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ON THE FUNDAMENTAL CONCEPTIONS UNDERLYING THE CHEMISTRY OF THE ELEMENT CARBON.[1]

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Two fundamental conceptions underlie our present system of carbon chemistry. First, the idea of the constant quadrivalence of carbon, which explains most adequately the existence of the vast array of carbon compounds. Second, the conception of substitution or metalepsis which gives us a basis for interpreting many of the reactions shown by these substances.

These ideas are, however, in the light of investigations of the past twenty years, inadequate; they must be replaced by the conception of a variable valence of carbon and by the conception of dissociation in its broadest sense.

A rigid application of the latter conceptions gives à far simpler basis for interpreting all the reactions of carbon chemistry; they are naturally also applicable to the chemistry of all the other elements.

I.   ON THE VALENCE OF THE CARBON ATOM.

The progress of organic chemistry since 1858 is due chiefly to the development of a few very simple ideas concerning the valence

of the elements, ideas which were first clearly and fully presented
at that time by Kekulé.

Hydrogen, oxygen and nitrogen are the elements which most
frequently combine with carbon to form the so-called organic
compounds. Since the compounds of one atom of oxygen, nitro-
gen, or carbon with hydrogen possess the empirical formulae,
$O=H_2$, $N\equiv H_3$, $C\equiv H_4$, the conception naturally presents itself
that the capacity of the various elements for holding hydrogen
atoms varies. Oxygen is capable of holding two such atoms,
nitrogen holds three, and carbon four atoms of hydrogen. There-
fore we assume, taking hydrogen as our unit, that the valence of

the element oxygen is two, $-O-$. of nitrogen, three, $-\overset{|}{N}-$,

and of carbon, four, $-\overset{|}{C}-$. Without going into much detail

concerning the nature of the valence, or what is the same thing
concerning the nature of the forces inherent in our atoms, we
assume briefly that every atom of an element possesses one, two,
three, four or more such units of force and we call the element
univalent, bivalent, trivalent, quadrivalent, etc., according to the
number of such units it possesses. It is by virtue of the existence
of these units of force that the compounds made up of the same
or of various elementary atoms exist. We assume that in such
a molecular compound the atoms are bound one to another in a
definite way by means of their affinity units.

Since the development of these ideas concerning the valence
of the elements there has been a great deal of work carried on
with the object of determining whether the valence of an element
is constant or whether it may vary; the majority of chemists are
now convinced that it may vary.

The valence of nitrogen may be three or five. The valences of
hydrogen. oxygen and carbon, on the other hand, have, until
recently, been assumed always to remain constant, i. e., one, two
and four, respectively.

Since the complexity, the very great variety and number of
existing compounds containing carbon are unquestionably to be
attributed to the peculiar nature of the forces inherent in the
carbon atom, let us consider a little more in detail what hypotheses
we make in our present system of carbon chemistry concerning

this element. We assume first that the valence of the carbon atom is always four; second, that the four valences or affinity units of the carbon atom are equivalent; third, that they are distributed in space in three dimensions and act in the direction of the axes of a tetrahedron; fourth, that the carbon atoms can unite with one another by means of one, two or three affinity units to form what we usually call chains. These chains may be open, or closed rings or cycles. The number of carbon atoms thus bound to one another may be exceedingly large. The closed chains usually contain three, four, five, six or seven carbon atoms in the ring. We may have in these chains, whether open or closed, some of the carbon atoms replaced by oxygen, nitrogen, sulphur or other elements. If now we unite the extra valences of each carbon or other atom—i. e., those affinity units which are not necessary for binding the atoms together in chains—with other atoms or radicals, it is at once evident that we can represent, theoretically, by so-called graphical formulae, molecules of great complexity.

It is also at once obvious that with a small number of atoms it must be possible to construct a relatively large number of aggregates which differ from one another simply in the way the atoms are bound together. In 1884, for instance, fifty-five totally different substances of the empirical formula $C_9H_{10}O_3$ were actually known. We call them isomers.

One of the chief problems of organic chemistry, since 1858, has been to determine on the basis of these ideas of valence the "constitution" of the carbon compounds. We determine by methods which are called synthetic, as well as by an exhaustive study of the reactions of a given compound, what may be called the "architecture" of its molecule, i. e., we determine how the various atoms of carbon, nitrogen, oxygen, hydrogen, etc., of which the substance may be composed, are joined together by virtue of their affinity units. How much has been accomplished on the basis of these ideas during the past forty-six years and how beautifully and simply all the facts known with regard to the almost countless carbon compounds are thus explained, only those can fully appreciate who have a detailed knowledge of the subject. Notwithstanding the large number of workers in the field, it has often required more than a decade of work to determine

the molecular architecture of one single carbon compound, and the question at times seriously presents itself whether we must not reach our limitations in this respect.

In any case, one point is deserving of especial emphasis: This idea of structure which has been applied chiefly to molecules containing the element carbon attributes to them a rigidity which is improbable from a purely dynamic standpoint.

The present system of organic chemistry is thus founded upon the assumption that the valence of all the atoms of carbon, wherever found, remains invariably four. In the earlier part of the last century many attempts were made to isolate the hydrocarbon methylene, $C=H_2$, which must contain bivalent carbon. Dumas and Peligot tried to obtain this substance from methyl alcohol,

$H_3C\diagup\stackrel{\textstyle H}{\diagdown}OH$, by loss of water. Perrot tried to isolate it from

methyl chloride, $H_3C\diagup\stackrel{\textstyle H}{\diagdown}Cl$, by dissociation into methylene and hy-

drogen chloride at a high temperature. Berthelot, Butlerow, Wurtz and Kolbe also made many fruitless attempts in this direction. As a final result of these repeated and negative efforts chemists finally became convinced that compounds containing bivalent carbon could not be isolated and the conclusion, therefore, that carbon was one of the few elements possessing a constant valence became very general.

There has, however, long existed one very simple compound of carbon which does not adjust itself to this system—namely, the inactive and poisonous carbon monoxide. If we assume the valence of oxygen as two, then we have here simply a derivative of methylene in which the two hydrogen atoms are substituted by oxygen, $C=O$. To be sure, there were many chemists who preferred to consider the valence of carbon in carbon monoxide as four, thus making the valence of oxygen four, $C\equiv O$; ard when we bear in mind that the other members of the oxygen group, sulphur, selenium and tellurium, exist as di-, tetra- and hexavalent atoms there is some justification for this interpretation. To me personally, however it seems in the highest degree improbable that two atoms should be thus bound to each other by four affinity units.

