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Charles S. Gibson
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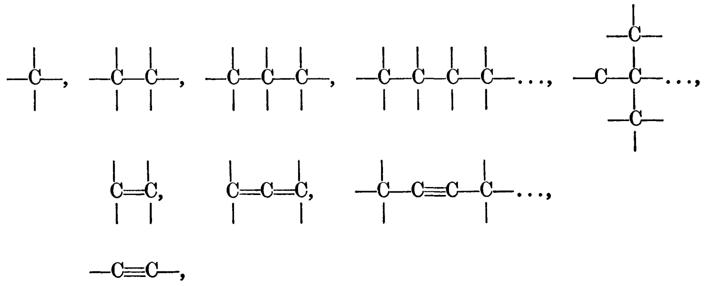
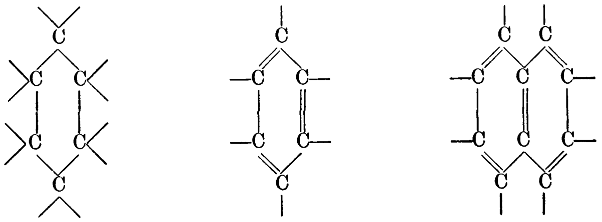
INTRODUCTORY

ORGANIC CHEMISTRY is the Chemistry of Carbon Compounds. It includes such compounds as carbon dioxide—the ultimate product of oxidation of the carbon in all organic compounds—carbon monoxide, carbon disulphide, cyanogen, hydrocyanic acid and its salts which may, for convenience, be studied along with typical inorganic substances. The great variety of organic compounds range from substances having relatively simple molecular constitutions, as those above mentioned, to the highly complex substances such as the polysaccharides (e.g. starch and cellulose) and rubber and the very great number of plant and animal products.

The great number of organic compounds is due to the capacity of the quadrivalent carbon atom in uniting with other carbon atoms and which no other element possesses in anything like the same degree. In this way, relatively simple organic compounds are built on such 'carbon skeletons' as



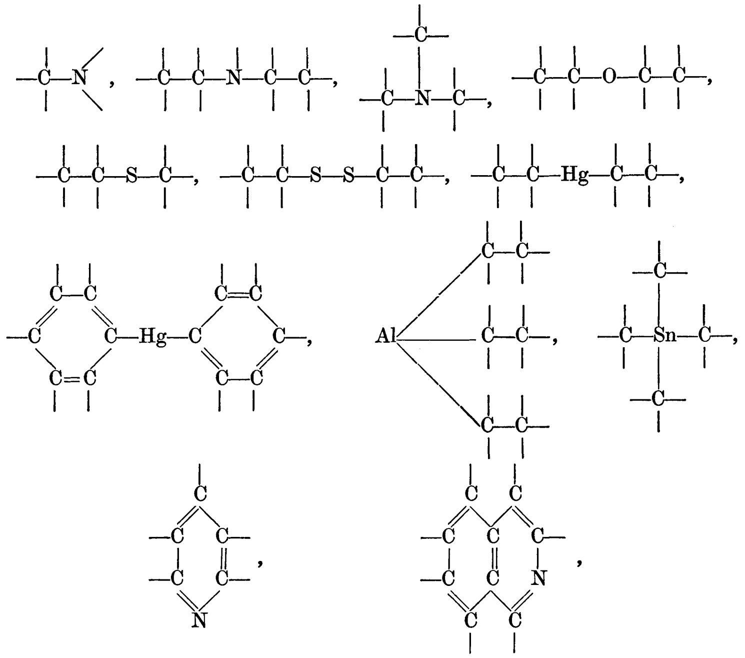
open chain compounds



ring or cyclic compounds

in all of which the quadrivalency of the carbon atom is preserved.

These 'skeletons' can be varied in an almost infinite number of ways, of which a few simple examples are



in which quadrivalent carbon is united to such elements as tervalent nitrogen, bivalent oxygen, bivalent sulphur and even to such metals as bivalent mercury, tervalent aluminium and quadrivalent tin.

