VIII. *On a New Series of Organic Compounds containing Boron.*

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Received May 15,—Read May 22, 1862.

The substitution of a compound organic radical for an elementary constituent in inorganic compounds has proved itself to be one of the most important and fertile fields of modern chemical investigation. The application of this species of substitution to the inorganic compounds of metals has called into existence an entirely new and extensive family of organic substances—the organo-metallic compounds, bodies never met with in nature, distinguished by their well-marked affinities, and capable in some instances of effecting, in their turn, numerous substitutions of a like character. The realization of a similar substitution in the case of certain inorganic compounds of nitrogen and phosphorus has, in the hands of Hofmann, not only enriched the science with a host of new and interesting compounds, but has also brought our knowledge of the organic bases to a degree of completeness, which cannot be rivalled in any other class of organic compounds. Lastly, attempts have not been wanting to extend these reactions to the oxygen compounds of the metalloids; and although this portion of the field presents difficulties of a somewhat more formidable character, yet these attempts have not unfrequently been attended with success. Thus nitric oxide has been transformed into dinitroethylic and dinitromethylic acids[*]; sulphurous anhydride into ethylodithionic and methylotrithionic acids[†]; and carbonic anhydride into propionic and acetic acids[‡].

The last-named reaction, confirming, as it did, the view previously expressed by Kolbe and myself[§], that organic compounds in general are nothing more than substitutions of this nature effected in carbonic oxide, in carbonic acid, and possibly in other inorganic compounds of carbon, naturally awakened a desire to extend this inquiry to the oxygen compounds of boron and silicon, which are usually regarded as possessing certain important analogies with carbonic anhydride. With this end in view, boracic ether was submitted to the action of zincethyl by Mr. Duppa and myself. We found that the whole of the oxygen in boracic acid became replaced by ethyl, and in a short communication to the Royal Society[||], we described some of the properties of the remarkable body, boric ethide, thus formed. In the further study of this substance, and the exten-

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[*] Philosophical Transactions for 1857, p. 59.

[†] Journal of Chemical Society, vol. x. p. 55, and p. 243.

[‡] Ibid. vol. xi. p. 103; and Proceedings of the Royal Society, vol. x. p. 4.

[§] Ann. der Chem. und Pharm. Bd. ci. s. 257. Proceedings of the Royal Institution of Great Britain for 1858.

[||] Proceedings of the Royal Society, vol. x. p. 568.

sion of the research to the homologous methyl compound, I much regret having been deprived of the cooperation of my friend and fellow-labourer who had rendered me such valuable assistance at the commencement of the investigation, but who was reluctantly compelled to abandon its further prosecution.

The first attempt to replace oxygen by ethyl in boracic anhydride was made by exposing the latter in a finely pulverized condition to the action of zincethyl at various temperatures, but it was found that the zincethyl was utterly powerless to effect the desired substitution; neither did the anhydrous acid yield in the slightest degree to Wanklyn's compound of sodiumethyl and zincethyl, although it was digested and heated with it for several days. There could scarcely be a doubt that the intractability of the anhydride was due in great measure to its total insolubility in the surrounding liquid, and therefore, in order to place it under conditions more favourable for the action of the organo-metallic body, it was converted into boracic ether.

The ether was prepared by Rose's process*, which consists in distilling an intimate mixture of sulphovinate of potash and dried borax. The best proportions were found to be two parts by weight of borax, and three parts of the sulphovinate; but the yield of ether was very small, the greater part of the product consisting of alcohol. The removal of the latter by rectification, as recommended by Rose, involved the loss of much ether; recourse was therefore had to chloride of calcium for its abstraction, a method which gave very satisfactory results, the product of pure ether being more than doubled. The following is a sketch of the process finally adopted. About 3 lbs. of the mixed borax and sulphovinate of potash were put into an ordinary Papin's digester, which was placed in a sand-bath and exposed to a very gradually increasing heat so long as volatile products came over. The crude distillate obtained from several such operations was then treated with about one-fourth of its weight of fused chloride of calcium, and agitated until the latter was dissolved. The liquid now separated into two layers, a lower one consisting of an alcoholic solution of chloride of calcium, and an upper one containing nearly all the boracic ether, which retained only a small proportion of alcohol in solution. The upper layer was decanted and submitted to distillation. It began to boil at about 85° C., but the thermometer soon rose to 118° C., between which temperature and 125° C. the greater part of the remaining liquid passed over and was reserved for the purposes of the investigation. A thick oily liquid remained in the retort, and appeared to consist of boracic acid united with a smaller proportion of oxide of ethyl.

On adding zincethyl to the boracic ether thus prepared, a considerable elevation of temperature gradually occurred, whilst at the same time a most penetrating and peculiar odour was developed, due apparently to the vapour of some volatile body, that not unfrequently burst into flame, when the cork was removed from the flask in which the reaction took place. Some preliminary experiments showed that this volatile body could be distilled unchanged from the mixture, and that it was neither miscible with, nor apparently decomposed by, water. It was also spontaneously inflammable, and the

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* Poggendorff's 'Annalen,' Bd. xcviii. s. 245.

beautiful green flame with which it burnt demonstrated the presence of boron as one of its constituents.

In order to prepare this body in sufficient quantity, several ounces of boracic ether were placed in a capacious flask closed by a doubly perforated cork. Through one of these perforations passed a thermometer, and through the other a short glass tube, one-fourth of an inch in diameter, and open at both ends: the bulb of the thermometer dipped into the boracic ether. Successive quantities of pure zincethyl were introduced through the short glass tube by means of a pipette, the elevation of temperature after each addition being allowed to subside before the next portion was added. The failure of a further addition of zincethyl to produce any rise of temperature was regarded as evidence of the completion of the reaction, which was not attained until a comparatively very large amount of zincethyl had been added.

