VIII. *An Account of the Artificial Formation of a Vegeto-Alkali.*

By GEORGE FOWNES, *Ph. D., F.R.S., Chemical Lecturer in the Middlesex Hospital Medical School. Communicated by* THOMAS GRAHAM, *Esq., F.R.S., &c.*

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A FEW months ago Mr. MORSON very kindly put into my hands, for examination, a quantity of dark-coloured, viscid oil, amounting to six or seven ounces, which was said to have been produced by the action of sulphuric acid upon bran. The tarry appearance of the oil was evidently the result of oxidation, for the bottle in which it had been preserved during a period of five years was very imperfectly closed, while a second and smaller portion, which had been kept in a stoppered bottle the same length of time, although dark in colour, was perfectly thin and fluid.

A portion of the oil was introduced into a retort, together with a quantity of water, and the whole submitted to distillation; water, accompanied by a heavy, pale-yellow volatile oil, came over. At the close of the process the retort was found to contain a solid, pitchy residue, insoluble in water, but dissolved in great measure by caustic potash, and again precipitable by the addition of an acid.

The distilled oil, separated by a funnel from the water under which it rested, after having been left a few days in contact with fused chloride of calcium, was distilled alone in a small retort fitted with a thermometer, the bulb of which dipped into the liquid. A little water came over at first with the oil, but this quickly ceased to appear, and then the temperature of ebullition remained quite constant to the close of the distillation, which was conducted nearly to dryness. It was inferred from this experiment that the oil was a single substance, and not a mixture of two or more different bodies.

The water which came over with the oil in the first distillation contained a very considerable quantity of that substance in a state of solution; it was strongly acid besides, from the presence of formic acid.

The purified oil was next submitted to analysis in the usual manner, by combustion with oxide of copper. The following were the results:—

	(1.)	(2.)	(3.)
Oil employed	5·73 grs.	7·79 grs.	5·547 grs.
Carbonic acid produced	13·18 grs.	17·74 grs.	12·64 grs.
Water produced . . .	2·27 grs.	2·96 grs.	2·12 grs.

Hence the composition in 100 parts*, nitrogen being altogether absent,—

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* The equivalent of carbon is taken throughout =6.

	(1.)	(2.)	(3.)
Carbon	62·73 grs.	62·11 grs.	62·14 grs.
Hydrogen	4·40 grs.	4·22 grs.	4·24 grs.
Oxygen	32·87 grs.	33·67 grs.	33·62 grs.
	100·00	100·00	100·00

The formula $C_{15} H_6 O_6$, calculated to 100 parts, gives numbers almost coincident with the above, viz.—

Carbon	62·50
Hydrogen	4·17
Oxygen	33·33
	100·00

The following is a summary of the chief properties of the oil:—

When free from water and freshly rectified, it is nearly colourless, but after a few hours acquires a brownish tint, which eventually deepens almost to blackness; when in contact with water, or when not purposely rendered anhydrous, it seems less subject to change, and merely assumes a yellow colour. Its odour resembles that of a mixture of bitter almond oil, and oil of cassia, but has less fragrancy. The specific gravity of this substance at 60° is 1·168; it boils at 323° Fahr., and distils at that temperature without alteration. Cold water dissolves the oil in question to a very large extent; by distillation, and fractioning the products, it can be again separated. In alcohol it dissolves with perfect facility. Concentrated sulphuric acid dissolves it in the cold with magnificent purple colour; the solution is decomposed by water, with separation of the oil. If heated with the acid, it is charred and destroyed with evolution of sulphurous acid. Strong hydrochloric acid behaves in a very similar manner. Nitric acid, by the aid of a little heat, attacks the oil with prodigious violence, evolving copious red fumes, and generating oxalic acid, which appears to be the only product.

Solution of caustic potash, in the cold, slowly dissolves the oil, forming a deep brown liquid, from which acids precipitate resinous matter; by the aid of heat, the same change ensues very rapidly. Metallic potassium was found to be slowly acted upon by the cold oil, but on slightly elevating the temperature, an explosion took place, attended by a voluminous flame and a large deposit of soot, my hand being at the same time severely burned by a portion of the projected potassium.

The most remarkable and characteristic reaction of this substance, however, is with ammonia. When placed in contact with five or six times its bulk of ordinary *liquor ammoniæ*, and left some hours, it is gradually, but in the end completely converted into a solid, yellowish-white, and somewhat crystalline mass, which is very bulky, and perfectly insoluble in cold water. It may be easily collected on a filter, drained from the ammoniacal mother-liquor, and dried *in vacuo* over a surface of oil of vitriol. This substance appears to be the only product of the action of ammonia on the volatile oil.