About fourteen years ago a series of systematic experiments was undertaken with the object of ascertaining whether carbon can exist in a bivalent condition. The experiments have established this point in a most decisive manner; we have now quite an array of substances which contain bivalent carbon.

Furthermore, it has been possible to prove, from the experience gained in their study, that methylene chemistry plays an important rôle in many of the simplest reactions of organic chemistry, reactions which have hitherto been explained on the basis of substitution.

At the time when these experiments were undertaken there existed, besides carbon monoxide, several substances which might contain bivalent carbon, namely, prussic acid and its salts, the cyanides, $HN{=}C$ and $M{-}N{=}C$. Also the so-called carbylamines, $RN{=}C$, discovered in 1866 by Gautier. These substances were, therefore, exhaustively studied in order to establish rigidly, by experiment, whether bivalent carbon was present or absent. The presence of dyad carbon in these compounds having been established and its properties thus being known, the problem then presenting itself was the isolation of methylene and its homologues.

You are probably all aware that Gay-Lussac established, in 1815, the existence of a radical, composed of one atom of carbon and one of nitrogen, in prussic acid and the cyanides. This radical, cyanogen, plays in its compounds a rôle similar to that of the elements of the halogen group. In 1832, Pelouse discovered the alkylcyanides, $R{-}C{\equiv}N$, by treating potassium cyanide with alkyliodides or with alkyl potassium sulphates,

$$KCN + RI \text{ or } ROSO_2OK \rightharpoonup R{-}C{\equiv}N + KI \text{ or } KOSO_2OK,$$

an apparent double decomposition reaction by which we obtain a compound in which the radical R $(= C_nH_{2n+1})$ is joined to the cyanogen group by means of carbon. The alkylcyanides thus obtained are neutral, pleasant smelling, harmless liquids resembling ether, chloroform and the alkylhaloids, $R{-}Cl$, $R{-}Br$ and RI.

In 1866, Gautier discovered a new class of organic compounds by treating cyanide of silver with alkyliodides,

$$R{-}I + Ag{-}(NC) \rightharpoonup AgI + R{-}N{=}C,$$
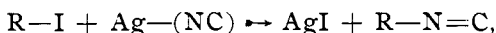
a reaction which is apparently a double decomposition reaction. They are isomeric, not identical, with the alkylcyanides of Pelouse. He called them the carbylamines or isonitriles and proved that

the alkyl group is bound to the cyanogen radical by means of nitrogen, $RN=C$ or $RN\equiv C$.

It thus became evident that we must distinguish between two cyanogen radicals, namely, one which in its compounds is bound to alkyl hydrogen or metal by means of carbon, $R-C\equiv N$, $H-C:N$, $M-C:N$, and another which is joined to these elements, or groups, by means of nitrogen, $RN=C$, $HN:C$, $MN:C$. We may call the former radical cyanogen, $-C:N$, and the latter iso-cyanogen, $-N:C$ or $-N\equiv C$; these radicals may, obviously, combine with each other to form three isomers of the empirical formula, C_2N_2. The substances discovered by Gautier, the alkyl-isocyanides, $RN=C$ or $RN\equiv C$, have properties strikingly different from those of their isomers—the alkylcyanides, $R-C\equiv N$, of Pelouse.

They are poisonous, nauseating compounds which affect the throat like prussic acid and color the blood intensely red; they produce violent headaches and vomiting. Their odor is most pronounced and persistent. Hofmann, who, in 1868, discovered another method for making them from primary amines, chloroform and caustic potash,

$$RNH_2 + 3KOH + CHCl_3 \rightarrow R-N:C + 3KCl + 3H_2O,$$
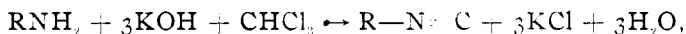
found it impossible to work with them except for very short periods.

An exhaustive study of the reactions of these alkylisocyanides, carried out in 1891-'92, led to the definite conclusion that they contain a dyad carbon atom, $i.\ e.$, they possess the constitution represented by the formula $RN=C$; the other possible formula with quadrivalent carbon and quinquivalent nitrogen, $R-N\equiv C$, is excluded by the facts.

The alkylisocyanides belong to the vast category of unsaturated compounds whose chemistry will be briefly discussed from a perfectly general standpoint below; they manifest their great chemical activity especially by absorbing other substances, forming new molecules in which the valence of carbon has changed from two to four. Such reactions we call additive. Two molecules simply unite to form one new molecule—the addition product.

A molecule containing an unsaturated carbon atom, $i.\ e.$, one with two of its valences latent or polarized, $RN\equiv C$ or $RN=C$ can not, $per\ se$, show any chemical activity whatever.

This is also true of a system containing a pair of doubly or triply bound carbon atoms, ethylene, $CH_2=CH_2$, and acetylene, $HC\equiv CH$; and finally of a saturated system which we may repre-

sent by a paraffine, C_nH_{2n+2}, for instance, marsh gas, $H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H$.

All these substances manifest chemical activity simply because they are, to a greater or less degree, in a dissociated, or what may be called an active, condition.

A given quantity of alkylisocyanide contains an extremely small per cent. of molecules with two free affinity units, $RN=C<$; these are in dynamic equilibrium with the absolutely inert molecules, $RN=C$, or better, $RN\equiv C^{|}$. That this percentage varies with the nature and mass of R is shown by the fact that various alkylated and arylated isocyanides manifest different degrees of chemical activity. Carbon monoxide possesses relatively a smaller number of such active particles, $O=C<$, and consequently is a comparatively inert substance, since the speed of addition reactions shown by unsaturated compounds must naturally be directly in proportion to the per cent. of active molecules present. A similar conception obviously explains the relative differences in reactivity shown by the various members of the olefine and acetylene series. Marsh gas, a saturated system, reacts with other substances because it is partially dissociated as follows:

$$CH_4 \rightleftarrows CH_3-+H- \text{ and } H_2C=+2H.$$
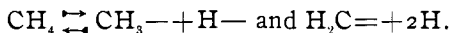
From this point of view chemical action depends entirely upon dissociation processes. The reactions often proceed with very great slowness because the percentage of dissociation is extremely low, possibly 0.1 to 0.001 per cent., or even less.

