

XX.—*Contributions to the knowledge of the Amyl group.*

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I.—NITRITE OF AMYL AND ITS DERIVATIVES.

Nitrite of Amyl.— $C_{10}H_{11}O,NO_3$.—As this body was made the starting point from which certain new compounds were formed, and as it belongs to a very interesting group of bodies which have not been much studied, I shall, in the first place, describe some of its properties which have hitherto remained unnoticed.

Nitrite of amyl, when perfectly dry, boils at $99^{\circ}C$. in a glass vessel, in contact with platinum wire, under a pressure of 756^{mm} . A small quantity of moisture depresses the boiling point two or three degrees, apparently by diminishing the cohesion of the liquid.

As a solvent, nitrite of amyl may be placed between oxide of ethyl and bisulphide of carbon. It is miscible in all proportions with these liquids, as also with the alcohols and ethers both single and double, with benzol, paraffin, naphthalin, and the hydrocarbons. It dissolves abundantly the fats, oils and fatty acids, and disintegrates gutta-percha and caoutchouc. Sulphur and

* J pr Chem lxxviii 65

† Pogg Ann ciii 184

phosphorus are dissolved sparingly; gun-cotton at ordinary temperatures and pressures remains unaffected by it.

One of the most prominent of its properties is the singular effect of its vapour, when inhaled, upon the action of the heart. If a piece of bibulous paper, moistened with two drops of the nitrite of amyl, be held to the nostrils, through which the breath is exclusively drawn, after the lapse of about fifty seconds, a sudden throbbing of the arteries of the neck is felt, immediately followed by a flushing of the neck, temples and forehead, and an acceleration in the action of the heart. These symptoms last for about a minute and then cease as suddenly as they began. By inhaling the vapour from the above quantity, the pulsation of the heart may be raised from 70 to 140 per minute, even when absolute rest is observed. The acceleration becomes painful if the inhalation be accompanied with, or immediately preceded by, violent muscular exertion. The effect is still more marked, if, the nostrils being held closed, the same quantity is dropped upon the back of the tongue, and the breath drawn deeply over it. To ascertain the effect of a larger quantity, a piece of cotton-wool was moistened with about twenty drops, and being placed in a paper cone, was held over the mouth and nostrils of a rabbit. The animal did not offer any resistance. On removing the cone after five minutes, no signs of uneasiness were observed until twenty minutes had elapsed, when the rabbit sprang up and, after running about for a few seconds, lay down on its stomach, stretching out its legs. The protrusion of its eyes and its cries showed that it suffered pain. The power of voluntary motion seemed almost suspended, especially on the left side, both the left legs being either insensible to pain or incapable of motion.

The animal appeared to have recovered completely in a quarter of an hour after the first symptom. Even when diluted with large quantities of air, the vapour of nitrite of amyl has a very unpleasant effect upon the head if breathed for a long time; but beyond a very slight tendency to headache, seems to be without any subsequent injurious effect.*

Two points are worthy of note in the above experiments; firstly,

* It may be proper to recall the fact, observed by Hofmann, that crude nitrite of amyl, as prepared by the action of nitrous acid upon amylic alcohol, contains hydrocyanic acid; this must of course be removed by caustic soda before experiments such as the above can be tried. The presence of this impurity was probably the cause of its discoverer, Balard, attributing to nitrite of amyl the power of producing violent headache. No such effect was experienced by the fifteen or twenty students, of ages varying from fifteen to twenty-five, whom I have induced to try it.

that the vapour of the nitrite of amyl has a different effect from that of its analogue in the ethyl series, nitrite of ethyl, the active constituent of sweet spirits of nitre, having rather an opposite or soothing effect. Secondly, that the time required to attain the maximum effect differs in the cases of the human subject and the rabbit;—the former, as mentioned, occurring in fifty seconds, the latter in twenty minutes.*

If a few drops of nitrite of amyl be heated in a flask till their ebullition has expelled all the air, and the heat be still applied after all the liquid has disappeared, a slight detonation occurs, accompanied by the livid flame of burning nitrogen compounds. This is doubtless due to the partial combustion of the vapour of the body at the expense of its own oxygen. To determine the precise temperature at which this decomposition occurs, a bath of fusible metal with inserted thermometer was gradually heated, and the nitrite of amyl allowed to drop upon it at regular intervals of such magnitude that the disturbance of temperature due to its evaporation might be supposed unimportant. As soon as the liquid took fire on coming into contact with the heated metal, the temperature was alternately depressed and elevated through the observed point. In this way the temperature 260°C . was found to be, within a few degrees, that necessary and sufficient to determine the combustion. Spongy platinum placed upon the surface seemed to exercise no influence upon the temperature required to effect the decomposition.