Portions of the new body, prepared in the manner above stated, and very carefully dried over sulphuric acid, gave the following results on analysis by combustion with oxide of copper. The proportion of nitrogen was determined by the excellent method of MM. Will and Varrentrapp.

	(1)	(2.)	(3.)
Substance employed . . .	7·94 grs.	6·37 grs.	4·195 grs.
Carbonic acid produced .	19·34 grs.	15·57 grs.	10·24 grs.
Water produced	3·24 grs.	2·59 grs.	1·69 grs.

Hence, in 100 parts—

	(1.)	(2.)	(3.)
Carbon	66·55 grs.	66·66 grs.	66·57 grs.
Hydrogen	4·53 grs.	4·52 grs.	4·47 grs.

Determination of nitrogen*:—

	(1.)	(2.)	(3.)
Substance employed . . .	6·02 grs.	4·65 grs.	4·45 grs.
Platinum-salt obtained . .	10·10 grs.	7·62 grs.	7·17 grs.
Per-centage of nitrogen .	10·58	10·54	10·16

These results lead directly to the formula $C_{15}H_6NO_3$; when this is reckoned to 100 parts, it gives—

Carbon	67·13
Hydrogen . . .	4·47
Nitrogen . . .	10·48
Oxygen	17·92
	100·00

Hence it is clear that the solid substance is produced from the oil by the assimilation of the elements of one equivalent of ammonia, and the separation of those of three equivalents of water.

$$\begin{array}{ll} \text{Oil . . . . . .} & C_{15}H_6\ O_6 \\ +1\text{ eq. ammonia .} & \underline{\ \ H_3N\ \ } \\ & C_{15}H_9NO_6 \end{array} \left.\vphantom{\begin{array}{l}a\\b\end{array}}\right\} = \left\{\vphantom{\begin{array}{l}a\\b\end{array}}\right. \begin{array}{ll} \text{solid . . . . . .} & C_{15}H_6NO_3 \\ \text{3 eq. water . . .} & \underline{\ \ H_3\ \ O_3} \\ & C_{15}H_9NO_6 \end{array}$$

The new substance belongs in fact to the class of the *amides*, which it resembles in many important particulars, as will be more apparent in the sequel.

In the year 1841 Dr. Stenhouse† published an interesting paper on a peculiar oily matter, first noticed by Doebereiner, which occasionally appears in very small quantity, in the preparation of artificial formic acid from sugar or starch, oxide of manganese, and dilute sulphuric acid, and to which he gave the name of *artificial oil of ants*. Dr. Stenhouse, in the investigation above referred to, succeeded in pre-

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* It may not be amiss perhaps to mention, that in the method adopted the organic substance is strongly heated in a hard glass tube with a mixture of hydrate of soda and quicklime. The whole of the nitrogen issues thence in the form of ammonia, and being condensed into hydrochloric acid, is afterwards converted into chloride of platinum and ammonium, from the weight of which that of the nitrogen is easily calculated.

† Philosophical Magazine for February 1841; also Annalen der Chemie und Pharmacie, xxxv. p. 301.

paring this substance at will, and in sufficient quantity to serve the purposes of experiment; he found it composed of carbon, hydrogen and oxygen, and, what appeared very extraordinary in such a body, the two latter elements were in the proportions to form water. The analytical results, reckoned to 100 parts, were as follows:—

	(1.)	(2.)	(3.)
Carbon	62·59	61·87	62·55
Hydrogen . . .	4·37	4·37	4·46
Oxygen	33·04	33·76	32·99
	100·00	100·00	100·00

These numbers agree very closely with those furnished by the assigned empirical formula $C_5 H_2 O_2$.

There could be but little doubt that the oil upon which I had been experimenting was identical with the substance above described; its properties agreed on the whole pretty well with those assigned by Dr. STENHOUSE to his interesting product, with the exception of its extraordinary behaviour with ammonia, which seems to have escaped notice, probably from time being required for the production of the *amide*. To complete the identification, therefore, a small portion of oil was prepared, the process described and recommended being closely followed. 2 lbs. of oatmeal, 2 lbs. of water, and 1 lb. of oil of vitriol, were well-mixed in a small copper still, and heated until the pasty mass became thin and fluid from the conversion of the starch into dextrine; the head was then applied and luted down, and distillation commenced. As soon as sulphurous acid began to appear, an additional lb. of water was introduced, and the distillation continued until that gas began to escape in large quantity. The liquid which came over was then rectified to one-half, the product neutralized with hydrate of lime to fix the sulphurous and formic acids, and again distilled, the first third only being collected. A small quantity of heavy yellow oil was thus procured, and an additional portion obtained by again subjecting the watery liquid to distillation. So far as could be seen, this oil corresponded in every particular with that examined by myself; when put into solution of ammonia it formed in a few hours the characteristic yellowish compound, identical in composition and properties with that already described.

