V. *Researches on Organo-metallic Bodies.*—Third Memoir. *On a New Series of Organic Acids containing Nitrogen.*

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In the progress made by Organic Chemistry during the past fifteen years, no generalization has perhaps contributed so extensively to the development of this branch of the science, as the doctrine of substitution. The value of this doctrine becomes even still more apparent, when it is remembered that chemists have, until very recently, possessed adequate means for following out its suggestions, in one direction only. The peculiar habits of chlorine render the substitution of an electro-positive constituent by this element, generally a work of little or no difficulty, and even the like substitution of other electro-negative for electro-positive elements in organic bodies, presents no insurmountable obstacles. But the inverse process has hitherto been successfully accomplished only in comparatively few cases, owing to the want of a body capable, like chlorine, of effecting such a replacement with facility. This want is now supplied in zincmethyl and its homologues; bodies which, on account of their intense affinities and peculiar behaviour, possess in an eminent degree the property of removing electro-negative constituents and replacing them by methyl, ethyl, &c. The action of zincmethyl upon water, attended as it is by the substitution of methyl for oxygen,

$$\left.\begin{matrix} C_2H_3Zn \\ HO \end{matrix}\right\} = \left\{\begin{matrix} C_2H_3, H \\ ZnO, \end{matrix}\right.$$

may be regarded as the type of these reactions, which open up a most extensive and perfectly new field of research, from the cultivation of which important discoveries cannot fail to spring. Amongst the reactions of this nature which promise most interesting results, are those with the chlorine and oxygen substitution products derived from the ethers and organic acids, which might lead to the higher members of each homologous series being produced from the lower ones, if not to the building up of some of those series from their inorganic types; a discovery which cannot now remain long in abeyance. Instead of immediately pursuing this line of investigation, however, I determined in the first place to confine my attention to the action of these organo-zinc bodies upon inorganic compounds.

In a former memoir* I endeavoured to give a general view of the rational constitution of all the organo-metallic bodies then known, by showing that they all possessed a molecular isonomy with the inorganic compounds of the respective metals. The only com-

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* Philosophical Transactions, 1852, page 438.

pound which at that time did not coincide with this view was Lövig's so-called ethostibylic acid, the formula of which, $SbC_4H_5O_5$, I suggested would probably be found to be erroneous*; and in fact, Lövig has since announced this to be the case: he now assigns to this compound the formula $Sb(C_4H_5)_3O_2$, $2SbO_3$, which harmonizes perfectly with the general view I ventured to propound. The recent researches of Merck† upon the compounds of stibethyl, although they probably prove the existence of certain new compounds of this radical, are by no means conclusive as to the non-existence of the bodies originally described by Lövig. With regard to those stanethyl compounds which have been since discovered, several of them correspond exactly with the known oxides of tin; the remainder are also by no means irreconcileable with my hypothesis, if we consider the polymeric attributes of stannic acid. Nevertheless, I conceive that the formulæ, and even the existence of some of the more complex stanethyl compounds, require confirmation before these bodies can be employed, either for the support or disproof of any general theory of the rational constitution of organo-metallic compounds.

Taking, then, this view of the organo-metallic compounds as my guide, I pointed out in a former memoir ‡ that the oxygen compounds of nitrogen might probably be represented by corresponding organic compounds, in which one or more equivalents of oxygen were replaced by an organic radical: thus, to take one example, nitric acid, by the substitution of methyl, should yield the following derivatives:—

$$\begin{array}{ccccc}
\text{I.} & \text{II.} & \text{III.} & \text{IV.} & \text{V.} \\
N\left\{\begin{array}{c} C_2H_3 \\ O \\ O \\ O \\ O \end{array}\right., &
N\left\{\begin{array}{c} C_2H_3 \\ C_2H_3 \\ O \\ O \\ O \end{array}\right., &
N\left\{\begin{array}{c} C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ O \\ O \end{array}\right., &
N\left\{\begin{array}{c} C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ O \end{array}\right., &
N\left\{\begin{array}{c} C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ C_2H_3 \end{array}\right.,
\end{array}$$

of which the fourth is already known as oxide of tetramethylammonium. My attempts to produce these derivatives from the oxygen compounds of nitrogen have hitherto been confined to the binoxide, in which I have succeeded in replacing oxygen by ethyl in the manner now to be described.

Action of Zincethyl upon Binoxide of Nitrogen.

If a small quantity of zincethyl, either pure or dissolved in ether, be passed up into dry binoxide of nitrogen confined over mercury, the binoxide is very slowly but completely absorbed in large quantity, without the production of any other gas. The solution may be accelerated by agitation, but even then it is exceedingly slow. At the expiration of from one to four days, rhomboidal crystals begin to be deposited, and increase in number until the liquid finally solidifies. To prepare these crystals in larger quantity, about an ounce of zincethyl, dissolved in an equal bulk of dry ether, was placed in a flat-bottomed flask and supplied with binoxide of nitrogen from a gas-holder,

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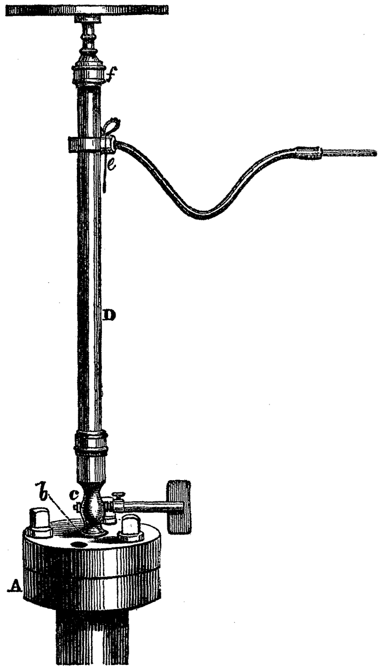
* Philosophical Transactions, 1852, page 442.

† Journal für Prak. Chemie, Bd. lxvi. S. 56.