The liquid in the flask was now submitted to distillation in an oil-bath. It began to boil at 94° C., and between this temperature and 140° C. a considerable quantity of a colourless liquid distilled over. The distillation then suddenly stopped, and, to avoid secondary products of decomposition by the application of a greater heat, the operation was interrupted. On cooling, the materials remaining in the flask solidified to a mass of large crystals of ethylate of zinc and zincethyl. On rectification, the distillate began to boil at 70° C., but the thermometer rapidly rose to 95°, at which temperature the last two-thirds of the liquid passed over and were received apart. The product thus collected exhibited a constant boiling-point on redistillation.

The combustion with oxide of copper of this liquid and the remaining boron compounds described in this paper presented some difficulties; owing partly to the volatility of boracic acid in aqueous vapour, and partly to the tendency of that acid when fused to encase particles of carbon and prevent their oxidation. Fortunately the errors thus introduced were not so considerable as to throw any doubts upon the analytical results, although in many cases the excess in the percentage of hydrogen and the deficiency in that of carbon are somewhat greater than usual. To estimate the boron in the liquid obtained as above described, advantage was taken of the complete decomposition of the compound when heated to 100° with concentrated nitric acid in sealed tubes. The whole of the boron was in this way converted into boracic acid, but the latter could not be determined by the direct evaporation of the nitric acid solution, the loss of boracic acid amounting in such an operation to 15 or 20 per cent. of the whole amount. None of the known processes for estimating this acid appeared to be eligible in the present instance, and it therefore became necessary to seek for a new one. After the trial of various methods with but indifferent success, the following experiments showed that the evaporation of the acid solution of boracic acid with a known weight of magnesia in excess, the residue being then ignited, presented a process which, although far from rigidly accurate, could not, in the case of the boron compound to be analysed, diminish the amount of boron to a greater extent than about 0·2 per cent.

I. 1·4310 grm. of boracic acid, treated as above described, suffered a loss equal to 2·55 per cent. of boracic acid, or ·73 per cent. of boron.

II. ·5957 grm. boracic acid, similarly treated, lost ·56 per cent. of boron.

III. 2·2477 grm. boracic acid, similarly treated, lost ·35 per cent. of boron.

IV. 1·1845 grm. boracic acid lost ·51 per cent. of boron.

V. ·4125 grm. boracic acid experienced neither loss nor gain.

VI. ·8398 grm. boracic acid lost ·48 per cent. of boron.

VII. 1·1637 grm. boracic acid lost ·58 per cent. of boron.

VIII. 1·4601 grm. boracic acid lost ·57 per cent. of boron.

IX. 1·6307 grm. boracic acid lost ·47 per cent. of boron.

Submitted to analysis, the new boron compound yielded the following results:—

I. ·1307 grm. gave ·3506 grm. carbonic acid and ·1818 grm. water.

II. ·1144 grm. gave ·3068 grm. carbonic acid and ·1625 grm. water.

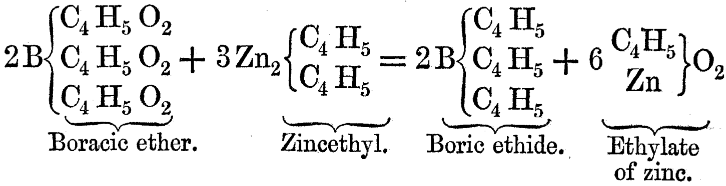
III. ·1071 grm. gave ·0380 grm. boracic acid.

These numbers agree with the formula

$$B\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5.\end{matrix}\right.$$

	Calculated.		Found.			
			I.	II.	III.	Mean.
C_{12} . . .	72	73·55	73·16	73·14	——	73·15
H_{15} . . .	15	15·42	15·45	15·78	——	15·61
B . . .	10·9	11·03	——	——	11·08	11·08
	97·9	100·00				99·84

The new body may be conveniently termed *boric ethide.* It is evidently formed by the replacement of the three atoms of oxygen in boracic acid by three atoms of ethyl, according to the following equation:—



$$\underbrace{2B\left\{\begin{matrix}C_4H_5O_2\\C_4H_5O_2\\C_4H_5O_2\end{matrix}\right.}_{\text{Boracic ether.}}+3\underbrace{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Zincethyl.}}=\underbrace{2B\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Boric ethide.}}+6\underbrace{\left.\begin{matrix}C_4H_5\\Zn\end{matrix}\right\}O_2}_{\text{Ethylate of zinc.}}.$$

The ethylate of zinc thus produced combines with zincethyl to form the crystalline compound above alluded to. Hence the very large amount of zincethyl which was found necessary to complete the reaction.

Boric ethide possesses the following properties:—It is a colourless mobile liquid of a pungent odour; its vapour is very irritating to the mucous membrane, and provokes a copious flow of tears. The specific gravity of boric ethide at 23° C. is ·6961; it boils at 95° C. A determination of the specific gravity of its vapour by GAY-LUSSAC'S method gave the following numbers:—

Weight of boric ethide	·2839 grm.
Observed volume of vapour	96·68 cub. centims.
Temperature of oil-bath	149° C.
Height of barometer	760·5 millims.
Height of mercury inside of tube above that outside	1·5 millim.
Height of column of oil	328·0 millims.