The nature of the oil so far elucidated, it will be proper to return to the subject of the *amide*, or ammonia-compound, the latter term being however hardly applicable. The mode of preparation of this substance has been already described; it is always produced when ammonia and the oil are brought into contact. It is very pale yellow, approaching to white, and nearly inodorous when dry and pure; in cold water it is insoluble; alcohol and ether, on the other hand, dissolve it freely. It may be obtained in tufts of small, short, acicular crystals, by allowing a hot, saturated alcoholic solution to cool; or whiter and purer, by adding ammonia to a saturated aqueous solution of the oil, and allowing the mixture to stand several days. In chemical characters this amide much resembles the *hydrobenzamide* of M. LAURENT, obtained by putting pure bitter almond oil into solution of ammonia. It is slowly decomposed by boiling water, and even by boiling alcohol, into free ammonia and volatile oil, and very slowly suffers the same kind of decomposition by moisture at the common temperature of the air. When heated, it melts, inflames, and burns with a smoky light, leaving a small deposit of charcoal. Acids decompose it immediately; a salt of ammonia is produced, and the original oil set free.

The action of alkalies on this substance is very remarkable, and well deserves attention. When boiled with a large quantity of dilute solution of caustic potash, it dissolves without the *least evolution of ammonia*, and the liquid deposits, on cooling, small, white, silky needles of a second new substance, having the *same composition* as the amide itself, but all the properties of a stable and exceedingly energetic organic base, possessing alkalinity, and having the power of forming with acids an extensive series of well-defined, and for the most part, crystallizable salts of great beauty.

Portions of the new salt-base, prepared at different operations with the greatest care, were submitted to ultimate analysis by burning with oxide of copper as before, the substance being dried *in vacuo* over a surface of oil of vitriol; the following results were obtained:—

	(1.)	(2.)	(3.)*
Substance employed . .	2·668 grs.	3·985 grs.	3·698 grs.
Carbonic acid produced .	6·53 grs.	9·74 grs.	9·06 grs.
Water produced . . .	1·12 grs.	1·63 grs.	1·51 grs.

Hence, in 100 parts,—

	(1.)	(2.)	(3.)
Carbon. . . .	66·75	66·66	66·82
Hydrogen . .	4·66	4·54	4·53

Estimation of nitrogen:—

	(1.)	(2.)
Substance employed. .	3·79 grs.	3·75 grs.
Platinum salt produced	6·12 grs.	6·11 grs.
Per-centage of nitrogen	10·18	10·28

The isomerism of the two substances is seen to be most complete; the numbers obtained by analysis absolutely coincide: and yet how discrepant their properties!

I am inclined to think that the nature of the isomeric change which the amide undergoes in presence of the alkali consists simply in a duplication of its elements; at least, this is the simplest view that can be taken. It is besides the only product. It will be seen from analyses of the salts formed by this substance, that the proportion of matter required to form a perfectly neutral compound with an acid, organic or inorganic, is expressed by the formula $C_{30}\,H_{12}\,N_2\,O_6$, which is the double of the *amide* $C_{15}\,H_6\,NO_3$. But then, as the constitution of this latter substance must be to some extent uncertain, since that of the oil is also unknown, and the *amide* forms no combinations, the above view must remain merely conjectural.

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* This specimen was prepared from the oxalate by precipitation by ammonia.

I pass now to a description of the properties of the new salt-base, of its principal salts yet studied, and of the best method of preparation on a considerable scale.

The substance itself crystallizes from boiling water in fine, soft, white, silky needles, much resembling those of cafeine, quite permanent in the air, and even in the dry vacuum. It has but little taste, although its salts are very bitter; they are far less so however than those of morphia, or of the bark-alkalies. It is inodorous. At a temperature rather below the boiling-point of water it melts to a heavy, nearly colourless, oily liquid, which on cooling assumes at first the consistence of a soft resin, but eventually becomes brittle and crystalline. When strongly heated in the air, the new substance inflames, burns with a red and smoky light, and leaves but very little charcoal. It is soluble in about 135 parts of boiling water, but after cooling, scarcely a trace remains dissolved. Alcohol and ether in the cold dissolve it with the utmost facility; the alcoholic solution deposits, on spontaneous evaporation, exceedingly brilliant silky crystals; the liquid has a great tendency to creep up the sides of the vessel. The alkaline reaction to test-paper, when dissolved in hot water or alcohol, is exceedingly strong and well-marked. Dilute acids dissolve this substance with the utmost ease, becoming thereby completely neutralized, unless employed in excess; from these combinations the base is precipitated in an unchanged state, by the addition of ammonia or of a fixed alkali. A salt of the new base gives no precipitate with solutions of peroxide of iron, oxide of copper or silver, lime or baryta; the hydrochlorate forms with corrosive sublimate, a white, and with chloride of platinum, a bright yellow, double salt. What is rather remarkable, it is not precipitated to any extent by tincture of galls. So powerful are the basic properties of this alkaloid, that when boiled with a solution of sal-ammoniac, it decomposes that salt with evolution of ammonia and formation of a hydrochlorate.