Turning now to a consideration of the reactions of alkylisocyanides, the substances which are absorbed by the unsaturated carbon atom present in the isonitriles are the following:

I. *Halogens* (chlorine, bromine, iodine; speed of reaction in the order named),

$$RN=C< + \underset{|\quad |}{X=X} \rightarrow RN=C\overset{X}{\underset{X}{<_{||}}} \rightarrow RN=C\overset{X}{\underset{X}{<}}.$$
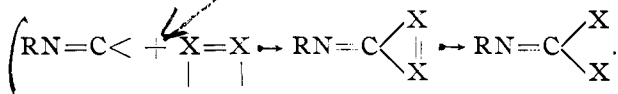
The reactions, especially those with chlorine and bromine, take place with great evolution of heat at —20°.

II. *Acid Chlorides*, such as $RCO—Cl$, $Cl—OC_2H_5$, $Cl—CO—Cl$, $Cl—CN$, $Cl—COOR$ to form the addition products,

$$RN\ C{<}^{Cl}_{COR}\ ,\quad {RN{:=}C{<}^{Cl}_{} \atop RN{=\!=}C{<}_{Cl}}{>}C:O,\ etc.$$
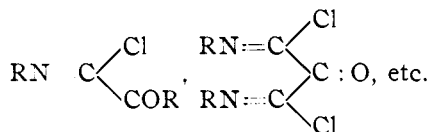
A hyphen denotes the point where the compounds are partially dissociated and consequently absorbed. These reactions, especially those with phosgene and ethyl hypochlorite, take place with great violence at —20°.

III. *Oxygen and Sulphur*, to form isocyanates and mustard oils, $RN{=}C{=}O$ and $RN{=}C{=}S$. Methylisocyanide unites directly at its boiling-point, 58°, with the oxygen of the air. The dry oxides of silver and mercury are reduced to metals with violence at 40°, alykylisocyanate being first formed. This shows the great affinity of bivalent carbon for oxygen.

IV. *Primary Amines and Hydroxylamine*,

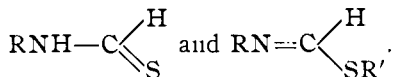$RN{=}C{<}$ + H—NHR or H—NHOH ↦

$$RN:C{<}^{H}_{NHR}\quad or\quad RN{=\!\!=}C{<}^{H}_{NHOH}\ ,$$
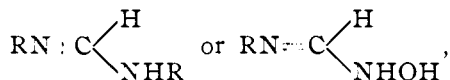
giving amidines of oxyamidines.

V. *Alcohols*, in the presence of an alkali, are absorbed, giving imido ethers,

$$RN{=\!\!=}C{<}^{H}_{OR}\ .$$
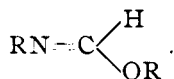
VI. *Hydrogen Sulphide and Mercaptans* give readily at 100° the addition products

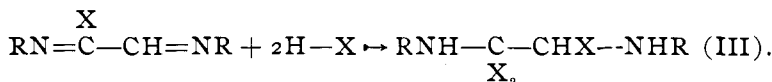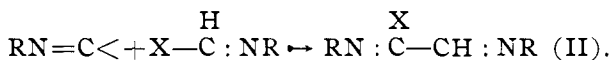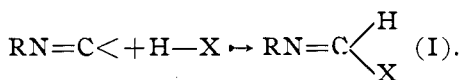$$RNH—C{<}^{H}_{S}\quad and\quad RN{=\!\!=}C{<}^{H}_{SR'}\ .$$

VII. *Acids*. Aqueous mineral acids act with great violence on the isonitriles, giving primary amines and formic acid,

$$RN{=}C{=} + 2H_2O ↦ RNH_2 + {H \atop HO}{>}C:O.$$
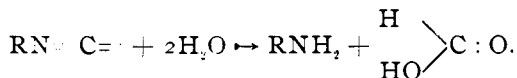
In the absence of water and on diluting the alkylisocyanides with absolute ether, perfectly dry halogen hydride causes the separation of white hygroscopic salt-like substances of the empirical formula $2RNC$, $3HX$ ($X=Cl$, Br or I). For this reason Gautier, as well as Hofmann, supposed the isonitriles to be basic compounds, *i. e.*, substances behaving like ammonia—hence the name carbyl-amine was given them by Gautier. Further study has shown, however, that this conclusion was erroneous. The isonitriles are entirely devoid of basic properties; the great violence with which they react with halogen hydrides is due to the presence of un-saturated carbon. The reaction probably takes place as follows:

$$RN{=}C{<}+H{-}X \rightarrowtail RN{=}C{\Big\langle}{\overset{H}{\underset{X}{}}} \quad (I).$$

$$RN{=}C{<}+\overset{H}{X}{-}\overset{X}{C}{:}NR \rightarrowtail RN{:}C{-}CH{:}NR \quad (II).$$

$$RN{=}\overset{X}{C}{-}CH{=}NR + 2H{-}X \rightarrowtail RNH{-}\underset{X_2}{C}{-}CHX{-}NHR \quad (III).$$

Reversibility of the Reactions.—The most striking property of these addition products of the isonitriles, $RN{:}C{\Big\langle}{\overset{X}{\underset{Y}{}}}$, is their low point of dissociation, *i. e.*, the carbon atom which has absorbed the X-Y thus becoming quadrivalent is unable to hold X-Y above certain temperature limits. There is consequently in every case a temperature varying with the nature and mass of X and Y, as well as with the nature and mass of the groups bound to the other two affinity units of carbon, at which the carbon atom becomes spontaneously dyad and is unable to remain in a quadrivalent condition; it was subsequently possible to prove that this is a perfectly general property of this atom.

All the addition products under discussion are partially dis-sociated,
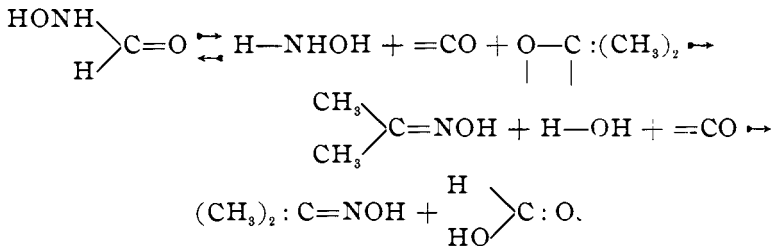
$$RN{:}C{\Big\langle}{\overset{X}{\underset{Y}{}}} \rightleftarrows RN{=}C{<} + X{-}Y,$$
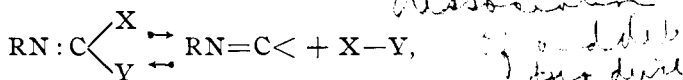
the dissociation increasing as the temperature is raised— in other words, the valence of carbon at temperatures below the dissocia-

tion point is an equilibrium phenomenon; dynamic equilibrium exists between bivalent and quadrivalent carbon.