Action of nascent Hydrogen.—It was to be expected that a body holding somewhat loosely a highly oxidized group, the latter being itself of unstable character, would undergo some change in the presence of nascent hydrogen. Into a flask provided with a funnel and exit-tube and containing three ounces of granulated zinc, an ounce of the nitrite of amyl was introduced; to this three ounces of alcohol at 50°B . were added, and then a mixture of equal parts of sulphuric acid and water allowed to enter slowly. The exit-tube was brought into a flask surrounded by a freezing mixture and the decomposition flask was immersed in cold water. When the zinc was nearly dissolved, the apparatus was disconnected. On adding water to the contents of the decomposition flask, an oily liquid, lighter than water, was separated, which on drying and rectifying gave a product boiling at 132°C . Burnt with oxide of copper, 0.3432 of this gave 0.8602 of carbonic acid and 0.4312 water.

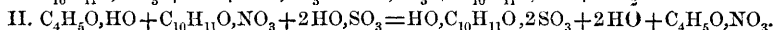
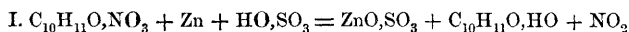
* It is probable that this body may find an application in medicine as a resuscitative, as in cases of suffocation, drowning or protracted fainting.

		Calculated.	Found.
C ₁₀	..	68·18	68·36
H ₁₂	..	13·64	13·96
O ₂			

It was therefore amylic alcohol. The aqueous solution from which it separated was evaporated to dryness with metallic zinc. The dry mass was shown to contain mere traces of organic matter, it consisted essentially of sulphate of zinc and sulphate of ammonia. The contents of the artificially cooled flask boiled on the application of the heat of the hand. It was distilled from a water bath at 40°. 0·3415^{grm.} gave on analysis 0·4606 carbonic acid, and 0·2168 water.

		Calculated.	Found.
C ₄	..	32·00	36·78
H ₅	..	6·66	7·05
N			
O ₄			

being therefore nitrite of ethyl containing alcohol. It has all the physical properties of such a liquid, and on boiling with alcoholic solution of caustic potash, yields nitrite of potash and a liquid wholly miscible with water. There are, therefore, in the first place, two simultaneous recompositions; the one, the formation of the amylic alcohol, being due to the action of the nascent hydrogen; the other, the formation of the nitrite of ethyl, being caused by the reaction upon the ethylic alcohol of the nitrous acid, as it is driven out of combination by the mineral acid employed.



But neither reaction stops here: the nitric oxide of the first is hydrogenated to ammonia, and the amylosulphuric acid of the second is decomposed as soon as formed. The above two curious reactions are of course independent of one another and the latter may be almost entirely prevented by using very dilute sulphuric acid. It is noteworthy, in the above reaction, that a body, nitrite of ethyl, is formed which is decomposable in alcoholic solution by sulphuric acid. That it nevertheless escapes decomposition is evidently owing to its volatility, by virtue of which it is removed as soon as formed from the field of chemical change.

Metallic Potassium effects an analogous reaction as far as the formation of amylic alcohol is concerned.

Action of Chlorine.—On passing pure and dry chlorine through

nitrite of amyl in an inverted retort connected with a condenser, heat was evolved and hydrochloric acid liberated, the contents of the retort changing in colour in succession from pale yellow to ruby red, olive green, and finally to pale, almost invisible green. The action was stopped at this point and a portion of the liquid being warmed and filtered to remove a small quantity of chloride of ammonium which separated out, was analysed. 0.2920gm. gave 0.0930gm. chloride of silver, 0.2039gm. gave 0.0707gm. chloride of silver. The two portions were from two separate preparations; the first contained accordingly 7.90 and the second 8.60 *per cent.* of chlorine. These numbers correspond most nearly with a substitution of one atom of chlorine for hydrogen in three atoms of the nitrite. This body has the specific gravity 0.909, but it is probably a mixture of the body next to be described, with undecomposed nitrite of amyl. If the current of chlorine be continued through the above liquid and its action be assisted by the heat of a water-bath, further evolution of hydrochloric acid results. When this has ceased, and the liquid and exit tubes show the presence of free chlorine, the action, as far at least as it goes in diffused daylight is complete. The contents of the retort are then shaken up with mercury and dilute ammonia to remove the excess of chlorine and hydrochloric acid, and dried over sulphuric acid in *vacuo*. 0.4561gms. gave 0.6109gms. carbonic acid and 0.2436gms. water. 0.2633gms. gave 0.3875gms. chloride of silver. The liquid has therefore the composition :—

	Calculated.	Found.
C_{10} .. 60	32.26	36.53
H_9 .. 9	4.84	5.93
Cl_2 .. 71	38.20	36.39
N		
O_4		

The above numbers show that the replacement was not quite complete; the substance analysed had been exposed for two hours to a rapid current of chlorine. This body is the *nitrite of bichloramyl*, $\left. \begin{array}{l} \text{C}_{10} \text{H}_9 \\ \text{Cl}_2 \end{array} \right\} \text{O,NO}_3$: that is, the nitrite of amyl wherein two atoms of hydrogen are replaced by chlorine. Nitrite of bichloramyl is a transparent colourless liquid of peculiar pine-apple odour, and very bitter and persistent taste. It is non-miscible with, and undecomposed by water: its specific gravity at 12°C. is

1.2333.* It is not volatile without partial decomposition. On distillation it begins to boil at 90°C. The boiling point rises to 200°C.: when this temperature is reached, the distillate is colourless, the residue black. Both are heavier than, non-miscible with, and undecomposed by, water.