From these data the specific gravity of the vapour was calculated to be 3·4006. This number agrees very closely with that calculated upon the supposition that boric ethide is volumetrically composed like terchloride of boron, as is seen from the following calculation:—

1 vol. Boron vapour	·75319
3 vols. Ethyl	6·0117
The 4 vols. condensed to 2 vols.	2)6·76489
	3·38244

The density of boric ethide vapour increases considerably as the temperature approaches the boiling-point; thus a determination made at 132° gave the number 3·5979, whilst a second showed the specific gravity of the vapour at 101°·6 to be no less than 3·757.

Boric ethide is insoluble in water, and is very slowly decomposed by prolonged contact with it. Iodine has scarcely any action upon it even at 100° C. It floats upon concentrated nitric acid for several minutes without change; but suddenly a violent reaction takes place, and crystals of boracic acid separate. When boric ethide vapour comes in contact with air, it produces slight bluish-white fumes, which in the dark are seen to proceed from a lambent blue flame. The liquid is spontaneously inflammable in air, burning with a beautiful green and somewhat fuliginous flame. In contact with pure oxygen it explodes. Excluded from the air, boric ethide is quite a stable body; a quantity of it kept in a sealed tube for two years exhibited, on examination, no evidence of any alteration.

When boric ethide is heated to 99° C. with strong hydrochloric acid over mercury, a considerable quantity of hydride of ethyl is slowly evolved; ·0517 grm. of boric ethide, thus treated as long as gas was evolved, gave 35·33 cubic centimetres at 11°·1 C. and 248·4 millimetres mercurial pressure, corresponding to 11·11 cub. centims. at 0° C. and 760 millims. pressure. The reaction

$$B\left\{\begin{array}{l}C_4H_5\\C_4H_5\\C_4H_5\end{array}\right. + HCl = B\left\{\begin{array}{l}C_4H_5\\C_4H_5\\Cl\end{array}\right. + \left.\begin{array}{r}C_4H_5\\H\end{array}\right\}$$

requires that 11·31 cub. centims. of hydride of ethyl at 0° C. and 760 millims. pressure should be liberated. That the gas thus evolved is hydride of ethyl is established by the following data:—

I.

	Millims.	Temp.
Pressure of gas used (dry)	225·3	at 13°·9 C.
Pressure after action of anhydrous sulphuric acid (dry)	223·9	at 13°·9 C.

II.

Pressure of gas used (dry)	23·7	at 14°·7 C.
Pressure after addition of oxygen (dry)	253·9	at 14°·7 C.
Pressure after explosion (dry)	195·6	at 14°·7 C.
Pressure after absorption of carbonic acid (dry)	147·7	at 14°·7 C.

No. I. proves the absence of members of the olefiant gas family. No. II. proves that the gas has the composition and condensation of hydride of ethyl, one volume of which consumes on combustion 3·5 volumes of oxygen, and generates twice its volume of carbonic acid; the following being the experimental numbers:—

Vol. of combustible gas.		Vol. of oxygen consumed.		Vol. of carbonic acid generated.
23·7	:	82·5	:	47·9
1	:	3·48	:	2·01

If boric ethide be heated with water to 99° C. for several hours, it also appears to suffer an analogous decomposition, although with extreme slowness; even with hydrochloric acid, the action is so tedious that I have not been able to prepare a sufficient quantity of boric chlorodiethide ($B(C_4H_5)_2Cl$) to examine its properties. In the cold, a strong solution of hydrofluoric acid has no action upon boric ethide, which also suffers scarcely any change by being heated to 99° C. for four hours with concentrated sulphuric acid. Gently heated for fourteen days with sodium in a sealed tube, boric ethide underwent no visible change.

Ammonia-Boric Ethide.

If a few drops of boric ethide be passed up into a dry eudiometer filled with mercury, and dry ammoniacal gas be then admitted into the same tube, each bubble of gas collapses with a shock, like that produced by a bubble of steam projected into cold water. A large quantity of ammonia is thus absorbed by boric ethide with extreme energy. To prepare the compound thus formed in larger quantity, several grammes of boric ethide were placed in a small flask filled with nitrogen and surrounded with ice: a current of dry ammoniacal gas was now passed into the flask so long as it was absorbed; finally, the product thus obtained was warmed to expel excess of ammonia, and then exposed *in vacuo* over sulphuric acid for twenty-four hours. It did not crystallize, and could not be distilled, except *in vacuo*, without decomposition. Submitted to analysis, it yielded 61·43 per cent. of carbon and 15·43 per cent. of hydrogen. The formula

$$NH_3+B(C_4H_5)_3$$

requires 62·66 per cent. of carbon and 15·66 per cent. of hydrogen. The unavoidable slight oxidation of the boric ethide during the necessary manipulations affords a sufficient explanation of the deficiency in the amounts of carbon and hydrogen exhibited by the analysis. I should, however, have made renewed attempts to obtain this body in a state of greater purity, had not the investigation of the corresponding crystalline methyl compound described below, left no doubt that the formula above given expresses the composition of ammonia-boric ethide.

Ammonia-boric ethide is a somewhat oily liquid, possessing an aromatic odour and an alkaline reaction. Carbonic acid has no action upon it, even in the presence of water, but other acids decompose it instantly and liberate boric ethide. When it is exposed to a measured quantity of atmospheric air, there is scarcely any perceptible absorption of oxygen even after the lapse of several hours.

Boric Dioxyethide.