Organic compounds obey the fundamental laws of chemistry, but in view of the capacity of the carbon atom to combine with itself, the Law of Multiple Proportions, in the case of most carbon compounds, cannot be stated so definitely as in the case of elements which form different series of compounds according to differences in the fundamental valency of the elements; thus, the above law in its simplest form is obeyed in the case of hydrocarbons (compounds containing carbon and hydrogen only) having the same number of carbon atoms in the molecule, such as those having the formulae:

C_2H_6	C_2H_4	C_2H_2
ethane	ethylene	acetylene

but, in its simple form, it does not apply in the case of such a series of hydrocarbons as

CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12} etc. (paraffins)

the composition of which differ from member to member by $=CH_2$.

In so far as organic compounds include solids, liquids and gases, the general methods of their physical investigation are the same as in the investigation of chemical compounds in general. Solid organic compounds may be, for example, crystalloids and colloids, electrolytes and non-electrolytes (non-electrolytes are relatively far more common among organic than among inorganic compounds). Consequently, as far as their nature permits, such solid compounds may be submitted to the methods usually employed for investigating these types of substances. On the other hand, the methods for investigating what may be described as 'the architecture of the molecules' or, as it is generally termed, 'the chemical constitution' (i.e. how the various atoms in the molecule are related to each other) of organic compounds are peculiar to organic chemistry and necessitate the study of the chemical behaviour of the numerous types of individual substances.

Apart from metallic radicals in salts of organic acids, in organo-metallic compounds (compounds containing metallic radicals directly united to carbon), in haemin (the red blood pigment containing iron) and in chlorophyll (the green colouring material of plants containing magnesium), the different elements in typical organic compounds are comparatively few. All organic compounds must contain carbon, the great majority contain hydrogen and oxygen, a very large number contain nitrogen and halogens (particularly chlorine, bromine and iodine), fewer contain sulphur and much fewer phosphorus. In view of the rapid increase in our knowledge, almost any element may be found sooner or later in organic compounds and, for example, organic compounds containing fluorine and other non-metallic elements are rapidly increasing in number. The principles of determining qualitatively and quantitatively the more typical elements in organic compounds will illustrate the general methods for these purposes.

Qualitative detection of the more usual elements in organic compounds

By definition, all organic compounds contain *carbon*, and when heated, after being intimately mixed with dry cupric oxide, evolve carbon dioxide, which may be made manifest by its forming a precipitate of calcium carbonate when passed into an aqueous solution of calcium hydroxide. If the compound contains *hydrogen*, water will be produced at the same time; it is, of course, essential that initially the materials used for the test for combined hydrogen should be dry. Not a few organic compounds are inflammable and burn in the presence of air or oxygen; the products of this combustion always contain carbon dioxide and water, proving the initial presence of combined carbon and hydrogen in the compound.

There is no satisfactory test for *oxygen* in organic compounds. Compounds which on being heated in the absence of oxygen evolve oxides of carbon and water obviously contain carbon, hydrogen and oxygen. Theoretically, a compound having the general formula $C_xH_yO_z$ should, on complete oxidation, yield carbon dioxide and water according to the following:

$$C_xH_yO_z \rightarrow xCO_2 + \frac{y}{2}H_2O.$$

In the great majority of cases $\frac{1}{2}z$ molecules of oxygen are less than $x+\frac{1}{4}y$ molecules of oxygen and, therefore, for the complete combustion of such an organic compound oxygen has to be supplied from an external source. If the amount of oxygen to be supplied could be measured accurately, and this was found to be less than the amount of oxygen present in the carbon dioxide and water obtained in the quantitative oxidation, the presence of oxygen in the original compound would be proved.