‡ Philosophical Transactions, vol. cxliii. page 442.

the gas being thoroughly dried, by bubbling through a long series of bulbs filled with concentrated sulphuric acid, which also served to absorb any traces of nitrous gas that might be formed by atmospheric oxygen gaining access to the interior of the apparatus. The gas was conducted into the flask by a tube which terminated just below the cork; whilst a provision was made for its exit by another tube continued to within a short distance of the surface of the liquid, and which terminated outside the cork in a capillary extremity, that could be readily sealed up by the blowpipe and reopened at pleasure. Binoxide of nitrogen, prepared from copper turnings and nitric acid, always contains a considerable per-centage of protoxide, and it was therefore necessary occasionally to allow a stream of the gas to flow through the flask, so as to prevent the absorption being hindered or stopped by the accumulation of protoxide of nitrogen: at other times the exit tube was hermetically sealed and the gas supplied only as it was absorbed. In this way, although the apparatus was in action day and night, six weeks elapsed before the absorption was completed. On another occasion, when the action was accelerated by violent agitation of the liquid for several hours each day, the zincethyl was saturated in about a fortnight. It was evident that such a process was little calculated for the production of considerable quantities of the new compound, and recourse was therefore had to mechanical means in order to expedite and facilitate the operation. Fig. 1 is from a photograph of the apparatus employed for this purpose, and as it will no doubt prove useful in other cases for experiments with sparingly soluble gases, I will describe it somewhat in detail. A is a copper digester similar to the one I have already described for the preparation of zincethyl*; into the aperture *b* is screwed the stopcock *c*, to which can be attached at pleasure the condensing syringe D made of gun-metal, 12 inches long and ·7 inch in diameter. In this syringe a solid steel piston $1\frac{3}{4}$ inch deep works air-tight, and the piston-rod passes through a stuffing-box *f*. The syringe is supplied with gas through the nozzle *e*, to which a flexible tube is attached. When the stopcock *c* is closed, the elevation of the piston produces a vacuum, which is instantly filled with gas, so soon as the piston has passed the nozzle *e*. Between *e* and *f* the interior of the syringe is grooved longitudinally, so as to prevent any compression of gas behind the piston, when it is drawn up to *f*. On forcing down the piston and opening the stopcock *c*, it is obvious that the gas occupying the syringe from *e* to *c* will be forced into A. By repeating this process, it is not difficult for one operator to compress about twenty atmospheres into A; such a degree of compression exerting upon the piston a pressure of about 114 lbs.

Fig. 1.



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* Philosophical Transactions, vol. cxlv. p. 261.

In each operation about three ounces of zincethyl in ethereal solution was placed in the copper cylinder A, and the condensing syringe being attached, about twenty atmospheres of dry binoxide of nitrogen were introduced; the syringe was unscrewed and the cylinder A agitated for two or three minutes by rolling upon the floor or otherwise; at the end of which operation, the pressure within A was found to be reduced to three or four atmospheres; the process of condensation and agitation being repeated five or six times, the copper cylinder becomes so much heated as to require immersion in cold water for a few minutes. At this stage of the process it is also desirable to allow the residual gas in A to escape.

This gas consists principally of protoxide of nitrogen and hydride of ethyl; the latter derived from the decomposition of zincethyl by a trace of aqueous vapour introduced with the binoxide of nitrogen. By repeating the above series of operations six or eight times, the zincethyl becomes saturated and the process is completed. If it be desired to obtain the crystalline compound in a state of perfect purity, it is better to place the zincethyl in a wide glass tube open at top and fitting into A; but in this case very moderate agitation only can be used, and consequently the absorption takes place more slowly, and the operation requires two or three days for its completion. It is, however, rarely necessary to have recourse to this modification of the process.

At the conclusion of an operation conducted as above, with the intervention of a glass tube, the contents of the latter consisted of a mass of colourless crystals immersed in an ethereal solution; the latter was poured off and the former were freed from ether, by plunging the tube in a water-bath at 90° C. and passing through it a stream of dry carbonic acid. The resulting crystalline mass attracted oxygen from the air with such avidity, as to burst into flame when any considerable quantity was freely exposed; it was also instantly decomposed by water, and was therefore transferred at once into small glass tubes, which were then immediately sealed hermetically.

Submitted to analysis these crystals yielded the following results:—

I. ·6476 grm., burnt with oxide of copper and free oxygen, the usual precautions being observed, yielded ·6101 grm. carbonic acid and ·3084 grm. water.

II. ·6110 grm. gave ·5836 grm. carbonic acid and ·2909 grm. water.

III. ·4988 grm. gave ·4588 grm. carbonic acid and ·2413 grm. water.

IV. ·8892 grm., treated first with water and then with boiling nitric acid, yielded on subsequent ignition ·3940 grm. oxide of zinc.

V. ·4179 grm., similarly treated, gave ·1837 grm. oxide of zinc.

VI. ·5900 grm. gave ·2585 grm. oxide of zinc.

VII. ·1155 grm., treated according to SIMPSON'S method, gave 52·5 cubic centimetres of dry nitrogen at 9°·2 C. and 210·3 mm. pressure, equal to 14·04 cubic centimetres at 0° C. and 760 mm. pressure, or ·0177 gramme*.

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* Considerable difficulty was at first experienced in determining the nitrogen in this and the following compounds. The method of WILL and VARRENTRAPP is quite inapplicable, as it does not in some cases convert more than one-half of the total nitrogen into ammonia. BUNSEN'S method also yields variable results,

VIII. ·3964 grm., similarly treated, gave 88·8 cubic centimetres dry nitrogen at 10°·0 C. and 412·4 mm. pressure, equal to 46·19 cubic centimetres at 0° C. and 760 mm. pressure, or ·05834 gramme.

IX. ·3712 grm. gave 84·0 cubic centimetres dry nitrogen at 411·8 mm. pressure and 15° C., or 43·02 cubic centimetres at 760 mm. pressure and 0° C., or ·05410 gramme.