When boric ethide is placed in a flask and allowed to oxidize gradually, first in dry air and finally in dry oxygen, it forms a colourless liquid, which boils at 125° C., but cannot be distilled under atmospheric pressure without partial decomposition. At the ordinary temperature, this product of oxidation evaporates without residue in a stream of dry carbonic acid. It can be distilled *in vacuo* without decomposition, and a portion so rectified yielded on analysis the following results:—

I. ·2681 grm., burnt with oxide of copper and oxygen, gave ·5359 grm. carbonic acid and ·2720 grm. water.

II. ·2246 grm., similarly treated, gave ·4376 grm. carbonic acid and ·2303 grm. water.

Owing to the causes already mentioned, the complete combustion of this body was very difficult, nevertheless the above numbers agree sufficiently well with the formula

$$B(C_4H_5)_3O_4,$$

as is evident from the following comparison:—

	Calculated.		Found.	
			I.	II.
C_{12} . . .	72·0	55·42	54·52	55·10
H_{15} . . .	15·0	11·54	11·27	11·92
B . . .	10·9	8·39	——	——
O_4 . . .	32·0	24·65	——	——
	129·0	100·00		

I regard this liquid as a compound of vinic ether, with a body having the formula

$$B\left\{\begin{array}{l}C_4H_5\\O\\O\end{array}\right.$$

and derived from boracic acid by the substitution of one equivalent of ethyl for one of oxygen. For this body the name *boric dioxyethide* is appropriate, whilst its ethereal compound may be conveniently termed diethylate of boric dioxyethide. The formula of the latter will therefore be

$$B\left\{\begin{matrix}C_4\,H_5\\O\\O\end{matrix}\right. + \left.\begin{matrix}C_4\,H_5\\C_4\,H_5\end{matrix}\right\}O_2, \text{ or } B\left\{\begin{matrix}C_4\,H_5\\C_4\,H_5\,O_2\\C_4\,H_5\,O_2.\end{matrix}\right.$$

The formation of diethylate of boric dioxyethide from boric ethide may be thus represented:—

$$B\left\{\begin{matrix}C_4\,H_5\\C_4\,H_5\\C_4\,H_5\end{matrix}\right. + O_4 = B\left\{\begin{matrix}C_4\,H_5\\C_4\,H_5\,O_2\\C_4\,H_5\,O_2.\end{matrix}\right.$$

This view of the constitution and mode of formation of the oxidized product is supported by its behaviour with water; for when diethylate of boric dioxyethide is placed in contact with water it is instantly decomposed, alcohol and *dihydrate of boric dioxyethide* being formed, according to the following equation:—

$$\underbrace{B\left\{\begin{matrix}C_4\,H_5\\C_4\,H_5\,O_2\\C_4\,H_5\,O_2\end{matrix}\right.}_{\text{Diethylate of boric dioxyethide.}} + 2\left.\begin{matrix}H\\H\end{matrix}\right\}O_2 = \underbrace{B\left\{\begin{matrix}C_4\,H_5\\H\,O_2\\H\,O_2\end{matrix}\right.}_{\text{Dihydrate of boric dioxyethide.}} + 2\left.\begin{matrix}C_4\,H_5\\H\end{matrix}\right\}O_2.$$

Dihydrate of boric dioxyethide may be conveniently prepared in a state of purity by agitating its aqueous solution with ether, which dissolves the boric compound. The ethereal solution must then be decanted, and on evaporation at common temperatures in a stream of dry carbonic acid, the new compound is left behind as a white and very volatile crystalline mass. The latter was sublimed at a gentle heat in a current of dry carbonic acid, and was made to condense in weighed tubes for analysis.

I. ·3870 grm., burnt with oxide of copper in a stream of air, gave ·4652 grm. carbonic acid and ·3285 grm. water.

II. ·5087 grm., oxidized with nitric acid in a sealed tube, the liquid supersaturated with a known weight of magnesia and then evaporated to dryness, gave ·2387 grm. boracic acid.

These numbers agree closely with the formula of dihydrate of boric dioxyethide:—

	Calculated.		Found.	
			I.	II.
C_4 . . .	24	32·47	32·78	——
H_7 . . .	7	9·47	9·43	——
B . . .	10·9	14·75	——	14·66
O_4 . . .	32	43·31	——	——
	73·9	100·00		

Dihydrate of boric dioxyethide is a colourless, volatile, crystalline body, very soluble in water, alcohol, and ether. It possesses an agreeable ethereal odour, and a most intensely sweet taste. Exposed to the air, it evaporates at ordinary temperatures, undergoing at the same time partial decomposition, and invariably leaving a slight residue of boracic acid. It may be sublimed without change at about 40° C. in a current of dry carbonic acid, and it then condenses in magnificent crystalline plates resembling naphthaline. It fuses at a gentle heat, and at a higher temperature boils with partial decomposition. Its vapour tastes intensely sweet.

Boric dioxyethide might be regarded as the anhydride of a bibasic acid: the diethylate of boric dioxyethide would then be the ether of this acid, whilst the volatile crystalline body just described would be the hydrated acid itself. The latter does in fact redden litmus paper, but in other respects its acid qualities are very obscure, and I have not been able to form definite salts with it. It therefore scarcely possesses a valid claim to a place amongst the acids.