The presence of *nitrogen* in an organic compound may be demonstrated by fusing the compound with sodium in a suitable hard glass tube, when sodium cyanide is produced. After getting rid of the excess of metallic sodium, the presence of sodium cyanide is demonstrated by extracting the product with warm water and filtering the solution. This strongly alkaline solution is treated with an aqueous solution of a ferrous salt, then with an aqueous solution of a ferric salt and, after addition of excess of hydrochloric acid to dissolve ferrous and ferric hydroxides, a blue precipitate of ferric ferrocyanide (insoluble Prussian Blue) is obtained if nitrogen is present in the original compound. Omitting the precipitation and solution of iron hydroxides, the reactions taking place are indicated:

$$\text{Organic compound containing nitrogen} + \text{Na, and fused} \rightarrow NaCN$$

$$2NaCN + FeSO_4 \rightarrow Na_2SO_4 + Fe(CN)_2$$

ferrous cyanide, unstable—cannot be isolated

$$4NaCN + Fe(CN)_2 \rightarrow Na_4[Fe''(CN)_6]$$

sodium ferrocyanide

$$3Na_4[Fe''(CN)_6] + 2Fe_2(SO_4)_3 \rightarrow 6Na_2SO_4 + Fe_4'''[Fe''(CN)_6]_3$$

ferric ferrocyanide or Prussian Blue—insoluble in hydrochloric acid

A few organic compounds when heated with alkali hydroxide evolve ammonia which, in those cases, obviously indicates the presence of nitrogen in the original substance. All nitrogenous organic compounds when heated for some time with concentrated sulphuric acid undergo oxidation and the nitrogen is converted into ammonium sulphate from which ammonia can be obtained. Finally, from all nitrogenous organic compounds when heated after being mixed with a large excess of cupric oxide so as to oxidise them, the nitrogen may be evolved as such and, partly, as oxides of nitrogen. If the resulting gaseous products of the oxidation are passed over heated metallic copper so as to reduce the oxides of nitrogen and then through a

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concentrated aqueous solution of potassium hydroxide, the gas collected is nitrogen coming from the original compound. These last three methods are not so satisfactory as the 'sodium-fusion' method for the mere testing for the presence of nitrogen in an organic compound.

The *halogens* usually present in organic compounds are chlorine, bromine and iodine, and their presence may be detected in three ways. Whilst not conclusive, the first depends on the fugitive green colour imparted to the Bunsen flame by copper halides. A copper wire heated in the oxidising flame becomes oxidised and ceases to impart a colour to the flame; when such an oxidised copper wire is dipped into an organic compound containing halogen so that a little adheres and is then placed in the Bunsen flame, the latter shows the characteristic transient green colour. Another test depends on the fact that many halogen-containing organic compounds when heated with *pure* calcium oxide convert the latter into calcium halide. The solid product is extracted with water and the filtered solution tested for halogen ions in the usual manner—colourless (chlorine), pale yellow (bromine) or yellow (iodine) precipitates of silver halide, darkening on exposure to light and insoluble in nitric acid. The most satisfactory test for halogen in an organic compound is to fuse the latter with sodium as in the nitrogen test. When the vigorous reaction is over the product is treated carefully with water (excess of sodium may remain) and warmed. The warm strongly alkaline solution containing sodium halide is filtered, acidified with nitric acid and treated with an aqueous solution of silver nitrate, when the silver halide is precipitated. The precipitate identified as silver chloride, bromide or iodide indicates the presence of chlorine, bromine or iodine in the original compound. All organic compounds when completely oxidised by concentrated nitric acid in the presence of silver nitrate yield up their halogens quantitatively as silver halides.

The presence of *sulphur* in an organic compound may also be qualitatively determined by fusing the compound with sodium. The essential product in such cases is sodium sulphide in the presence of an excess of sodium hydroxide. The product is treated carefully with water (probable excess of sodium) and then the mixture is warmed. To the filtered alkaline solution is added a fresh aqueous solution of sodium nitroprusside or sodium nitrosoferricyanide,

$$Na_2[Fe'''(NO)(CN)_5].2H_2O,$$

when a characteristic intense purple colour is produced in the solution. The actual nature of the water-soluble intensely coloured compound is not definitely established; it may be a compound having the constitution

$$Na_3[Fe'''(O:N.S.Na)(CN)_5],$$

but its production is characteristic of alkaline sulphides. The sulphur in all organic compounds containing this element when completely oxidised with concentrated nitric acid is quantitatively converted into sulphuric acid, which may be identified by the production of barium sulphate, which is insoluble in water and mineral acids.