The point of complete dissociation of the various addition products of the isonitriles has not yet been accurately determined in every case. The following data with reference to the dissociation points of carbon monoxide addition products are of interest and therefore used for illustration in this connection:

Dissociation point.

Formaldehyde, $O : C{<}^H_2$,   600°

Formamide, $O{=}C{<}^H_{NH_2}$,   250° (about)

Formic acid, $O{=}C{<}^H_{OH}$,   169°

Formhydroxamic acid, $O{=}C{<}^H_{NHOH}$,   85°

Formylchloride, $O : C{<}^H_{Cl}$,   —20° (below)

Since these substances containing quadrivalent carbon decompose spontaneously into carbon monoxide, i. e., can not exist in the quadrivalent condition at temperatures above those indicated, it is self-evident that at lower temperatures the addition products must be partially dissociated and that in the future we must be able to determine, in each case with absolute accuracy, the per cent. of dissociation at any temperature. A striking experiment with formhydroxamic acid, dissociation point 85°, proves the correctness of this conclusion; on allowing this crystalline substance to stand at 20° in acetone solution the following reaction takes place quantitatively:

$$\underset{H}{\overset{HONH}{>}}C{=}O \ \overset{\rightarrow}{\leftarrow}\ H{-}NHOH + {=}CO + \underset{|}{O}{-}\underset{|}{C} :(CH_3)_2 \rightarrowtail$$

$$\underset{CH_3}{\overset{CH_3}{>}}C{=}NOH + H{-}OH + {=}CO \rightarrowtail$$

$$(CH_3)_2 : C{=}NOH + \underset{HO}{\overset{H}{>}}C : O.$$

In a similar manner we can prove that the isonitrile addition products, many of which have definite boiling-points and are quite stable, are partially dissociated at ordinary temperatures. Thus the addition products with halogens, $RN{=}C\big\langle{}^{X}_{X}$, are all converted back quantitatively into the alkylisocyanides by treatment with finely divided metals, zinc dust or sodium, which simply abstract the free halogen.

Many of the acylhalide addition products dissociate spontaneously into the components on distillation; these phenomena are perfectly analogous to the dissociation of dry ammonium chloride,

$$H_3N{\big\langle}^{H}_{Cl} \; \underset{\leftarrow}{\overset{\rightarrow}{\;}} \; NH_3 + HCl.$$
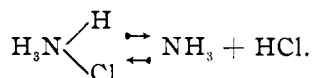
For this reason the majority of the addition products of the isonitriles can be kept only for a short time; this property rendered futile many attempts to isolate definite addition products. The continual dissociation of such products sets free active or dissociated alkylisocyanide particles, and these slowly condense with one another,

$$XRN{=}C{<} \; \mapsto \; (RN{=}C)_x,$$
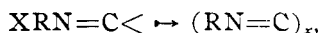
giving rise to the so-called alkylisocyanide resins (non-reversible) —products whose molecular weight has not yet been determined and which are perfectly analogous to azulmic or polymerized prussic acid. Consequently, in carrying out an addition reaction with an isonitrile, especially if it requires much time or a temperature above 20°, large quantities of these resinous polymers are formed from which it is possible to isolate the addition product only with great difficulty. Many of the isonitriles themselves, even when perfectly pure, undergo rapid polymerization to resins so that they can be kept only for a very short time. Phenylisocyanide, $C_6H_5N{=}C^j$, is the most striking instance, as it changes in a few minutes from a colorless to a dark blue liquid and in a few days condenses to a dark brown resin.

Have we not here a possible explanation of the fact that it is impossible to isolate methylene and a large number of its derivatives, although marsh gas, methyl alcohol and chloride of methyl,

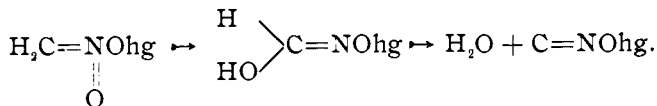$$H_2C{<}^H_H, \quad H_2C{<}^{OH}_H, \quad H_2C{<}^H_{Cl},$$
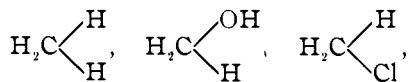
each contain a relatively small per cent. of active methylene particles at ordinary temperatures?

The presence of bivalent carbon in the alkylisocyanides having been established, the next question presenting itself was whether prussic acid and its salts contain the cyanogen or the isocyanogen radical. In the latter case, $HN:C$, $MN:C$, these substances must be analogous to Gautier's isonitriles. It had hitherto been considered as established, but without sufficient evidence, that prussic acid and the cyanides were cyanogen compounds analogous to the nitriles of Pelouse.

When one considers the physical and physiological properties of prussic acid (boiling-point $25°$, sp. gr. 0.7, a violent poison) and contrasts these with the corresponding properties of methylcyanide (boiling-point $81°$, sp. gr. 0.81, sweet smelling, harmless oil) and of methylisocyanide (boiling-point $58°$, sp. gr. 0.75, a poison) one at once comes to the conclusion that prussic acid, as well as its salts, must belong to the isocyanogen compounds and consequently must contain bivalent carbon.

An exhaustive study of prussic acid and the cyanides establishes this sharply, especially in the case of the salts, from a chemical standpoint. The relation of fulminic acid to prussic acid corroborates the evidence.

You are all familiar with fulminate of mercury—a substance which is made on a commercial scale and used for explosives. It was discovered in 1800 by Howard, and analyzed in 1824 by Liebig in Gay-Lussac's laboratory. We obtain it by dissolving mercury in concentrated nitric acid and adding the resulting solution to ordinary alcohol. It has the empirical formula $HgC_2N_2O_2$, and being obtained from ethyl alcohol, CH_3—CH_2—OH, fulminic acid was supposed to have two carbon atoms in its molecule, $H_2C_2N_2O_2$. The constitution of this substance was, for a long time, a great puzzle to chemists. That we have here a substance very closely related to prussic acid was discovered by accident. In working with the mercury salt of isonitromethane it was found that this compound is spontaneously converted at $0°$ into fulminate of mercury, according to the equation,

$$H_2C=NOhg \rightarrowtail \begin{matrix} H \\ \\ HO \end{matrix}\Big\rangle C=NOhg \rightarrowtail H_2O + C=NOhg.$$
$$\underset{O}{\overset{\|}{}}$$