Considering boric ethide to be formed by the substitution of the ethyl in zincethyl for the oxygen in boracic acid, Mr. Duppa and myself expressed the reaction as follows:—

$$\underbrace{2B\left\{\begin{matrix}C_4H_5O_2\\C_4H_5O_2\\C_4H_5O_2\end{matrix}\right.}_{\text{Boracic ether.}} + \underbrace{3Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Zincethyl.}} = \underbrace{2B\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Boric ethide.}} + \underbrace{6\;\left.\begin{matrix}C_4H_5\\Zn\end{matrix}\right\}O_2.}_{\text{Ethylate of zinc.}}$$

Another but less probable view of the change presents itself in the supposition that the three atoms of ethyl in boric ethide were already present in the boracic ether, the action of the zincethyl being simply to remove the whole of the oxygen from the boracic ether. Kekulé[†] has in fact adopted this latter view of the reaction.

So long as the organic radical of the zinc compound and that of the boracic ether are identical, it is impossible to prove whether the three individual atoms of ethyl in boric ethide were originally present in the boracic ether, or have been derived from the zincethyl. Indicating by an asterisk the atoms of ethyl which finally become part of the boric ethide, it is impossible to prove conclusively whether the reaction takes place according to the first or second of the following equations:—

$$(1)\quad 2B\left\{\begin{matrix}C_4H_5O_2\\C_4H_5O_2\\C_4H_5O_2\end{matrix}\right. + 3Zn_2\left\{\begin{matrix}C_4H_5*\\C_4H_5*\end{matrix}\right. = 2B\left\{\begin{matrix}C_4H_5*\\C_4H_5*\\C_4H_5*\end{matrix}\right. + 6\;\left.\begin{matrix}C_4H_5\\Zn\end{matrix}\right\}O_2.$$

$$(2)\quad 2B\left\{\begin{matrix}C_4H_5*O_2\\C_4H_5*O_2\\C_4H_5*O_2\end{matrix}\right. + 3Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right. = 2B\left\{\begin{matrix}C_4H_5*\\C_4H_5*\\C_4H_5*\end{matrix}\right. + 6\;\left.\begin{matrix}C_4H_5\\Zn\end{matrix}\right\}O_2.$$

Although we cannot thus label, as it were, the atoms taking part in the reaction, we can unerringly trace the movements of the alcohol radicals, if we secure their identification by varying their composition in the two compounds used in the process. The

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[†] Lehrbuch der org. Chemie, p. 489.

study of the action of zincmethyl upon boracic ether would obviously decide between these views. If boric ethide were produced from these materials, KEKULÉ'S hypothesis would be established; but if, on the other hand, boric methide were the result of the reaction, then the correctness of the view originally taken by Mr. DUPPA and myself would be proved to be correct. The following are the results obtained in pursuing this inquiry.

Boric Methide.

When a strong ethereal solution of zincmethyl is added to boracic ether, an elevation of temperature to the extent of 8° or 10° C. is observed, whilst at the same time a most intensely pungent odour is developed; this odour, although it resembles that of boric ethide, is far more powerful, and more persistently irritating to the mucous membrane. A slow evolution of a spontaneously inflammable gas, burning with a splendid green flame, was also noticed; and this evolution of gas became more rapid when the warmth of the hand was applied to the flask containing the ingredients. Preliminary experiments proved that this gas was nearly insoluble in water, but almost completely soluble in alcohol, the residue remaining undissolved being marsh-gas derived from the action of the alcohol upon traces of zincmethyl vapour with which the gas was contaminated. The gas was not condensed by a freezing mixture of ice and salt. It was, with the exception of a small percentage of marsh-gas, instantaneously dissolved by solution of ammonia, which yielded the gas again unchanged when neutralized by an acid. Concentrated sulphuric acid was without action upon the gas.

These data led to the following plan for collecting the gas in a state of purity. About two ounces of boracic ether were mixed in a small flask with rather more than their own bulk of an ethereal solution of zincmethyl, of such strength as to be spontaneously inflammable in a high degree. The flask, loosely corked, was placed in ice-cold water, and allowed to stand for a couple of hours until the reaction was complete: it was then furnished with a bent tube passing through a cork, and designed to conduct the gas into a second flask placed in a freezing mixture of ice and salt; from this flask the gas passed into a third containing about half an ounce of strong solution of ammonia. The air in the whole of the apparatus was now displaced by nitrogen, and the flask containing the boracic ether and zincmethyl removed from the ice-cold water. A slow evolution of gas immediately commenced, and was kept up at a convenient speed by plunging the generating flask into cold water, to which heat was very slowly applied. The gas, in passing through the freezing mixture, deposited nearly the whole of the ether and zincmethyl vapour with which it was contaminated; and on reaching the solution of ammonia, the boron compound was instantaneously absorbed, whilst other gases, if present, passed through the ammonia unacted upon, and escaped into the atmosphere. The solution of ammonia soon became covered with a stratum of a lighter liquid, which increased in quantity until the stream of gas ceased to pass through. The ammonia-flask was now disconnected with the rest of the apparatus, and reserved for the next operation. The residue in the generating flask solidified to a crystalline mass on cooling.

It now only remained to disengage the gaseous boron compound from its combination with ammonia. For this purpose the ammonia-flask was fitted with a funnel-tube terminating beneath the surface of the liquid, and a gas-delivery tube, the latter leading to a LIEBIG'S potash apparatus charged with concentrated sulphuric acid; finally, the opposite extremity of the latter apparatus was connected with a mercurial gas-holder. To prevent dangerous explosions, on the elimination of the spontaneously inflammable gas from its ammonia compound, the whole of the air-spaces of the apparatus were filled with nitrogen. Everything being thus prepared, dilute sulphuric acid was gradually poured into the ammonia-flask through the funnel-tube, the contents of the flask being frequently agitated. No gas was evolved until the excess of ammonia was saturated; then, however, it was given off abundantly, and the addition of a few drops of sulphuric acid, from time to time, through the funnel-tube served to keep up a convenient current. The gas was allowed to pass freely through the depressed mercurial gas-holder until a sample of it proved, by its perfect solution in ammonia, that all nitrogen had been swept from the apparatus. The exit-tube of the gas-holder was now closed, and the gas collected in sufficient quantity for subsequent experiments.