The salts formed by this curious body are exceedingly numerous, and would in all probability well repay a more extended investigation; the few yet examined are the following:—

Hydrochlorate.—This is easily prepared by dissolving the alkaloid in dilute, warm hydrochloric acid, to saturation. The salt, which is perfectly neutral to test-paper, forms tufts of fine, silky, acicular crystals, like those of hydrochlorate of morphia. It is very soluble in pure water, but far less so in an excess of hydrochloric acid. The crystals retain their brilliancy when dried *in vacuo* over sulphuric acid. An analysis of this salt gave the following results:—

(Carbon and hydrogen.)	(1.)	(2.)	(3.)
Salt employed	5·855 grs.	5·435 grs.	6·115 grs.
Carbonic acid produced . .	12· grs.	11·12 grs.	12·55 grs.
Water produced	2·49 grs.	2·27 grs.	2·56 grs.

	(1.)	(2.)	(3.)
Carbon. . . .	55·89	55·62	55·97
Hydrogen. . .	4·72	4·64	4·65

6·027 grs. salt gave of chloride of silver 2·65 grs. = 10·67 per cent. chlorine.

6·68 grs. salt gave of chloride of silver 2·92 grs. = 10·60 per cent. chlorine.

6·147 grs. salt gave of double chloride of platinum and ammonium 8·24 grs. = 8·45 per cent. nitrogen.

The formula $C_{30} H_{12} N_2 O_6, HCl+2HO$, reckoned to 100 parts, gives numbers closely agreeing with the preceding; viz.—

Carbon	55·81
Hydrogen . . .	4·65
Nitrogen	8·72
Chlorine	10·98
Oxygen	19·84
	100·00

When a solution of the hydrochlorate of the new base is mixed with one of bichloride of platinum, an insoluble, or sparingly-soluble, bright yellow, crystalline precipitate falls, which is a compound of the two bodies. It is blackened and decomposed by boiling. When heated in the dry state, it melts, blackens, and swells up to a prodigious extent, evolving fumes of sal-ammoniac; the incineration of the charcoal is slow and difficult. Examined by analysis, the double salt gave the following results:—

Salt employed	7·28 grs.
Carbonic acid produced . .	10·16 grs.
Water produced	1·97 grs.

In 100 parts,—

Carbon.	38·06
Hydrogen.	3·

16·43 grs. salt gave of metallic platinum 3·36 grs., or 20·45 per cent.

The formula $C_{30} H_{12} N_2 O_6, HCl+PtCl_2$, calculated to 100 parts, gives—

Carbon	37·97
Hydrogen	2·74
Platinum	20·90

Nitrate.—This is a very beautiful salt; it forms hard, transparent, colourless, and very brilliant crystals, whose form yet remains to be determined. It is freely soluble in pure water, but very sparingly soluble in excess of nitric acid. The crystals effloresce and become opake in a dry atmosphere. In this state they contain $C_{30} H_{12} N_2 O_6, NO_5+HO$, as shown by the result of an analysis given below.

Nitrate employed . . .	5·62 grs.
Carbonic acid produced .	11·19 grs.
Water produced . . .	2·02 grs.

or, in 100 parts,—

Carbon	54·30
Hydrogen	3·99

The theoretical quantities are—

Carbon	54·35
Hydrogen	3·93

Oxalates.—The neutral oxalate is a very soluble salt, crystallizing, when the solution is sufficiently concentrated, in tufts of fine needles, like the hydrochlorate. The binoxalate is very sparingly soluble in the cold, and crystallizes remarkably well when a hot saturated solution is left slowly to cool. It forms transparent plates, like those of oxalate of urea, which have a strong acid reaction when dissolved, and retain their lustre in the dry vacuum. This substance gave on analysis the results stated below, leading to the formula $C_{30} H_{12} N_2 O_6, 2C_2 O_3 + 2HO$.