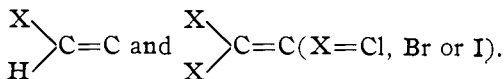This synthesis led directly to the conclusion that fulminate of mercury possesses a constitution entirely analogous to cyanide of mercury, $C=Nhg$, i. e., that it contains the isocyanogen radical with bivalent carbon. A further study of the fulminates established this point with precision. Especially striking is the behavior of fulminates towards dilute acids. Liebig and Gay-Lussac stated, in 1824, judging from the odor, that fulminate of silver gives prussic acid with dilute hydrochloric acid. A more careful study of this reaction, in 1894, proved that not a trace of prussic acid, but a substance, formyl chloride oxime, $\begin{matrix} H \\ \\ Cl \end{matrix}\Big\rangle C=NOH$, is formed, which possesses the following remarkable properties. Long needles, clear as glass, which decompose and explode with violence at 20°; extremely volatile even at 0° and having an odor similar to prussic acid, which is obviously due to a partial dissociation into fulminic acid. Aqueous silver nitrate converts it quantitatively into chloride and fulminate of silver,

$$\begin{matrix} H \\ \\ Cl \end{matrix}\Big\rangle C=NOH + 2AgNO_3 \rightarrowtail AgON:C + AgCl + 2HNO_3.$$
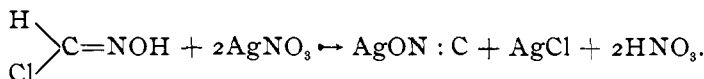
Up to 1897 the presence of bivalent carbon had been established in the following compounds: 1, Carbon monoxide, $O:C$; 2, the alkyl and aryl isocyanides, $R-N:C$; 3, prussic acid and the cyanides, $NH:C$, $MN=C$; 4, fulminic acid and the fulminates, $(HO)N:C$, $M-O-N=C$. 2, 3 and 4 are all compounds containing the isocyanogen radical. In 1897 the presence of bivalent carbon was established in a series of nitrogen-free carbon compounds obtained from acetylene. They are the mono- and di-halogen substituted acetylidenes,

$$\begin{matrix} X \\ \\ H \end{matrix}\Big\rangle C=C \text{ and } \begin{matrix} X \\ \\ X \end{matrix}\Big\rangle C=C(X=Cl, Br \text{ or } I).$$

The corresponding members of the acetylene series, $XC\equiv CH$ and $XC\equiv CX$, do not exist, although we have substances like $CH_3C\equiv CI$, $C_6H_5C\equiv C-X$, whose properties are in marked contrast to those of the acetylidene derivatives.

Diiodacetylidene, which possesses an odor deceptively like that of the isonitriles, dissociates at 100° with violence into iodine and diatomic carbon,

$$I_2C = C \rightarrow I_2 + C = C ;$$
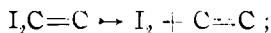
the latter can not be isolated as such, but polymerizes explosively to graphite and amorphous carbon. The mono- and dihalogen substituted acetylidenes are all poisonous and spontaneously combustible compounds, possessing, therefore, like methylisocyanide, a marked affinity for oxygen.

Up to the present time it has not been possible to isolate compounds containing bivalent carbon, other than those mentioned above. We are, however, now in a position to explain clearly why we can not hope, by methods now known, to isolate methylene and its homologues as such, although these substances play a great rôle in many of the fundamental reactions of organic chemistry.

In order to approach this point more intelligently let us first consider briefly the properties of unsaturated compounds in general, their possibility of existence, etc.

II. ON THE UNSATURATED COMPOUNDS.

The unsaturated compounds may, first of all, be divided into three categories, namely: I. Those in which two atoms, which may be the same or different, are bound doubly or triply to each other by two or three affinity units, such as olefines; acetylenes; chlorine, $Cl \equiv Cl$; oxygen, $O = O$; aldehydes, $\begin{matrix} R \\ H \end{matrix} \! \! \diagdown \! \! \diagup C : O$; alkyl-cyanides, $R - C \equiv N$; nitric acid, $HON \! \! \diagup_{\diagdown O}^{O}$; sulphur trioxide, $O = S \! \! \diagup_{\diagdown O}^{O}$; etc. II. Those in which an atom itself is unsaturated, i. e., does not exert its maximum valence capacity, as for instance, amines, $R_3 \equiv N$; thioethers, $R_2 = S$; methylene derivatives; etc. We must assume that the remaining affinity units are latent, or what is far more probable, especially where two or four affinity units are available, that they mutually polarize each other in a manner entirely similar to unsaturated compounds containing doubly or triply linked atoms.

Finally we have a third class of unsaturated compounds: III. Those containing closed atomic chains, such as trimethylene,

$$CH_2 \overbrace{\qquad}^{} $$

$CH_2—CH_2$; propylenoxide, $CH_3CH \overset{O}{\overbrace{\qquad}} CH_2$; etc., which show apparently a saturated molecular system like the paraffines, and yet react in a manner perfectly analogous to olefines and methylene derivatives.

Fundamentally considered these three classes of unsaturated compounds manifest their chemical activity in the same way; they absorb a great variety of other molecules and thus form combinations, called addition products. How does this union take place? An unsaturated compound with its affinities polarized represents, in reality, a saturated system; it can not, *per se*, show chemical activity. This is also true of molecular systems in which the atoms are bound to one another by single affinity units. The sole basis for reactivity in either case is the presence of a relatively greater or smaller number of dissociated particles. The reactivity of any unsaturated, as well as of a saturated compound, must, in fact, be directly proportional to the ratio of such active particles present. If that ratio is very small, the substance may be entirely inert; if it is greater, absorption of reagents proceeds with regularly increasing speed.

Experience has shown, furthermore, that many unsaturated compounds can not be isolated; but polymerize spontaneously. It is clear that when the per cent. of active particles present in an unsaturated compound becomes relatively great the possibility of their uniting with each other to form condensed molecules increases—in fact, we may imagine a condition in which the active molecules simply can not be prevented from combining with each other. This shows us why we can not isolate and keep substances like formaldehyde, $H_2C=O$, or alkylcyanates, $ROC≡N$, in the monomolecular form. Similarly in many cases where attempts were made to isolate methylene derivatives, like mono- and diphenylmethylene, benzoyl and acetylmethylene,

cyanmethylenecarboxylate, $\overset{CN}{\underset{COOR}{>}}C_1$, a spontaneous polymerization to the di- or trimolecular systems,

$$X \diagdown \diagup X \qquad X \diagdown \diagup C \diagup X$$
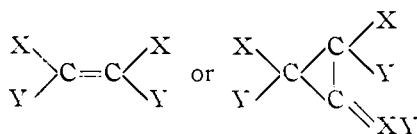
took place. One further point with reference to unsaturated compounds must now be presented.