These numbers correspond with the formula

$$C_4 H_5 Zn N O_2,$$

as is seen from the following comparison:—

	Calculated.		Found.								
			I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
C_4 .	24	26·22	25·69	26·05	25·09						
H_5 .	5	5·46	5·29	5·29	5·38						
N .	14	15·30							15·32	14·72	14·63
Zn .	32·52	35·53				35·63	35·28	35·16			
O_2 .	16	17·49									
	91·52	100·00									

The substance used for these analyses was prepared in several different operations. That used for Nos. III. and IV. had undergone considerable oxidation, as it was finely powdered before being weighed, which will account for the deficiency in the per-centage of carbon. These results prove that the new body is formed by the union of an equal number of atoms of zincethyl and binoxide of nitrogen; but from considerations given below, the above formula requires to be doubled, and I shall presently show that the body is a compound of zincethyl with the zinc-salt of a new acid, for which I propose the name *Dinitroethylic acid.* Its formula is therefore

$$N_2 C_4 H_5 O_4 Zn + Zn C_4 H_5,$$

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owing to the formation of some carbonate of zinc, which requires a higher heat for complete decomposition. SIMPSON'S absolute method gave very good results without the use of peroxide of mercury, but it was found impossible to prevent the occurrence of a considerable amount of binoxide of nitrogen in the resulting gas. Even when it was made to stream over 12 inches of an intensely ignited mixture of copper turnings and copper reduced from the oxide, the resulting nitrogen still contained 10·9 per cent. of binoxide. It was therefore necessary to estimate the volume of the latter gas by means of solution of protosulphate of iron, and to deduct half its volume from the observed amount of the mixed gases. The presence of protoxide of nitrogen would not interfere with the accuracy of the result, as this gas is unaffected by solution of protosulphate of iron, and contains exactly its own volume of nitrogen. By the observance of this precaution, SIMPSON'S absolute method not only appears to be capable of great accuracy, but it also requires much less expenditure of time, whilst it is easier of execution than any of the other methods, if it be employed in conjunction with the gas analysis apparatus, which I always use in eudiometrical operations (see Journal of the Chemical Society, vol. vi. p. 200); the absorption-tube, containing a layer of concentrated caustic potash solution, being used to receive the products of combustion, at the conclusion of which, the determination of the absolute volumes of nitrogen and binoxide of nitrogen is effected with this apparatus in a few minutes.

This compound is produced from zincethyl and binoxide of nitrogen according to the following equation:—

$$\left.\begin{matrix}2(\mathrm{Zn\,C_4\,H_5})\\ 2\mathrm{NO_2}\end{matrix}\right\}=\mathrm{N_2\,C_4\,H_5\,O_4\,Zn+Zn\,C_4\,H_5}.$$

Dinitroethylate of zinc and zincethyl is deposited from its ethereal solution in large colourless and transparent rhomboidal crystals, which instantly become opake on exposure to the air, owing to the formation of an oxidized product. These crystals are tolerably soluble in anhydrous ether without decomposition, but they are instantly decomposed by anhydrous alcohol and by water. Exposed to the gradually increasing heat of an oil-bath, dinitroethylate of zinc and zincethyl fuses at 100° C., froths up and begins slowly to evolve gas. At 180° C. the colour darkens, and a small quantity of a yellowish liquid of a penetrating odour, free from zincethyl and possessing a very powerful alkaline reaction, distils over. This liquid, neutralized with hydrochloric acid and treated with bichloride of platinum, yielded a splendidly crystalline platinum salt, which was obtained, however, in too small quantity to allow of its composition being determined. From 180° to 190^{c}, dinitroethylate of zinc and zincethyl evolved gas very rapidly, and the experiment was then interrupted. The gas consisted of 18·4 per cent. carbonic acid, 23·66 per cent. olefiant gas, and 57·94 per cent. of a mixture of hydride of ethyl, nitrogen and protoxide of nitrogen.

When brought into contact with water, dinitroethylate of zinc and zincethyl is immediately decomposed with lively effervescence. A large quantity of inflammable gas is evolved, and a white flocculent substance formed. At the conclusion of the reaction the latter dissolves almost completely, forming an opalescent solution resembling milk, possessing a powerfully alkaline reaction and a peculiarly bitter taste.

In order to ascertain the exact nature of the gas evolved in this reaction, some crystals of dinitroethylate of zinc and zincethyl were passed up into an inverted receiver filled with mercury, and were then brought into contact with a small quantity of water. The gas thus collected over mercury possessed an ethereal odour, burnt with a slightly luminous flame, and was completely soluble in an equal volume of alcohol. It was perfectly neutral, and underwent no change on being treated successively with caustic potash solution and dilute sulphuric acid.

A specific gravity determination gave the following numbers:—

Temperature of room	7°·7 C.
Height of barometer	761·3 mm.
Height of internal column of mercury . . .	6·5 mm.
Weight of flask and gas	31·2294 grms.
Temperature in balance-case	10°·7 C.
Weight of flask and dry air	31·2199 grms.
Temperature of balance-case	11°·0 C.
Capacity of flask	141·0 cub. cent.

From these data the specific gravity was calculated to be 1·0515.

Submitted to eudiometrical analysis the following data were obtained:—

I.		Temp.
Pressure of gas used (dry)	200·9 mm.	3°·6 C.
Pressure after action of fuming sulphuric acid (dry)	200·9	3°·6

II.		
Pressure of gas used (dry)	20·0 mm.	3°·5
Pressure after admission of oxygen (dry)	267·6	3°·5
Pressure after explosion (dry)	217·9	3°·5
Pressure after absorption of carbonic acid (dry) . .	177·7	3°·5
Pressure after admission of hydrogen (dry) . . .	845·6	3°·5
Pressure after explosion	312·2	3°·5

These numbers prove that neither nitrogen nor any member of the olefiant gas family is present; they also prove that one volume of the combustible gas consumed almost exactly 3½ volumes of oxygen and generated two volumes of carbonic acid, as seen by the following proportions:—

Vol. of combustible gas.		Vol. of oxygen consumed.		Vol. of CO_2 generated.
20·0	:	69·9	:	40·2
1	:	3·495	:	2·01

These are exactly the results obtained by the combustion of hydride of ethyl, one volume of which consumes 3½ volumes of oxygen and generates two volumes of carbonic acid. This result is also confirmed by the determination of the specific gravity of the gas, for the theoretical specific gravity of hydride of ethyl is 1·03652, which agrees very nearly with the number obtained in the above determination.