The presence of *phosphorus* in an organic compound may be detected by fusing the latter with a mixture of potassium nitrate and sodium carbonate when oxidation takes place, the phosphorus becoming converted into water-soluble phosphate. The filtered aqueous extract is tested for phosphate with an aqueous solution of ammonium molybdate or with magnesia-mixture (ammoniacal solution of magnesium chloride and ammonium chloride) in the usual way. The phosphorus in an organic compound may also be quantitatively converted into phosphoric acid by the complete oxidation of the compound with concentrated nitric acid.

The *metallic radicals* in organic compounds may be detected as metallic oxides or carbonates remaining after 'destroying' the compound by heating it in air. The 'ash' is, of course, submitted to the usual methods of analysis and the methods can be made quantitative.

As a general rule the *Quantitative Analysis of Organic Compounds* is carried out by determining the amount of products obtained by completely oxidising weighed quantities of the compounds. Microanalytical methods are now extensively employed when possible and, although they involve special technique, they yield highly satisfactory results in the hands of trained operators. The principles involved are comparatively simple.

Determination of carbon and hydrogen. The weighed quantity of the substance is oxidised in a current of oxygen or air which is dry and free from carbon dioxide and also in the presence of a suitable oxidising agent such as cupric oxide or potassium dichromate. The products of oxidation or 'combustion', viz. water (formed from the hydrogen in the compound) and carbon dioxide (produced from the carbon in the compound), are collected in previously weighed tubes containing suitable absorbing material. The water is absorbed in calcium chloride or pumice saturated with concentrated sulphuric acid and then the carbon dioxide is absorbed either in solid potassium hydroxide or soda-lime. If nitrogen be present in the compound, the products of combustion, before being collected, are allowed to pass over heated copper which reduces any oxides of nitrogen and then the nitrogen passes through the absorption apparatus without change. If halogen be present in the original compound, lead chromate may be used as the additional oxidising agent, when the halogen is retained as lead halide; or, the products of combustion before passing to the absorption apparatus are allowed to pass over heated silver which retains the halogen as silver halide so that the halogen does not pass into the absorption apparatus. Generally, special precautions have to be taken in the quantitative oxidation or 'combustion' of substances which on oxidation may yield substances in addition to water and carbon dioxide and which, like these, may be retained in the absorption apparatus. The result of a typical analysis of a simple substance is the following:

> 7·200 mg. of an organic compound gave on combustion 4·320 mg. of water and 10·56 mg. of carbon dioxide.

Assuming the atomic weights of hydrogen, carbon and oxygen to be 1, 12 and 16 respectively,

7·200 mg. of the compound contains

$$\frac{2}{18} \text{ or } \frac{1}{9} \times 4{\cdot}320 \text{ mg. hydrogen and } \frac{12}{44} \text{ or } \frac{3}{11} \times 10{\cdot}56 \text{ mg. carbon,}$$

i.e. 100 parts of the compound contain

$$\frac{1 \times 4{\cdot}320 \times 100}{9 \times 7{\cdot}200} \text{ parts of hydrogen}$$

and

$$\frac{3 \times 10{\cdot}56 \times 100}{11 \times 7{\cdot}200} \text{ parts of carbon.}$$

That is, the compound contains 6·67 per cent. of hydrogen and 40·0 per cent. of carbon.

In the absence of further information, it must be assumed that the deficiency, viz. $100 - 6{\cdot}67 - 40{\cdot}0 = 53{\cdot}33$ per cent., is oxygen. The result of this analysis shows that the compound contains carbon $= 40{\cdot}0$ per cent., hydrogen $= 6{\cdot}67$ per cent. and oxygen $= 53{\cdot}33$ per cent.