*Intramolecular Rearrangement Shown by Unsaturated Systems.*

From the discussion presented above it is obvious that trimethylene and propylenoxide, belonging to class III, must contain a small percentage of active particles; the dissociation of the triatomic ring in the former case can lead to only one form of active molecule, namely, $-CH_2-CH_2-CH_2-$; whereas propylenoxide may give the following three active molecules:

$$\begin{array}{c} O- \\ | \\ CH_3CH-CH_2- \ (A) \end{array} ; \quad CH_3\overset{|}{C}H-CH_2-O- \ (B) ;$$

and

$$CH_3CH-O-CH_2- \ (C).$$
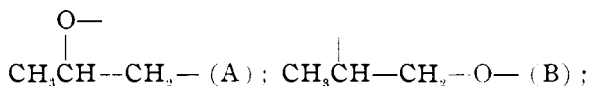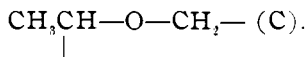
Since propylenoxide absorbs dry ammonia or hydrogen chloride, as was proved by especially careful and exhaustive experiments, giving addition products of the general formula

$$CH_3CHOH-CH_2X \ (X=Cl \text{ or } NH_2),$$
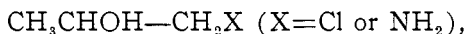
the only possible conclusion that can be reached is that propylenoxide contains relatively more active (A) than active (B) or (C) molecules; consequently the absorption reactions proceed by preference in *only one* of three theoretically possible directions.

When trimethylene or propylenoxide is heated or placed in contact with various catalytic agents, the per cent. of active particles must naturally increase and when a definite limit has been reached a spontaneous transformation of trimethylene into propylene and of propylenoxide into propionicaldehyde ($^2/_3$) and acetone ($^1/_3$) takes place; both reactions are non-reversible.

These results can only be explained in the following manner: aside from the increase in active particles, dissociation in other parts of the molecule and especially of hydrogen from carbon must also take place. Consequently the following intramolecular addition reactions finally occur spontaneously:

$$\text{CH}_2\text{—CH—CH}_2 \rightarrowtail \text{CH}_3\text{CH—CH}_2 \overset{\leftarrow}{\underset{\rightarrow}{}} \text{CH}_3\text{CH}=\text{CH}_2$$
$$ \overset{|}{\text{H}}$$
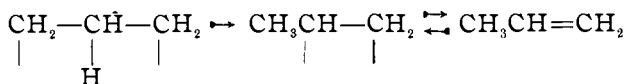
Active trimethylene particles.   Propylene.

$$\text{CH}_3\text{—C}\overset{\nearrow\text{H}}{\underset{\text{O—}}{\text{—CH}_2}} \rightarrowtail \text{CH}_3\overset{|}{\text{C}}\text{—CH}_3 \overset{\leftarrow}{\underset{\rightarrow}{}} \text{CH}_3\text{—}\overset{\overset{\text{O}}{\|\,}}{\text{C}}\text{—CH}_3 \;[\tfrac{1}{3}]$$

Active propylenoxide, particles (A).   Acetone.

$$\text{CH}_3\text{CH—CH—O—} \rightarrowtail$$
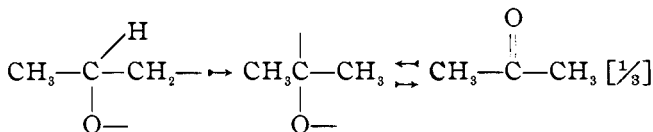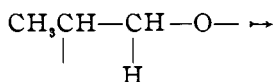$$\overset{|}{}\quad\overset{|}{\text{H}}$$

Active propylenoxide

$$\text{CH}_3\text{CH}_2\text{—CH—O—} \overset{\leftarrow}{\underset{\rightarrow}{}} \text{CH}_3\text{CH}_2\text{CH}=\text{O}\;[\tfrac{2}{3}]$$
$$\overset{|}{}$$
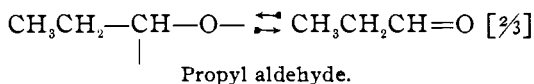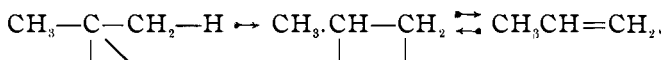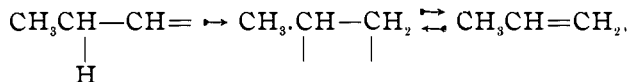
particles (B).   Propyl aldehyde.

It is interesting to note that the active (B) propylenoxide molecules which are present in smaller ratio suffer rearrangement more readily than the active (A) molecules. The active (C) molecules, on the other hand, must be present in far smaller amount and certainly no transformation of propylenoxide to vinyl-methyloxide, $\text{CH}_2=\text{CH—OCH}_3$, takes place.

It is important to realize that propylenoxide, acetone and propionaldehyde are isomers, but do not stand in a tautomeric relation to one another. This is also true of trimethylene and propylene, as well as of a- and β-amylene and isoamylene, etc.

Similarly it can be rigidly shown by experiment that a- and β-propylidene, $\text{CH}_3\text{CH}_2\text{CH}=$ and $(\text{CH}_2)_2\text{C}=$, which are spontaneously combustible substances not capable of isolation as such, transform themselves by intramolecular addition,

$$\text{CH}_3\text{CH—CH}= \rightarrowtail \text{CH}_3.\text{CH—CH}_2 \overset{\leftarrow}{\underset{\rightarrow}{}} \text{CH}_3\text{CH}=\text{CH}_2.$$
$$\overset{|}{\text{H}}$$

$$\text{CH}_3\text{—C—CH}_2\text{—H} \rightarrowtail \text{CH}_3.\text{CH—CH}_2 \overset{\leftarrow}{\underset{\rightarrow}{}} \text{CH}_3\text{CH}=\text{CH}_2.$$
$$\overset{|\diagdown}{}$$

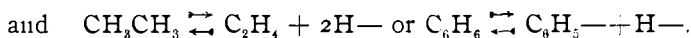into propylene (non-reversible).

There is not the slightest doubt that such intramolecular addition reactions are the basis of the majority of our synthetic methods for making cyclic compounds. The cycloparaffines in Russian petroleum are probably formed from ordinary paraffines

by dissociation into hydrogen and methylene derivatives and the latter then spontaneously transform themselves, by intramolecular addition, into penta- and hexamethylene rings.
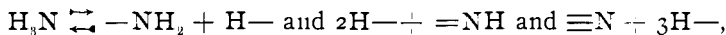
On the Reactions of Paraffines and Benzene Derivatives.