On submitting the milky solution, formed by the decomposition of dinitroethylate of zinc and zincethyl in water, to a stream of carbonic acid, a copious precipitate of carbonate of zinc, free from organic matter, was thrown down; the liquid was then heated to boiling and filtered. The filtrate, evaporated almost to dryness in a water-bath, yielded a white radiated crystalline mass, which, after being reduced to powder, pressed between blotting-paper, and dried over sulphuric acid, was submitted to analysis and yielded the following results:—

I. ·9042 grm., exposed to a current of dry air at ordinary temperatures and afterwards at 100° C., at which temperature it fused, lost ·0360 grm. water.

II. ·2843 grm., burnt with oxide of copper with the usual precautions, gave ·1963 grm. carbonic acid and ·1180 grm. water.

III. ·3540 grm. gave ·2410 grm. carbonic acid and ·1518 grm. water.

IV. ·2785 grm., dissolved in water, treated with nitric acid and afterwards ignited, gave ·0910 grm. oxide of zinc.

V. ·3074 grm., similarly treated, gave ·0975 grm. oxide of zinc.

VI. ·2577 grm., similarly treated, gave ·0825 grm. oxide of zinc.

VII. A nitrogen determination according to BUNSEN'S method yielded the following results:—

		Temp.
Pressure of mixed gases (dry).	184·2 mm.	13°·7 C.
Pressure after absorption of CO_2 (dry) . . .	65·0	13°·7

The atomic relation of carbonic acid to nitrogen is therefore as follows:—

$$CO_2 : N = 119{\cdot}2 : 65,$$

or

$$CO_2 : N = 2 : 1{\cdot}09.$$

VIII. 2·1023 grms., dried at 100° C. until the weight ceased to diminish, lost ·0788 grm. water.

These numbers correspond with the formula

$$2(N_2C_4H_5O_4Zn)+HO,$$

as is seen from the following comparison:—

	Calculated.		Found.					
			II.	III.	IV.	V.	VI.	VII.
C_8 .	48	19·04	18·83	18·57				
H_{11} .	11	4·36	4·61	4·76				
N_4 .	56	22·22						23·78
Zn_2 .	65·04	25·81			26·23	25·46	25·69	
O_9 .	72	28·57						
	252·04	100·00						

These results prove that the action of water upon dinitroethylate of zinc and zincethyl consists in the transformation of the zincethyl into oxide of zinc and hydride of ethyl, thus

$$\left.\begin{array}{r} N_2C_4H_5O_4Zn+C_4H_5Zn \\ HO \end{array}\right\} = \left\{\begin{array}{l} C_4H_5, H \\ N_2C_4H_5O_4Zn \\ ZnO. \end{array}\right.$$

The neutral dinitroethylate of zinc, however, thus set at liberty, immediately unites with a second equivalent of oxide of zinc, to form the basic salt $N_2C_4H_5O_4Zn+ZnO$, which is decomposed by carbonic acid into carbonate of zinc and the neutral salt.

Estimations Nos. I. and VIII. prove that dinitroethylate of zinc crystallizes with half an equivalent of water, which is expelled at 100° C., the loss in drying being 3·98 per cent. and 3·75 per cent. respectively, whilst the theoretical number is 3·57.

In order to establish beyond doubt the nature of the transition from dinitroethylate of zinc and zincethyl, to dinitroethylate of zinc, a known quantity of the former compound was treated with water, and the amount of zinc separated by carbonic acid and of that left in solution, separately estimated. The following numbers were obtained:—·5654 grm. dinitroethylate of zinc and zincethyl gave, when treated with carbonic acid, a quantity of carbonate, which yielded on ignition ·1204 grm. oxide of zinc. The filtrate precipitated by carbonate of soda gave ·1148 grm. oxide of zinc. These numbers are equivalent to

21·30 per cent. of oxide of zinc precipitated by carbonic acid, and 20·35 per cent. oxide of zinc left in solution; numbers which nearly approach to equality, and do not differ from the theoretical amount in each case (22·14) more widely than might be expected when it is stated that the dinitroethylate of zinc and zincethyl used, had become partially oxidized before being weighed.

Dinitroethylate of zinc is also produced by the direct oxidation of dinitroethylate of zinc and zincethyl in a stream of dry air, ethylate of zinc being at the same time formed: the completion of the oxidation is known by the product ceasing to effervesce in contact with water. This reaction is expressed by the following equation:—

$$\left.\begin{array}{r} N_2\,C_4\,H_5\,O_4\,Zn + C_4\,H_5\,Zn \\ O_2 \end{array}\right\} = \left\{\begin{array}{l} N_2\,C_4\,H_5\,O_4\,Zn \\ ZnO,\ C_4\,H_5\,O. \end{array}\right.$$

When this product is treated with water, alcohol and bibasic dinitroethylate of zinc are produced,

$$\left.\begin{array}{r} N_2\,C_4\,H_5\,O_4\,Zn \\ ZnO,\ C_4\,H_5\,O \end{array}\right\} = \left\{\begin{array}{l} N_2\,C_4\,H_5\,O_4\,Zn + ZnO \\ C_4\,H_5\,O,\ HO. \end{array}\right.$$

One of the equivalents of base being removed by carbonic acid, the filtered solution of the neutral salt thus obtained was evaporated to crystallization, and the crystals heated to 100° for some time; at this temperature they fused and afterwards solidified in cooling to a gummy mass, which is the anhydrous dinitroethylate of zinc, as is seen from the following analyses:—

I. ·3964 grm., burnt with oxide of copper and oxygen, gave ·2880 grm. carbonic acid and ·1540 grm. water.

II. ·0835 grm. gave ·0610 grm. carbonic acid and ·0338 grm. water.

III. ·2885 grm., treated with nitric acid and afterwards ignited, gave ·0988 grm. oxide of zinc.

IV. ·3501 grm., similarly treated, gave ·1182 grm. oxide of zinc.

These numbers agree sufficiently with those calculated from the formula of anhydrous dinitroethylate of zinc,

$$N_2\,C_4\,H_5\,O_4\,Zn.$$

	Calculated.		Found.			
			I.	II.	III.	IV.
C_4 . . .	24	19·75	19·81	19·92		
H_5 . . .	5	4·11	4·32	4·50		
N_2 . . .	28	23·04				
Zn . . .	32·52	26·76			27·49	27·10
O_4 . . .	32	26·34				
	121·52	100·00				

Finally, dinitroethylate of zinc and zincethyl is produced by adding an ethereal solution of zincethyl to anhydrous dinitroethylate of zinc, and corresponding compounds appear to be formed under similar circumstances, with other salts of dinitroethylic acid. These compounds are evidently of the same nature as that produced by the union of zincethyl with iodide of zinc, which is formed in such large quantity during the preparation of zincethyl.