The amount of *nitrogen* in a compound is always determined separately. For this purpose, the weighed quantity of the compound is intimately mixed with a large excess of a suitable oxidising agent (e.g. cupric oxide) and heated in a current of carbon dioxide; the resulting gaseous products are passed over heated copper and then through a concentrated aqueous solution of potassium hydroxide over which the nitrogen is collected in a suitable 'nitrometer'—an apparatus for measuring the volume of nitrogen. The potassium hydroxide absorbs all the carbon dioxide and, after making allowance for the vapour tension of the solution of potassium hydroxide, the weight of the nitrogen obtained and the percentage of nitrogen in the substance are calculated as illustrated in the following example:

> 6·720 mg. of a compound gave 1·91 ml. of nitrogen at 15° C. and 752 mm.
>
> i.e. 6·720 mg. gave $\frac{1{\cdot}91 \times 273 \times 752}{288 \times 760} = 1{\cdot}791$ ml. of nitrogen at 0° C. and 760 mm. pressure.

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Assuming that 1 litre of nitrogen at N.T.P. weighs 1·2507 grams, the compound contains

$$\frac{1{\cdot}2507 \times 1{\cdot}791 \times 100}{1000 \times 0{\cdot}00672} = 33{\cdot}3 \text{ per cent. of nitrogen.}$$

Another method of estimating nitrogen consists in oxidising a weighed quantity of the compound by digesting it with concentrated sulphuric acid, whereby, when the compound is completely oxidised, the whole of the nitrogen is retained as ammonium sulphate. The ammonia is liberated from this by making strongly alkaline and boiling and is absorbed in a known excess of a standard aqueous solution of sulphuric acid. This is Kjeldahl's method; it is rarely used for the analysis of pure compounds, but is the routine method for determining the nitrogen content of highly complex materials such as proteins, feeding stuffs, etc.

The amount of *halogen* may be determined by Carius' original method by sealing in a suitable glass tube a weighed quantity of the compound with an excess of concentrated nitric acid and silver nitrate and heating the whole in a closed or 'bomb' furnace at a temperature of about 250° when, after a time, the oxidation is complete. The halogen is converted into silver halide which, by careful manipulation, can be weighed directly. An example of the analysis of a compound containing bromine is the following:

0·2680 gram of the compound gave 0·2507 gram of silver bromide.

Assuming the atomic weights of bromine and silver to be 80 and 108 respectively,

the substance analysed contains

$$\frac{0{\cdot}2507 \times 80 \times 100}{188 \times 0{\cdot}2680} = 39{\cdot}8 \text{ per cent. of bromine.}$$

The amount of *sulphur* may also be determined by Carius' original method, in which the weighed quantity of the compound is heated in a suitably sealed tube with an excess of concentrated nitric acid. The sulphur is quantitatively converted into sulphuric acid, which is precipitated as barium sulphate and weighed as such. A typical example of the results of such a determination is

0·1440 gram of a compound gave 0·2801 gram of barium sulphate.

Assuming the atomic weights of oxygen, sulphur and barium to be 16, 32 and 137·4 respectively,

the substance contains

$$\frac{0{\cdot}2801 \times 32 \times 100}{233{\cdot}4 \times 0{\cdot}1440} = 26{\cdot}7 \text{ per cent. of sulphur.}$$

These examples indicate the principles involved in determining the percentage composition of organic compounds. From such results,

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the relative number of the different atoms in a molecule of a compound can be determined as indicated by the following simple example:

An organic compound contained 9·1 per cent. of hydrogen and 54·5 per cent. of carbon.

In the absence of further information it must be assumed that the deficiency, viz. $100-9{\cdot}1-54{\cdot}5=36{\cdot}4$ per cent., must be oxygen.

