}$
Bisulphimethylate of baryta	$\text{C}_2 \text{H}_3 \text{S}_2 \text{O}_4, \text{BaO} + \text{aq.} ?$
Bisulphimethylate of lead	$\text{C}_2 \text{H}_3 \text{S}_2 \text{O}_4, \text{PbO} + \text{aq.}$

* Ann. de Pharm. 61-2, p. 93.

Bisulphimethylate of copper $C_2 H_3 S_2 O_4, CuO + aq. ?$

Hyposulphamethylate of baryta $C_2 H_3 S_2 O_5, BaO + aq.$

Hyposulphamethylate of lead $C_2 H_3 S_2 O_5, PbO + aq.$

Hyposulphamethylate of copper $C_2 H_3 S_2 O_5, CuO + 5 aq.$

I hope that I shall soon be enabled to present this Society with another treatise upon these compounds.