Dinitroethylate of zinc crystallizes in minute colourless needles containing half an equivalent of water, which they retain when exposed over sulphuric acid *in vacuo*. They fuse below 100° C., and gradually become anhydrous at this temperature. They are very soluble in water and in alcohol. The concentrated aqueous solution solidifies on cooling to a white fibrous crystalline mass. Heated suddenly in air to a temperature of about 300°, this salt does not deflagrate, but it inflames, burning rapidly with a beautiful bluish green flame. When dry dinitroethylate of zinc is treated with concentrated sulphuric acid, and the vessel containing those ingredients is placed in a freezing mixture, dinitroethylic acid is liberated; but it is so unstable, that when the temperature rises a few degrees it begins to effervesce violently, and is rapidly decomposed with the evolution of gases and white vapours. A dilute solution is somewhat more stable; it may be prepared either by decomposing a dilute solution of dinitroethylate of zinc with dilute sulphuric acid and then distilling *in vacuo*, or by adding to a dilute solution of the baryta-salt just sufficient sulphuric acid to precipitate the base. Dilute dinitroethylic acid thus prepared possesses a pungent odour, somewhat resembling that of the nitro-fatty acids, and an acid taste. It reddens litmus-paper strongly, and gradually decomposes even at ordinary temperatures.

The acid procured by distillation *in vacuo* being treated with carbonate of silver, the latter dissolved with evolution of carbonic acid. The filtered solution, evaporated over sulphuric acid, deposited light flocculent crystals of dinitroethylate of silver, which blackened rapidly. They gave, by treatment with nitric acid and subsequent ignition, 55·85 per cent. of metallic silver. The formula $N_2 C_4 H_5 O_4 Ag$ requires 54·82 per cent. Another portion of the dilute acid, procured by the decomposition of the baryta-salt as described above, was saturated with magnesia, evaporated to dryness, and the residue treated with strong alcohol. The filtered alcoholic solution, which contained no trace of sulphuric acid, gave, on evaporation, dinitroethylate of magnesia, which, by treatment with nitric acid and ignition, yielded 19·64 per cent. of magnesia. The formula $N_2 C_4 H_5 O_4 Mg$ requires 19·80 per cent.

The salts of dinitroethylic acid are all soluble in water and alcohol, and most of them crystallize with more or less difficulty. They are all violently acted upon by concentrated nitric acid, the dinitroethylic acid being entirely decomposed and a nitrate of the constituent base produced. Dilute nitric acid acts in the same manner, but more slowly. They all fuse at a temperature little above 100° C. The potash, soda, lime, and baryta salts deflagrate explosively, like loose gunpowder, at a temperature considerably below redness.

Dinitroethylate of Baryta.

$N_2 C_4 H_5 O_4 Ba$.

This salt is produced by adding caustic baryta in excess to a solution of dinitroethylate of zinc, carbonic acid being passed through the solution until the excess of baryta is precipitated. It is then treated with sulphuretted hydrogen to remove a trace of oxide of zinc, which is still held in solution. After being heated to boiling for a few minutes, and then filtered, the solution is concentrated by evaporation, and finally dried down to a gummy mass, which does not crystallize on cooling. This is anhydrous dinitroethylate of baryta. It yielded the following analytical results:—

I. ·8228 grm., burnt with chromate of lead, gave ·4420 grm. carbonic acid and ·2428 grm. water.

II. ·3675 grm., treated with dilute sulphuric acid and ignited, gave ·2737 grm. sulphate of baryta.

These numbers agree with the formula

$N_2 C_4 H_5 O_4 Ba$.

	Calculated.		Found.	
			I.	II.
C_4 . . .	24	15·23	14·65	
H_5 . . .	5	3·17	3·28	
N_2 . . .	28	17·77		
Ba . . .	68·59	43·52		43·82
O_4 . . .	32	20·31		
	157·59	100·00		

Dinitroethylate of baryta is uncrystallizable, very deliquescent, and very soluble in water. Its solution reacts perfectly neutral.

Dinitroethylic Ether.

Several attempts were made to prepare this compound by the usual methods of etherification, but with only very partial success. When crystallized, dinitroethylate of lime is distilled with sulphovinate of potash, alcohol comes over mixed with an ethereal liquid which dissolves in water, but separates again on the addition of chloride of calcium, in the form of oily drops of a peculiar ethereal odour. I only succeeded, however, in obtaining such minute quantities of this body as to preclude the possibility of fixing its composition.

Dinitroethylate of Lime.

$N_2 C_4 H_5 O_4 Ca + 3HO$.

This salt is readily prepared by treating solution of dinitroethylate of zinc with excess of hydrate of lime, passing carbonic acid through the solution, and then heating to boiling for a few minutes. The filtered solution deposits, on evaporation, beautiful silky needles of dinitroethylate of lime, which contain three atoms of water, two of which are expelled at 100° C. An estimation of lime in this salt gave 20·76 per cent.; the above formula requires 20·59 per cent.

Dinitroethylate of Silver

is produced by double decomposition from dinitroethylate of baryta and sulphate of silver. It is very soluble in water, crystallizes in very light scales, and is so speedily decomposed, even with little exposure to light, that no satisfactory analysis could be made.

Double Nitrate and Dinitroethylate of Silver.

$$Ag\,O\,N\,O_5 + Ag\,O\,N_2\,C_4\,H_5\,O_3.$$

This salt is very sparingly soluble in water; it is precipitated in a crystalline granular form when concentrated solutions of dinitroethylate of zinc and nitrate of silver are mixed. The precipitated salt, washed on a filter with distilled water and dried by pressure between bibulous paper, yielded the following analytical results:—

I. ·3850 grm., burnt with oxide of copper, gave ·0941 grm. carbonic acid and ·0500 grm. water.

II. ·1817 grm. gave, on ignition, ·1070 grm. metallic silver.

These numbers agree closely with the above formula.