The reactions of paraffines and benzene derivatives towards halogens, nitric and sulphuric acids, whereby substitution products are formed are still interpreted in the text-books from the standpoint of metalepsis or substitution, although a vast amount of evidence has accumulated which makes this axiomatic assumption improbable.
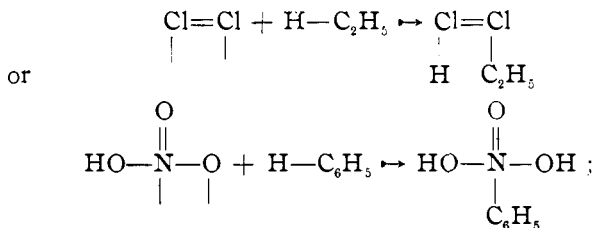
The fact that ethane and benzene, for instance, decompose into hydrogen and into ethylene and diphenyl at 800° and 600°, respectively, proves that an extremely small per cent. of these molecules must exist at ordinary temperatures in an active or dissociated cond'tion,

$$CH_3CH_3 \rightleftarrows CH_3CH_2{-} {+} H{-} \; ;$$

and $CH_3CH_3 \rightleftarrows C_2H_4 + 2H{-}$ or $C_6H_6 \rightleftarrows C_6H_5{-}{+}H{-}.$
The same is true of ammonia,

$H_3N \rightleftarrows {-}NH_2 + H{-}$ and $2H{-}{+} {=}NH$ and $\equiv N + 3H{-},$

and of a great variety of other non-ionizable hydrogen compounds. Consequently, when chlorine or nitric acid reacts with benzene or ethane to give the monochlor or mononitro substitution products we have these reagents, in the *active molecular* condition, simply uniting by addition with the dissociated ethane or benzene particles,

$$
\begin{array}{ccc}
Cl{=}Cl + H{-}C_2H_5 \rightarrowtail & Cl{=}Cl \\
\;|\quad\; | & \;|\quad\; | \\
 & H\quad C_2H_5
\end{array}
$$

or

$$
\begin{array}{ccc}
O & & O \\
\| & & \| \\
HO{-}N{-}O + H{-}C_6H_5 \rightarrowtail & HO{-}N{-}OH \; ; \\
|\quad\; | & & | \\
 & & C_6H_5
\end{array}
$$

the resulting addition products then lose hydrogen chloride and water respectively, and thus give the monochlor or nitro substitution product of the mother substance. From this point of view all so-called substitution reactions belong to the category of addition reactions.

What is now especially needed in order to place the reactions

of organic chemistry on an exact mathematical basis is a precise method of determining the ratio of active particles present at various temperatures in the case of the unsaturated, as well as the saturated, compounds.
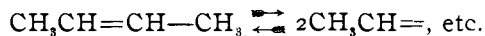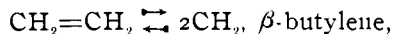
As the substances under discussion are almost exclusively non-electrolytes, the sole methods that suggest themselves for this purpose are determinations of the speed of decomposition, as well as of addition reactions.

The above discussion makes it evident that all unsaturated compounds belonging to classes I and III contain a small and relatively varying per cent. of active particles with one or more carbon atoms temporarily in an active or *trivalent* condition; the same is true of compounds containing hydrogen bound to carbon—paraffines, C_nH_{2n+1}—H, benzene derivatives, etc. The isolation of compounds containing trivalent carbon as such, I believe, however, to be an impossibility. Gomberg's triphenylmethyl, for instance, has recently been proved by him to be a bimolecular aggregate, $C_{38}H_{30}$—not identical with hexaphenylethane—which, however, like the above-mentioned compounds, contains a very small percentage of active triphenylmethyl, $(C_6H_5)_3{\equiv}C$—, particles in dynamic equilibrium with the bimolecular aggregate; as soon as the percentage of triphenylmethyl particles is increased by heat or by means of catalytic agents a spontaneous polymerization to the real hexaphenylethane (non-reversible) takes place.

We are now in a position to consider the evidence showing that methylene and its homologues play a great rôle in many of the fundamental reactions of organic chemistry which have hitherto been explained on the basis of substitution.

III.   ON THE REACTIONS OF THE MONATOMIC ALCOHOLS AND THE ALKYLHALOIDS.

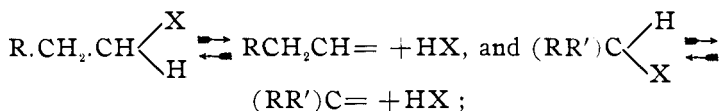The experiments which first suggest themselves as a means of isolating methylene and its homologues are: 1, Dissociation of olefines as ethylene,

$$CH_2{=}CH_2 \rightleftharpoons 2CH_2, \quad \beta\text{-butylene},$$

$$CH_3CH{=}CH{-}CH_3 \rightleftharpoons 2CH_3CH{=}, \text{ etc.}$$
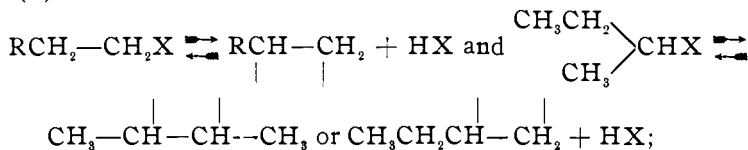
Since ethylene gives hydrogen and acetylene by heat and the higher olefines also decompose with evolution of hydrogen, there

was little prospect of success by experiments in this direction. 2, Dehydration of the mon-atomic alcohols, $C_nH_{2n+1}OH$, or removal of halogen hydride from the alkylhalides, $C_nH_{2n+1}X$; naturally only primary and secondary derivatives, RCH_2X and

$$\underset{R'}{\overset{R}{\diagdown}}CHX \;(X=OH,\; Cl,\; Br\; or\; I),\; and\; not\; tertiary\; compounds,$$

$R_3{\equiv}C{-}X$, can yield methylene and its homologues. Furthermore, since many of the alcohols and alkylhalides containing more than one carbon atom in the molecule are known to give olefines by dissociation, dehydration, or treatment with alcoholic potash respectively, the conclusion might naturally at first be drawn that only a direct olefine dissociation existed in these cases. From a purely theoretical standpoint, however, it is clear that a primary or secondary alkylhalide or a corresponding alcohol with more than one carbon atom in the molecule may dissociate with loss of halogen hydride or water in two possible ways: It may undergo (1) methylene dissociation, as

$$R.CH_2.CH{\diagdown}^{X}_{H} \rightleftarrows RCH_2CH= \;+HX,\; and\; (RR')C{\diagdown}^{H}_{X} \rightleftarrows$$

$$(RR')C= \;+HX\;;$$

or (2) olefine dissociation, as

$$RCH_2{-}CH_2X \rightleftarrows RCH{-}CH_2 \;+\; HX\; and\; \underset{CH_3}{\overset{CH_3CH_2}{\diagdown}}CHX \rightleftarrows$$

$$CH_3{-}\overset{|}{C}H{-}\overset{|}{C}H{-}CH_3\; or\; CH_3CH_2\overset{|}{C}H{-}\overset{|}{C}H_2 \;+\; HX;$$

or both kinds of dissociation may take place simultaneously.