Therefore if the molecular weight of the compound were 100, there would be in such a molecule

$$\frac{9{\cdot}1}{1}=9{\cdot}1 \text{ atoms of hydrogen,}$$

$$\frac{54{\cdot}5}{12}=4{\cdot}54(2) \text{ atoms of carbon}$$

and $$\frac{36{\cdot}4}{16}=2{\cdot}27(5) \text{ atoms of oxygen,}$$

the atomic weights of hydrogen, carbon and oxygen being assumed to be 1, 12 and 16 respectively. Such fractions of atoms cannot exist in the molecule of a compound, and in the molecule there must be at least one atom of the element present in the least atomic proportion, in this case, oxygen. These numbers also indicate that the molecular weight of the compound cannot be 100. By inspection, the above atomic proportions are almost completely divisible by 2·27, thus

$$\frac{9{\cdot}1}{2{\cdot}27}=4, \qquad \frac{4{\cdot}54}{2{\cdot}27}=2, \qquad \frac{2{\cdot}27}{2{\cdot}27}=1,$$

and therefore the relative numbers of atoms of carbon, hydrogen and oxygen in the compound are expressed by the formula C_2H_4O. At the same time, there is no apparent reason why the above atomic proportions should not be divided by 1·135, or by 0·756 or by 0·567 or by any submultiple of 2·27, in which cases the formulae arrived at would be $C_4H_8O_2$, $C_6H_{12}O_3$, $C_8H_{16}O_4$, etc. instead of the simplest formula C_2H_4O.

The simplest formula which can be deduced from the results of analysis of a compound is known concisely as the Empirical Formula, and, from the above, the empirical formula may be the molecular formula or a submultiple of it; and therefore to determine the molecular formula it is necessary to determine the molecular weight of the compound.

The methods of *Determination of the molecular weights of organic compounds* are those in general use for all types of compounds. If the particular compound can be vaporised without decomposition or dissociation, the vapour density can be determined by Victor Meyer's method, by Dumas' method or by Hofmann's method, whichever may be found the most convenient and suitable for the

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compound under investigation. Victor Meyer's method is frequently used and, although the value of the vapour density obtained by this method is only approximate and hence the molecular weight calculated from this (by multiplying by 2) according to Avogadro's Law is also approximate, it will be sufficiently accurate to determine whether it is the molecular weight corresponding to the empirical formula or to one of its multiples. In the case of the compound having the empirical formula C_2H_4O, it was found that the vapour density as determined by Victor Meyer's method was approximately 43, indicating an approximate molecular weight of 86. This indicates that the molecular formula must be twice the empirical formula, i.e. $C_4H_8O_2$, of which the true molecular weight is 88 ($H=1$, $C=12$, $O=16$).

In the case of compounds whose molecules dissolve without dissociation or association in liquids and which obey the gas laws as applied to dilute solutions, the molecular weight may be determined from (*a*) the depression of the freezing point of a suitable solvent, (*b*) the elevation of the boiling point of a suitable solvent, (*c*) the lowering of the vapour pressure of a suitable solvent and (*d*) the osmotic pressure of a suitable solution. In actual practice, the usual methods employed are determinations of the depression of the freezing point and elevation of the boiling point of suitable solvents (cf. p. 507).

Further information concerning the molecular weights of organic compounds can be obtained in special cases by what may be described as chemical methods. For example, the equivalents of compounds which are acids can generally be determined by titration with a suitable alkali. The equivalent of a monobasic acid of the general formula, AH, is the same as its molecular weight; generally, the molecular weight of an acid is $n \times$ its equivalent weight, where n represents the basicity of the acid. Again, the silver salts of all typical organic acids when completely decomposed by heat leave a quantitative residue of silver, and the equivalents of such organic acids can be determined from the relationship

$$A\mathrm{Ag} - \mathrm{Ag} + \mathrm{H} = A\mathrm{H},$$

where AAg represents the equivalent weight of silver salt or the molecular weight of the silver salt of a monobasic acid, AH. If the basicity, n, of the acid is known, the molecular weight of an organic acid of the formula, $A'\mathrm{H}_n$, is determined from the relationship

$$A'\mathrm{Ag}_n - n\mathrm{Ag} + n\mathrm{H} = A'\mathrm{H}_n,$$

where $A'\mathrm{Ag}_n$ represents the molecular weight of the normal silver salt of the n-basic acid, $A'\mathrm{H}_n$. It is only necessary to prepare the normal silver salt of the acid, determine the amount of silver in a weighed amount and calculate the amount of the silver salt which contains the atomic weight of silver or n times the atomic weight of