	Calculated.		Found.	
			I.	II.
C_4 . . .	24	6·54	6·67	
H_5 . . .	5	1·36	1·36	
N_3 . . .	42			
Ag_2 . . .	215·94	58·85		58·89
O_{10} . . .	80			
	366·94			

Dinitroethylate of Copper.

$$2(N_2\,C_4\,H_5\,Cu\,O_4) + HO.$$

This salt is prepared by mixing solutions of dinitroethylate of baryta and sulphate of copper. The filtered solution is of a magnificent purple colour; on evaporation *in vacuo* it yields splendid purple needles, which contain half an equivalent of water, and may be obtained several inches in length; they are four-sided prisms. These crystals, separated from the mother-liquor, and dried by exposure over sulphuric acid *in vacuo*, gave the following numbers on analysis:—

I. ·2249 grm., burnt with oxide of copper, gave ·1616 grm. carbonic acid and ·0795 grm. water.

II. ·3038 grm. yielded by SIMPSON'S method 84 cubic centimetres dry nitrogen at

493 mm. pressure and 13° C., or 55·13 cubic centimetres at 760 mm. pressure and 0° C., equal to ·06628 grm.

III. ·1913 grm., treated with dilute nitric acid, evaporated to dryness and ignited, gave ·0593 grm. oxide of copper.

IV. ·1780 grm., dissolved in water and precipitated with caustic potash, gave ·0556 grm. oxide of copper.

The formula above given requires numbers which sufficiently correspond with those obtained:—

	Calculated.		Found.			
			I.	II.	III.	IV.
C_8 . . .	48	19·18	19·60			
H_{11}. . .	11	4·39	3·93			
N_4 . . .	56	22·37		21·82		
2CuO . .	79·30	31·68			31·00	31·24
O_7 . . .	56	22·38				
	250·30	100·00				

Dinitroethylate of Magnesia.

$N_2(C_4H_5)MgO_4$.

Prepared by treating the solution of dinitroethylate of zinc with excess of caustic magnesia, boiling and filtering. The filtered solution, concentrated in a water-bath, yielded granular crystals, which fuse at 100° C. and dry up to a solid amorphous mass. This is the anhydrous salt.

I. ·2504 grm., moistened with nitric acid and cautiously ignited, gave ·0496 grm. magnesia.

II. ·3782 grm., similarly treated, gave ·0758 grm. magnesia.

III. ·0950 grm., treated by SIMPSON'S method, gave 52·5 cubic centimetres nitrogen at 337·0 mm. pressure and 14°·1 C., equal to 22·08 cubic centimetres at 0° C. and 760 mm. pressure, or ·02787 grm.*

The following is a comparison of these results with the theoretical numbers:—

	Calculated.		Found.		
			I.	II.	III.
C_4	24	23·76			
H_5	5	4·95			
N_2	28	27·72			29·37
MgO . . .	20	19·80	19·81	20·04	
O_3	24	23·77			
	101	100·00			

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* This determination was made before it was discovered that the nitrogen was always contaminated with binoxide of nitrogen, and hence the number obtained is considerably too high.

Dinitroethylate of Soda.

$N_2 C_4 H_5 O_4 Na$.

Prepared by precipitating dinitroethylate of lime with carbonate of soda, and evaporating the filtrate in a water-bath. The residue being treated with strong alcohol, the dinitroethylate of soda dissolves, and is thus separated from the excess of carbonate of soda. The alcoholic solution, evaporated to dryness in a water-bath, yielded minute scaly crystals, which were anhydrous. They gave the following analytical results:—

I. ·1650 grm., treated by SIMPSON's method, gave 84 cubic centimetres of dry nitrogen at 316·2 mm. pressure and 13° C., or 33·28 cubic centimetres at 760 mm. pressure and 0° C., equal to ·04201 grm.

II. ·2368 grm., moistened with nitro-hydrochloric acid and ignited, gave ·1227 grm. chloride of sodium.

III. ·2337 grm., treated with dilute sulphuric acid and ignited, gave ·1494 grm. sulphate of soda.

The following numbers agree closely with the above formula:—

	Calculated.		Found.		
			I.	II.	III.
C_4	24	21·43			
H_5	5	4·46			
N_2	28	25·00	25·46		
NaO . . .	31	27·68		27·48	27·91
O_3	24	21·43			
	112	100·00			

Products of the Decomposition of Dinitroethylic Acid.

I have stated that when dinitroethylic acid is liberated from its salts, by the addition of concentrated sulphuric acid, it is rapidly decomposed even at 0° C. I have examined the products of this decomposition in the case of the lime-salt, with the following results. A quantity of crystals of dinitroethylate of lime in coarse powder was placed in an apparatus, in which it could be gradually decomposed by concentrated sulphuric acid, the gaseous products collected, and their weight accurately ascertained. The rapidity of decomposition was moderated by the external application of cold water. At the conclusion of the decomposition, it was found that the weight of the gaseous products evolved was equal to 30·6 per cent. of the weight of the lime-salt employed. The weight of gaseous products is therefore almost exactly one-half of the weight of the anhydrous acid contained in the lime-salt (59·6 per cent.). The liquid and solid products of the operation contained sulphate of lime, sulphovinate of lime, and sulphate of ammonia or ethylamine. These gaseous products, after streaming through concentrated sulphuric acid, were collected over mercury and submitted to eudiometrical investigation. The determination of the specific gravity gave the following numbers:—

Temperature of room	16°·0 C.
Height of barometer	762·8 mm.
Height of inner column of mercury	8·3 mm.
Weight of flask and gas	31·7280 grms.
Temperature in balance-case . .	15°·0 C.
Weight of flask and air	31·6665 grms.
Temperature in balance-case . .	15°·0 C.
Capacity of flask	141·5 cubic centimetres.

From these data the specific gravity was calculated to be 1·3601.

About nine-tenths of the gas was absorbed by an equal volume of recently boiled absolute alcohol. A preliminary examination proved the presence of binoxide of nitrogen, a combustible gas absorbable by fuming sulphuric acid, and an incombustible residue containing combined oxygen.