The following determinations, together with the analysis of its ammonia compound, prove that this gas is *boric methide*, and that its formula is

$$B\begin{cases}C_2H_3\\ C_2H_3\\ C_2H_3.\end{cases}$$

I. An indefinite quantity of the gas was cautiously led over ignited oxide of copper, the carbonic acid and water produced being collected and weighed in the ordinary manner. 0·5875 grm. of carbonic acid and 0·3664 grm. of water were obtained. These numbers show that the atomic relation of carbon to hydrogen is as 2 : 3.

$$C:H=2:3{\cdot}04.$$

II. A determination of the specific gravity of the gas gave the following results:—

Temperature of room at the moment of closing the flask	12°·2 C.
Height of barometer	759·4 millims.
Height of column of mercury in neck of flask above outer level of metal	4·5 millims.
Weight of flask and gas	28·7500 grms.
Temperature in balance-case	16°·1 C.
Weight of flask filled with dry air*	28·5882 grms.
Temperature in balance-case	15°·0 C.
Capacity of flask	141·7 cub. centims.

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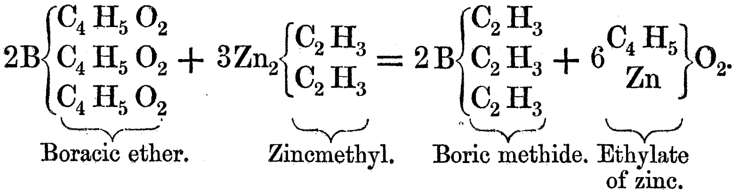
* The gas in the flask was replaced with dry air, by plunging the flask into a large beaker filled with carbonic acid, and then directing a rapid stream of the dry acid gas into the flask, so as to remove the spontaneously inflammable gas, which, rushing out of the neck of the flask with considerable velocity, reached the surface of the carbonic acid, and there formed beautiful wreaths of green flame. The flask was now several times exhausted and filled with dry air.

From these data the specific gravity of the gas was calculated to be 1·9108—a number which closely coincides with the calculated specific gravity of boric methide, which contains 1 volume of boron vapour and 3 volumes of methyl, the four volumes being condensed to two.

1 vol. Boron vapour . . .	·75319
3 vols. Methyl	3·10956
	2)3·86275
	1·93137

Boric methide is produced from boracic ether and zincmethyl by the following reaction:—



$$2B\underbrace{\left\{\begin{matrix}C_4H_5O_2\\C_4H_5O_2\\C_4H_5O_2\end{matrix}\right.}_{\text{Boracic ether.}} + 3Zn_2\underbrace{\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Zincmethyl.}} = 2B\underbrace{\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Boric methide.}} + 6\underbrace{\left.\begin{matrix}C_4H_5\\Zn\end{matrix}\right\}}_{\text{Ethylate of zinc.}}O_2.$$

The formation of boric methide under these circumstances proves conclusively that the corresponding ethyl compound is formed, not by the removal of the whole of the oxygen from boracic ether, but by the actual substitution of the three atoms of oxygen in boracic acid by three atoms of ethyl, whilst boric methide is in like manner produced by the similar substitution of methyl for oxygen,—a kind of substitution which is quite in harmony with the mode of formation of very numerous compounds in the organo-metallic family.

Boric methide exists at ordinary temperatures as a colourless and transparent gas, possessing a peculiar and intolerably pungent odour, irritating the mucous membrane, and provoking a copious flow of tears. Its specific gravity is 1·93137. It retains its gaseous condition when exposed to a cold of −16° C.; but at 10° C., and under a pressure of three atmospheres, it condenses to a colourless, transparent, and very mobile liquid. It is very sparingly soluble in water, but very soluble in alcohol and in ether. In contact with atmospheric air it takes fire spontaneously, burning with a bright green flame, which is very fuliginous if the volume of the flame be considerable. If the gas issue into the air through a tube $\frac{1}{10}$th of an inch in diameter, the amount of smoke is surprisingly great, two or three cubic inches of gas, when consumed in this way, filling the atmosphere of a capacious room with large comet-like flocks of carbonaceous matter. This curious phenomenon is probably due, in part at least, to the formation of a superficial coating of boracic acid, which envelopes the particles of carbon and prevents their combustion. Suddenly mixed with atmospheric air or oxygen, boric methide explodes with great violence. In contact with air, both boric methide and the vapour of boric ethide exhibit two distinct kinds of spontaneous combustion. Thus, when these bodies issue very slowly from a glass tube into the air, they burn with a lambent blue flame invisible in daylight, and the temperature of which is so low that a finger may be held in it for some time without much inconvenience. Under these circumstances partial oxidation only takes place, and it is to the products thus formed that the peculiar pungent odour of boric ethide and boric methide is due. When, on the other hand, these bodies issue into the air more rapidly, the lambent blue and nearly cold flame changes to the green and hot flame above mentioned. I have not examined the spectra of the two differently coloured flames from the same compound, but they doubtless present a widely different appearance, thus affording another instance of the dependence of the spectra of bodies upon temperature,—a phenomenon to which Dr. TYNDALL and myself recently called attention in the case of lithium[*].