Action of Phosphorus.—In the cold or at temperatures just sufficient to melt phosphorus, nitrite of amyl, as mentioned above, acts as a solvent. But at a temperature above this and below the boiling point of the nitrite, a true chemical action commences, the basis of which is the oxidation of the phosphorus at the expense of the oxygen of the organic nitrite. When the action has once commenced, which is seen by the evolution of a permanent gas, sufficient heat is evolved to carry it on without the application of external heat. If some ounces of the nitrite be employed, the temperature towards the end rises to 121°C., soon after which the action ceases abruptly. In order to trace this reaction, weighed quantities of nitrite of amyl and of phosphorus were employed, and the evolved gas was passed through two bulb wash-tubes, the first containing alcohol and the second water, and then through a chloride of calcium tube. The three tubes were all weighed. The flask containing the phosphorus and the nitrite was immersed in a water bath, the temperature of which was so regulated as to effect a regular disengagement of gas. When the reaction was finished, the residual phosphorus, the liquid residue in the flask, and the three tubes, were again weighed. In an experiment of this kind, after making the proper corrections, it was found that 18.53gms. of nitrite of amyl were acted on by 2.00gms. of phosphorus. As 16.00gms. of residual liquid remained in the flask, it follows that 4.53gms. of gas had been evolved; but as the gas so formed still contained organic matter, the latter number is probably somewhat too high. The gas was collected over mercury, and washed first with alcohol, then with water. The portion first collected contained about 70 per cent. of nitrogen, 4 per cent. of nitric oxide,

* The following simple device may be sometimes conveniently employed in determining the specific gravity of small quantities of liquids which are neither miscible with, nor decomposed by water, and whose specific gravities do not greatly exceed unity (say from 1 to 2). A single drop of the liquid to be examined is brought into a tall cylinder glass containing a little water, and immersed in a large beaker glass. A strong clear solution of chloride of calcium is added in small quantities at a time, care being taken not to break the drop of the liquid being examined, and to allow the solution to regain the temperature of the surrounding water. When such quantity has been added that the drop is in indifferent equilibrium, the specific gravity of the chloride of calcium solution is taken in the ordinary way with the specific gravity bottle, and it is of course identical with that of the liquid under examination.

and 26 of nitrous oxide: the latter portions were richer in nitrous oxide.* The reaction is therefore not a simple one. In two other experiments, in which the gas was not passed through wash-tubes, 1 part by weight of phosphorus gave rise to 8, and to 6·7 of residual liquid respectively.

The residual liquid was exposed to the air for several weeks to oxidize the free phosphorus which it held in solution, then heated to 150° to expel any unchanged nitrite of amyl, and finally repeatedly dissolved in alcohol and reprecipitated by water and dried in *vacuo* over sulphuric acid. Thus purified, a light brown oily liquid is obtained, which is quite insoluble in, and undecomposed by, water. Its specific gravity at 20°C. is 1·02; but it expands more rapidly than water, and at 70°C. has the specific gravity 1.

On analysis it showed the following composition:—

·5470gm.	gave	·9598gm.	carbonic acid and	·4458gm.	water
·4676gm.	gave	·8102gm.	carbonic acid and	·3885gm.	water
·4702gm.	gave	·1989gm.	pyrophosphate of magnesia		
·1947gm.	gave	·0116gm.	nitrogen.		

These numbers agree best with the formula $C_{20}H_{23}PNO_8$.

	Calculated.		Found.		
C_{20} ..	47·61	47·25	47·86		—
H_{23} ..	9·12	9·19	9·06		—
P ..	12·30	—	—	12·08	—
N ..	5·55	—	—	—	6·0
O_8 ..	25·43				

It is difficult to see what the rational formula of this body should be. Until some further light be thrown upon it, it may be called *amylonitro phosphorous acid*. It may be heated to 160°C. without decomposition; above this temperature it blackens and gives off hydride of amyl.

Amylo-nitrophosphite of potash is prepared by digesting the acid with alcoholic solution of caustic potash, passing carbonic acid through to neutralize the excess of potash, digesting with alcohol, filtering and evaporating. Dried in *vacuo* over sulphuric acid, it is a yellowish, finally granular, highly deliquescent body, soluble in water and alcohol. Dilute mineral acids separate out the

* The presence of nitrous oxide enabled me to determine the nitric oxide by combustion with hydrogen.

organic acid in heavy drops. Heated by itself it swells up and finally deflagrates.

The baryta, silver, lead, and copper salts are prepared from the potash salt on adding a soluble salt of the respective bases. They are all precipitated at first as light, flocculent, amorphous bodies. On agitating or warming them, they adhere together, forming tenacious gummy substances, which become dry and brittle under the air-pump. The silver salt cannot be dried without partial decomposition. Analysis showed all the above salts to be bibasic, with the exception of the lead salt, which gave discordant results on analysis, and whose composition is therefore doubtful. The acid is separated from all its salts on the addition of sulphuric or hydrochloric acid.