The estimation of binoxide of nitrogen was effected by adding an excess of oxygen to a known volume of the gas in presence of caustic potash, the excess of oxygen being subsequently removed by pyrogallate of potash. Three determinations gave the following results:—

I.

Pressure of gas used (dry)	178·9 mm.	14°·0 C.
Pressure after absorption of binoxide of nitrogen (dry)	164·3	14°·0

II.

Pressure of gas used (dry)	104·7	13°·0
Pressure after absorption of NO_2 (dry)	95·2	13°·0

III.

Pressure of gas used (dry)	147·8	13°·0
Pressure after absorption of NO_2 (dry)	133·8	13°·0

Estimation of gas absorbed by fuming sulphuric acid, subsequent to the removal of binoxide of nitrogen.

IV.

Pressure of gas used (dry)	243·3 mm.	13°·5 C.
Pressure after action of fuming SO_3 (dry)	177·8	13°·5

V.

Pressure of gas used (dry)	164·3	14°·0
Pressure after action of fuming SO_3 (dry)	121·1	14°·0

The gaseous mixture therefore consisted of—

	I.	II.	III.	IV.	V.	Mean.
Binoxide of nitrogen	8·16	9·07	9·47			8·90
Gas absorbed by fuming SO_3 . .				24·53	23·95	24·24
Gas unabsorbable by fuming SO_3				66·57	67·15	66·86
						100·00

The gas remaining after the action of fuming sulphuric acid yielded the following eudiometrical results:—

VI.

Pressure of gas used (dry)	36·9 mm.	12°·8 C.
Pressure after admission of oxygen (dry)	144·5	12°·8
Pressure after admixture of hydrogen (dry) . . .	191·8	12°·8
Pressure after explosion (dry)	121·8	12°·8
Pressure after action of caustic potash (dry) . . .	121·3	12°·8

VII.

Pressure of gas used (dry)	119·9	14
Pressure after admission of hydrogen (dry)	340·6	14
Pressure after explosion (dry)	231·8	14
Pressure after admission of oxygen (dry)	401·8	14
Pressure after explosion	234·4	14

Analysis No. VI. shows that the gas left unabsorbed by fuming sulphuric acid contains no combustible constituent; for it did not explode with oxygen, and on ignition with hydrogen in presence of excess of oxygen, it neither generated water nor carbonic acid; the diminution of pressure produced on explosion with hydrogen (70·0 mm.) being almost exactly equal to that which ought to be produced by the 47·3 mm. of hydrogen added. Analysis No. VII. proves that on explosion with excess of hydrogen 119·9 volumes of the gas consumed 108·4 volumes of hydrogen, leaving 119·5 volumes of free nitrogen. The gas therefore contained 108·4 volumes of protoxide of nitrogen and 11·5 volumes of nitrogen.

In order to ascertain the composition of the combustible gas removed by fuming sulphuric acid, the original gas, after the removal of binoxide of nitrogen, was exploded with excess of oxygen, so as to determine the amount of oxygen consumed and of carbonic acid generated.

VIII.

Pressure of gas used (dry)	104·3 mm.	14° C.
Pressure after admission of oxygen (dry)	371·5	14
Pressure after explosion (dry)	317·0	14
Pressure after absorption of carbonic acid (dry) . .	260·7	14

IX.

Pressure of gas used (dry)	55·7 mm.	13°·1 C.
Pressure after admission of oxygen (dry)	223·8	13°·1
Pressure after explosion (dry)	193·1	13°·1
Pressure after absorption of carbonic acid (dry)	164·5	13°·1
Pressure after admission of hydrogen (dry)	709·8	13°·1
Pressure after explosion (dry)	339·5	13°·1
Pressure after admission of oxygen (dry)	749·1	13°·1
Pressure after explosion (dry)	295·7	13°·1

Analysis No. VIII. shows that 104·3 volumes of gas, containing 27·8 volumes of the body removed by fuming sulphuric acid, consumed 83·0 volumes of oxygen and generated 56·3 volumes of carbonic acid. In analysis No. IX. 55·7 volumes, containing 14·3 volumes of the gas absorbable by fuming sulphuric acid, consumed 44·5 volumes of oxygen and generated 28·6 volumes of carbonic acid. The last three readings in this analysis also prove that the body removed by fuming sulphuric acid is free from nitrogen. The two analyses give the following proportions between the volumes of combustible gas, oxygen consumed, and carbonic acid generated:—

	Volume of combustible gas.			Oxygen consumed.			CO$_2$ generated.	
	I.	II.		I.	II.		I.	II.
	27·8	14·3	:	83·0	44·5	:	56·3	28·6
or								
	1	1	:	2·99	3·007	:	2·02	1·93

The body removed by fuming sulphuric acid is therefore olefiant gas, one volume of which consumes three volumes of oxygen and generates two volumes of carbonic acid.

The whole of these eudiometrical experiments give the mean per-centage composition of the original gas as follows:—

Binoxide of nitrogen	8·90
Olefiant gas	24·24
Protoxide of nitrogen	60·65
Nitrogen	6·21
	100·00

This result is confirmed by the above determination of the specific gravity of the gas, as is seen from the following calculations:—

	Per-centage amount.	Specific gravity.		
Binoxide of nitrogen	8·90	×1·0365=	9·2249	
Protoxide of nitrogen	60·65	×1·5202=	92·2001	
Nitrogen	6·21	× ·9674=	29·4573	
Olefiant gas	24·24			
	100·00		130·8823	
			100	=1·3088
Found by experiment				1·3601

I had anticipated that the decomposition of dinitroethylate of lime by sulphuric acid would yield either protoethide of nitrogen ($N C_4 H_5$) or ethoprotoxide of nitrogen ($N C_4 H_5 O$), but the action of the concentrated acid evidently proceeds too far for the production of this result. Further experiments must decide whether or not the employment of a more dilute acid for the decomposition will not lead to the production of one of these compounds.

Action of Zincmethyl upon Binoxide of Nitrogen.