Boric methide is not acted upon by binoxide of nitrogen or by iodine. Solution of bichromate of potash scarcely affects it, but the addition of concentrated sulphuric acid at once determines the reduction of the chromic acid. When boric methide is allowed to bubble through water into chlorine, each bubble burns explosively with a bright flash of light and the separation of carbon. It has no tendency to unite with acids. Concentrated sulphuric acid has no action upon it; when mixed with hydriodic acid gas, it suffers no change; but, on the other hand, it is freely absorbed by solutions of the fixed alkalies, and by ammonia. If a very rapid current of the gas, mixed with half its volume of marsh-gas, be passed through a stratum of strong solution of ammonia only half an inch deep, not a trace of boric methide escapes absorption.

Ammonia-Boric Methide.

When dry ammoniacal gas is mixed with an equal volume of dry boric methide, both gases instantly disappear with the evolution of a considerable amount of heat, and the production of a white, volatile, crystalline compound. The latter is also formed when boric methide is passed into solution of ammonia. The colourless liquid stratum which forms upon the surface soon solidifies when it is placed over sulphuric acid *in vacuo*. A quantity of the compound obtained by this latter process was purified by solution in ether and subsequent recrystallization. On being submitted to analysis, it yielded the following results:—

I. ·2652 grm., burnt with oxide of copper, gave ·4862 grm. carbonic acid and ·401 grm. water.

II. ·2809 grm. gave ·5105 grm. carbonic acid and ·4217 grm. water.

III. ·2124 grm., decomposed by dilute hydrochloric acid in a stream of carbonic acid, gave a solution of chloride of ammonium, which, treated in the usual manner, yielded ·6450 grm. of chloride of platinum and ammonium.

These numbers lead to the formula

$$NH_3 + B(C_2H_3)_3,$$

as is seen from the following comparison of calculated numbers with experimental results:—

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[*] Philosophical Magazine, S. 4. vol. xxii. p. 472.

	Calculated.		Found.			
			I.	II.	III.	Mean.
C_6 .	36	49·39	49·99	49·56	——	49·77
H_{12} .	12	16·46	16·80	16·68	——	16·74
N. .	14	19·20	——	——	19·07	19·07
B. .	10·9	14·95	——	——	——	14·42
	72·9	100·00				100·00

The excess of carbon, and to some extent also that of hydrogen, in these analyses is doubtless due to the retention of a small amount of ether by the crystals, the great volatility of the latter preventing any protracted exposure over sulphuric acid; but the substance used in No. II. was exposed for a much longer time than that employed in No. I.

Ammonia-boric methide is deposited from its ethereal solution in magnificent arborescent crystals, which rapidly volatilize without residue when exposed to the air. They possess a caustic and bitter taste, and a very peculiar odour, in which both the smell of ammonia and of boric methide can be recognized. Ammonia-boric methide fuses at 56° C. and boils at about 110° C. In a current of air, or better, of carbonic acid, it sublimes at a very gentle heat, and condenses in magnificent arborescent crystals. Determinations of the specific gravity of its vapour, at three different temperatures, gave the following results:—

Weight of ammonia-boric methide used . . . . ·0580 grm.

	I.	II.	III.
Observed volume of vapour . .	57·9 cub. cent.	58·6 cub. cent.	59·9 cub. cent.
Temperature of oil-bath . . .	119°·0 C.	130°·0 C.	139° C.
Height of mercury inside of tube above that outside	99·9 millims.	93·1 millims.	88·5 millims.

Height of barometer . . . . 751·8 millims.

Height of column of cold oil . . . . 307 millims.

From these data the specific gravity of the vapour was calculated to be

I.	II.	III.
1·251	1·258	1·250

These numbers indicate that the vapour of ammonia-boric methide consists of equal volumes of boric methide and ammonia united without condensation:—

1 vol. Boric methide . . .	1·93137
1 vol. Ammonia	·5873
	2)2·51867
	1·25933

Thus the formula of ammonia-boric methide is a four-volume formula*, a state of

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* H_2O_2= 2 vols.

condensation which is usually considered to be abnormal, and which, where it occurs, is generally explained by the assumption of a decomposition of the body at the moment of conversion into vapour. The proof of the disunion or integrity of the vaporous molecule of ammonia-boric methide would be interesting in connexion with these so-called anomalous vapour-densities, but I have to regret my inability to offer any sufficiently decisive solution of this problem. The difficulty to be overcome is the finding of a reagent that will not decompose ammonia-boric methide at elevated temperatures, but which would absorb ammonia only, out of a mixture of this gas with boric methide, at a temperature above the boiling-point of ammonia-boric methide. Chloride of calcium does not decompose ammonia-boric methide; but although it readily absorbs ammonia at ordinary temperatures, yet it allows the whole of it to escape again at 110° C. Chloride of zinc decomposes ammonia-boric methide before the latter volatilizes. The same effect is produced by all the strong acids, which are therefore also inadmissible, whilst dry boracic acid does not absorb ammonia even at ordinary temperatures. The substance which appeared to be best adapted for this reaction was dry and recently fused chloride of copper. This salt does not decompose ammonia-boric methide below the boiling-point of the latter, whilst it readily absorbs ammonia, and retains it at a temperature of 160° C. I will now describe the mode in which an experiment with this substance was conducted, and the results which were obtained. A quantity of ammonia-boric methide was introduced into a graduated tube filled with mercury, and inverted in a vessel containing the same metal. The whole was now immersed in an oil-bath, and heat applied until the boron compound was converted into vapour, the volume of which, at a known temperature and pressure, was then observed. After the apparatus had been allowed to cool, a fragment of chloride of copper was passed up into the tube, and heat again applied. The boron compound soon melted and enveloped the fragment of chloride of copper: as the temperature approached the boiling-point of ammonia-boric methide, the latter slowly boiled off from the chloride of copper, and the vapour then occupied the same volume as that read off before the introduction of the chloride of copper. The mercury in the tube remained steady for two or three minutes; it then gradually ascended, and the contraction of the vapour-volume continued until it was reduced to exactly one-half, as indicated by the following numbers:—

Corrected volume of vapour before treatment with chloride of copper	35·67 cub. centims.
Ditto after treatment with chloride of copper	17·85 cub. centims.