Salt employed	4·808 grs.
Carbonic acid produced	10·05 grs.
Water produced	1·76 grs.

4·85 grs. salt gave of double chloride of platinum and ammonium 5·95 grs., or 7·74 per cent. nitrogen.

Hence, in 100 parts,—

Carbon	57·01
Hydrogen	4·06
Nitrogen	7·74
Oxygen	31·19
	100·00

The theoretical numbers are—

Carbon	56·96
Hydrogen	3·91
Nitrogen	7·85
Oxygen	31·28
	100·00

The *acetate* is very soluble, and apparently uncrystallizable, or at least crystallizable with great difficulty.

The following is an excellent and easy method of preparing the vegeto-alkali in a state of purity and whiteness. The *amide,* dried in the air, or better, over oil of vitriol in the vacuum of the air-pump, is thrown into a large quantity of boiling-hot dilute solution of caustic potash contained in a capacious glass flask placed over a lamp or chauffer. After ten or fifteen minutes' ebullition the change is complete, the great bulk of the new substance appearing in the form of a heavy, yellowish oil, which, on the removal of the vessel from the fire, collects at the bottom of the flask, and on cooling, solidifies, while that which had been dissolved by the liquid crystallizes out. When perfectly cold, the whole is thrown upon a cloth filter, slightly washed with cold water, and then dissolved in a large quantity of dilute boiling solution of oxalic acid, the acid being kept in considerable excess. The liquid, filtered hot, deposits on cooling a large crop of crystals of the acid oxalate of the base, dark-coloured, however, and impure. The salt may then be collected on a cloth filter, slightly washed and pressed, redissolved in boiling water, and heated for a few minutes with a little good animal charcoal, deprived of its earthy phosphates, &c., by washing with hydrochloric acid. The filtered solution now deposits the acid oxalate in a state of perfect whiteness and purity; from the pure salt the alkali may be obtained in crystals by solution in a large quantity of boiling water, addition of excess of ammonia, and rapid filtration at a high temperature. The crystals which form on cooling require of course washing with distilled water until all the ammoniacal and other salts are removed, and a portion of the alkaloid taken from the filter is found to leave no residue when completely burned on platinum.

I am in great doubt as to the most appropriate names to be bestowed on these curious bodies, and this doubt will remain until more is known respecting the real origin of the oil. This substance has no apparent connection with formic acid, except the accidental one of contemporaneous production. It is allied in *constitution* to the sugar and starch series, inasmuch as it contains oxygen and hydrogen in the proportions to form water, and in *properties* to bitter almond oil and the essential oils in general. So far as my own experiments go, it seems to be produced most freely and in greatest abundance from bran, 1 lb. of that substance distilled with half its weight of sulphuric acid and 3 lbs. of water having yielded nearly a drachm of oil, while mere indistinct traces could be obtained from similar quantities of rice- and potatoe-starch. Under these circumstances, perhaps the name "Furfurol" (from *furfur*, bran, and *oleum*) might be applied provisionally, and I am informed that this is the name which was proposed by the party who several years ago prepared a considerable quantity of the oil (a portion of which came into my hands, as mentioned at the commencement of this paper), and endeavoured to discover for it economical applications.

The following, therefore, will be the provisional nomenclature:—

Oil produced by the action of sulphuric acid on bran, &c., termed "furfurol," $C_{15} H_6 O_6$.

Product of the action of ammonia on furfurol, or "furfurolamide," $C_{15} H_6 NO_3$.

Vegeto-alkali, "furfurine," produced by the duplication of the elements of furfurolamide, $C_{30} H_{12} N_2 O_6$.

In conclusion, I beg to direct attention to the large and promising field of investigation offered by the study of the action of ammonia on the volatile oils, and on other allied bodies.

Middlesex Hospital,
Jan. 9, 1845.

NOTE ADDED DURING THE PRINTING.

Since the preceding paper was read I have received a communication from the gentleman just referred to, Mr. WILLIAM COLEY JONES, late of Plymouth, who has directed my attention to an article in the Polytechnic Journal, April 1840, in which he has described some of the more important properties of the oil in question, and among others, its power of generating a solid compound with ammonia, which when distilled with dilute sulphuric acid reproduced the furfurol. Mr. JONES prepared furfurol on a very extensive scale from the waste "lignin," or bran, separated from wheat in the process of starch-making; the details of the method however are not given, and there are no analyses of the products. I feel no hesitation in expressing my opinion that the honour of the independent discovery of this most curious body is justly due to Mr. JONES, and it is much to be regretted that it did not receive greater publicity.

Aug. 12, 1845.