Dinitromethylate of Zinc and Zincmethyl.—Zincmethyl absorbs binoxide of nitrogen much more slowly than zincethyl takes up the same gas; nevertheless at the ordinary atmospheric pressure, the two bodies gradually unite and form colourless crystalline needles, closely resembling, in all their reactions, the dinitroethylate of zinc and zincethyl. I have made no analyses of this body, but considering the homology existing between zincethyl and zincmethyl, together with the product of its decomposition by water, there can scarcely be a doubt that it is dinitromethylate of zinc and zincmethyl, and that its formula is

$$N_2 C_2 H_3 O_4 Zn + C_2 H_3 Zn.$$

It rapidly oxidizes in the air, and takes fire when exposed in considerable quantity. It is instantly decomposed by water, giving light carburetted hydrogen and an opalescent solution of basic dinitromethylate of zinc.

$$\left.\begin{array}{r} N_2 C_2 H_3 O_4 Zn + C_2 H_3 Zn \\ HO \end{array}\right\} = \left\{\begin{array}{l} C_2 H_3, H \\ N_2 C_2 H_3 O_4 Zn + ZnO. \end{array}\right.$$

Dinitromethylate of Zinc.

$$N_2 C_2 H_3 O_4 Zn + HO.$$

A quantity of the dinitromethylate of zinc and zincmethyl was prepared by the action of compressed binoxide of nitrogen upon zincmethyl, in the strong copper vessel above described. The resulting crystalline compound was decomposed by water, and the opalescent solution being treated with carbonic acid, boiled, and filtered, yielded, on evaporation, minute crystals of dinitromethylate of zinc. These crystals, dried at 100° C. and submitted to analysis, gave the following results:—

I. 1·4200 grm., burnt with oxide of copper, gave ·5872 grm. carbonic acid* and ·4473 grm. water.

II. ·3585 grm., treated with nitric acid and ignited, gave ·1212 grm. oxide of zinc.

III. ·0982 grm., similarly treated, gave ·0333 grm. oxide of zinc.

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* This analysis exhibits a considerable excess of carbon, which is due to the passage of binoxide of nitrogen into the potash bulbs, and the consequent formation of nitrite of potash. It appears to be impossible to decompose the whole of this gas by ignited copper turnings, in conducting the combustion of substances so rich in oxidized nitrogen as the dinitroethylates, and especially the dinitromethylates; hence, in the analyses of the salts of both these acids, the per-centage of carbon is almost invariably too high.

These numbers lead to the formula

$$N_2 C_2 H_3 O_4 Zn + HO,$$

which requires the following values:—

	Calculated.		Found. I.	Found. II.	Found. III.
C_2 . .	12	10·30	11·28		
H_4 . .	4	3·43	3·50		
N_2 . .	28	24·03			
ZnO . .	40·52	34·77		33·81	33·91
O_4 . .	32	27·47			
	116·52	100·00			

Dinitromethylate of Soda.

$$N_2 C_2 H_3 O_4 Na + 2HO.$$

This salt is formed by treating a solution of dinitromethylate of zinc with carbonate of soda, evaporating to dryness, and treating the residue with strong alcohol. Dinitromethylate of soda dissolves, and the filtered solution, on evaporation, deposits crystals, which, after drying at 100° C., yielded 25·83 per cent. of soda; the above formula requires 26·72 per cent. Dinitromethylate of soda is very soluble both in water and alcohol; it deflagrates violently when heated, and in other respects closely resembles the corresponding salt of dinitroethylic acid.

These determinations, although very imperfect and incomplete, establish the existence of a class of salts containing dinitromethylic acid, homologous with the dinitroethylates; and there can be little doubt that the zinc compounds of the other alcohol radicals will yield corresponding acids, when treated with binoxide of nitrogen.

It is difficult to form any satisfactory hypothesis relative to the rational constitution of this series of acids: they may be regarded as belonging to the type of nitrous acid containing a double atom of nitrogen, and in which one atom of oxygen has been replaced by an alcohol radical, thus—

$$N_2\begin{cases} C_n H_{(n+1)} \\ O \\ O \\ O \end{cases}$$

or they may be viewed as constructed upon the hyponitrous acid type, one equivalent of oxygen being replaced by an alcohol radical, and a second atom by binoxide of nitrogen, thus—

$$N\begin{cases} C_n H_{n+1} \\ NO_2 \\ O \end{cases}$$

Without attaching much value to either hypothesis, I prefer the latter.

By analogous processes, there can be little doubt that many new series of organic acids may be derived from inorganic acids, by the replacement of one or more atoms of oxygen by an alcohol radical; in fact, my pupil Mr. HOBSON is now studying a new series containing sulphur, produced by the action of zincethyl and its homologues upon sulphurous acid: the ethyl acid of this series is formed by the replacement of one equivalent of oxygen, in three equivalents of sulphurous acid, by an alcohol radical.

The following Table exhibits the compounds of the new series of acids, which have been described in the foregoing pages.

	Formulæ.
Dinitroethylic acid	$N_2 C_4 H_5 O_4 H$.
Dinitroethylate of silver	$N_2 C_4 H_5 O_4 Ag$.
Dinitroethylate of copper	$2(N_2 C_4 H_5 O_4 Cu)+HO$.
Dinitroethylate of zinc (crystallized)	$2(N_2 C_4 H_5 O_4 Zn)+HO$.
Dinitroethylate of zinc (anhydrous)	$N_2 C_4 H_5 O_4 Zn$.
Dinitroethylate of baryta	$N_2 C_4 H_5 O_4 Ba$.
Dinitroethylate of lime	$N_2 C_4 H_5 O_4 Ca+3HO$.
Dinitroethylate of magnesia	$N_2 C_4 H_5 O_4 Mg$.
Dinitroethylate of soda	$N_2 C_4 H_5 O_4 Na$.
Double nitrate and dinitroethylate of silver	$NO_6 Ag+N_2 C_4 H_5 O_4 Ag$.
Dinitroethylate of zinc and zincethyl	$N_2 C_4 H_5 O_4 Zn+C_4 H_5 Zn$.

Dinitromethylic acid	$N_2 C_2 H_3 O_4 H$.
Dinitromethylate of zinc	$N_2 C_2 H_3 O_4 Zn+HO$.
Dinitromethylate of soda	$N_2 C_2 H_3 O_4 Na+2HO$.
Dinitromethylate of zinc and zincmethyl	$N_2 C_2 H_3 O_4 Zn+C_2 H_3 Zn$.