By treatment with chloride of copper, 100 volumes of vapour were therefore reduced to 50·04 vols., the residue consisting of pure boric methide gas. It is obvious that this absorption may be due either to decomposition of the vapour of ammonia-boric methide *by chloride of copper* at an elevated temperature, or to the decomposition *by heat* of the boric compound into equal volumes of boric methide and ammonia, the latter being then absorbed by the chloride of copper. Unfortunately, the result of the experiment is not sufficiently decisive to compel the adoption of either of these hypotheses, although the formation of the vapour and its existence for a few minutes in contact with chloride of copper favour the first more than the second; thus indicating that the vapour of ammonia-boric methide consists of equal volumes of ammonia and boric methide united without condensation, a result which would harmonize with the very generally observed rule, that when two gases or vapours unite in equal volumes, the volume of the compound is equal to that of its constituents.

Ammonia-boric methide scarcely absorbs a perceptible amount of oxygen at ordinary temperatures, even after several days' exposure to the gas; but it takes fire below 100° C. when heated in contact with the air. Its vapour is also very inflammable; thus, when ammonia-boric methide is placed under the receiver of an air-pump, and the air is being withdrawn, the explosion of the mixture of air and vapour in the cylinders of the pump is frequently determined by the rise of temperature consequent upon the depression of the pistons when the rarefaction has become considerable.

Boric methide is also absorbed by aniline with great avidity. Acids expel the gas from this compound unchanged.

Terhydride of phosphorus has no action upon boric methide. A mixture of equal volumes of the two gases is spontaneously inflammable, burning with a yellowish-white flame, in which the characteristic green tinge attending the combustion of boric methide is no longer perceptible.

Compounds of Boric Methide with Potash, Soda, Lime, and Baryta.

Solution of caustic potash absorbs boric methide with great energy. The saturated solution, exposed over sulphuric acid *in vacuo*, dries down to a gummy mass, which scarcely exhibits signs of crystallization. The same body may be more conveniently formed by decomposing ammonia-boric methide with alcoholic solution of potash, taking care to employ an excess of the former. On evaporation over sulphuric acid *in vacuo*, the excess of the ammonia compound volatilizes, and is decomposed by the sulphuric acid with the elimination of boric methide: thus the potash compound evaporates in an atmosphere of boric methide. Nevertheless even by this method I did not succeed in obtaining the potash compound in a state of purity; potash-boric methide thus prepared yielding on analysis 47·93 per cent. of potash, and 42·86 per cent of boric methide, numbers only very remotely indicating the formula

$$KO\,B(C_2H_3)_3,$$

which requires 45·67 per cent. of potash and 54·33 per cent. of boric methide. The appearance of the compound, even after exposure to gentle heat *in vacuo*, suggested the presence of water, which could not, however, be expelled at a temperature below that at which potash-boric methide itself is decomposed.

Boric methide is also readily absorbed by solution of neutral carbonate of potash, bicarbonate of potash and potash-boric methide being apparently formed. Although boric methide and potash unite with remarkable energy, yet they are separated by acids with the greatest readiness; even carbonic acid in the presence of water can expel boric methide from its potash compound; thus, if an aqueous solution of potash-boric methide be passed into carbonic acid standing over mercury, the acid gas soon becomes replaced by pure boric methide.

Soda-boric methide, baryta-boric methide, and lime-boric methide are similar bodies, produced by the absorption of boric methide gas by caustic solutions of soda, baryta, and lime; they are all readily soluble in water and react alkaline.

Boric methide in combination with the alkalies and alkaline earths has almost entirely lost its powerful affinity for oxygen; nevertheless, when these bodies are placed in contact with a known quantity of oxygen over mercury for several days, the volume of the gas perceptibly diminishes.

The great difficulty, not to say danger, attending the gradual oxidation of considerable quantities of a gaseous and spontaneously inflammable body like boric methide, has prevented me from following this compound into its products of oxidation, as was done in the case of boric ethide. With a graduated supply of oxygen, however, boric methide appears to comport itself like boric ethide, and the compounds formed are probably homologous with diethylate and dihydrate of boric dioxyethide.

In conclusion, it can scarcely be doubted that the action upon boracic ether of the zinc compounds of the remaining alcohol radicals would produce the homologues of the bodies described in the foregoing pages. It may also be remarked, that the existence of bodies like boric dioxyethide, in which one-third of the oxygen in boracic anhydride is replaced by ethyl, altogether abolishes any supposed analogy between carbonic and boracic acids, whilst it proves that the composition of the latter acid is expressed by the formula BO_3, or some multiple of that formula. I am at present engaged in studying the action of zincethyl and sodiumethyl upon the ethers of silicic, carbonic, oxalic, and acetic acids.