A third kind of dissociation where the hydrogen atom does not come from the atom containing the X or from a carbon atom adjacent to it is also possible and at times important, but it need not be considered in this connection.

An exhaustive study of the primary and secondary alcohols and alkylhalides, covering a period of nine years, has proved very conclusively that these substances undergo methylene dissociation only.

Preliminary experiments with alcohols and alkylhalides where no olefine dissociation is possible, i. e., in the methane,

$CH_2{\Large<}^H_X$, toluene, $C_6H_5CH{\Large<}^H_X$, diphenylmethane, $(C_6H_5)_2C{\Large<}^H_X$,

acetone and acetophenone, $CH_3COCH{\Large<}^H_X$, and $C_6H_5COCH{\Large<}^H_X$,

malonic and cyanacetic ester series,

$$(COOR)_2C{\Large<}^H_X \quad \text{and} \quad {}^{CN}_{COOR}{\Large>}C{\Large<}^H_X ,$$
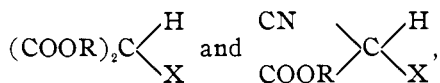
have proved that all these compounds have very low dissociation points—never above 300° in the aromatic nor, with few exceptions, in the aliphatic series. Nevertheless it was found impossible to isolate the methylene derivative as such in any case; there was either a spontaneous conversion to a di- or trimolecular polymer, an olefine or a trimethylene derivative, or a conversion to resinous polymers analogous to azulmic acid and the alkyliso-cyanide resins. Most important was the discovery that these nascent or active methylene residues, ${}^Z_Y{\Large>}C=$, are always spontaneously combustible, burning often with marvelous evolution of heat to the corresponding oxides, ${}^Z_Y{\Large>}C=O$; this was not surprising in view of the properties of the methylene derivatives described above. Furthermore, the affinity of unsaturated carbon for oxygen is strikingly shown by the fact that these residues have the power of decomposing water,

$$\frac{Z}{Y}{\Large>}C= \; + \; O=H_2 \; \longrightarrow \; \frac{Z}{Y}{\Large>}C=O \; + \; 2H—,$$
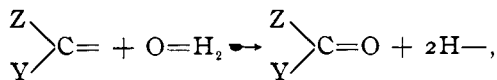
with evolution of hydrogen.

A subsequent investigation of the primary and secondary alcohols and alkylhalides containing more than one carbon atom proved, first of all, that all these substances have comparatively low points of dissociation. In no case was the decomposition point found to be higher than 700°; it was often as low as 160° to 300°. The products of dissociation are water or halogen hydride and C_nH_{2n} respectively; and the latter, as emphasized

above, is invariably methylene or a homologue and never an
olefine. This naturally means that all these compounds are par-
tially dissociated in this way at ordinary temperatures.

$$\underset{R'}{\overset{R}{>}}C\underset{X}{\overset{H}{<}} \rightleftarrows \underset{R'}{\overset{R}{>}}C= +HX,$$
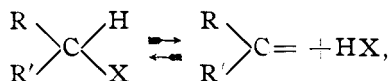
relatively more the lower the actual decomposition point.

It is, therefore, possible that in all the interactions of the primary
and secondary alkylhalides with other substances, such as salts,
ammonia, metals, benzene, etc., they do not act as such, but by
virtue of being partially dissociated. An enormous amount of
evidence has accumulated in favor of this conclusion. Let us
consider chiefly the results obtained in the ethyl series, including
ethyl alcohol and its derivatives. The dissociation or decomposi-
tion point of the following compounds containing ethyl has been
determined with a fair degree of accuracy:

Ethane, $CH_3CH\underset{H}{\overset{H}{<}}$,   800°

Ethyl alcohol, $CH_3CH\underset{OH}{\overset{H}{<}}$,   650°

Sodium and potassium ethylate, $CH_3CH\underset{H}{\overset{OM}{<}}$.   250°

Ethyl ether, $CH_3CH\underset{O}{\overset{H}{<}}$ 550°
$CH_3\overset{}{C}H-H$

Ethyl chloride, $CH_3CH\underset{Cl}{\overset{H}{<}}$,   600°

Ethyl bromide, $CH_3CH\underset{Br}{\overset{H}{<}}$,   500°

Ethyl iodide, $CH_3CH\underset{I}{\overset{H}{<}}$.   400° (?)

Diethyl sulphate, $CH_3CH\!\!\begin{smallmatrix}H\\O\!-\!SO_2\end{smallmatrix}$,   200°

$$CH_3.CH\!\!\begin{smallmatrix}O\\H\end{smallmatrix}$$

Monoethyl sulphate, $CH_3CH\!\!\begin{smallmatrix}H\\OSO_2OH\end{smallmatrix}$,   160°

Ethyl potassium sulphate, $CH_3CH\!\!\begin{smallmatrix}H\\OSO_2OK\end{smallmatrix}$, 250°

Ethyl nitrate, $CH_3CH\!\!\begin{smallmatrix}H\\ONO_2\end{smallmatrix}$,   200° (?)

Ethane, ethyl chloride and bromide, when heated to the temperatures named, give ethylene and hydrogen or halogen hydride respectively, and on cooling these products do not again recombine. We can, therefore, obtain ethylene quantitatively from chloride or bromide of ethyl by simply passing their vapors through tubes heated to the decomposition point. Nevertheless it is impossible to obtain more than very small amounts of ethylene from the ethylhalides by means of alcoholic potash, caustic potash or quicklime; in these cases ethyl ether or ethyl alcohol is the chief reaction product even when the ethyl halide is passed over quicklime in tubes heated to from 300° to 500°.

Furthermore, the per cent. of ethylene obtained varies remarkably with the temperature, the concentration and with the nature of the halogen in the alkylhalide used.

The conclusions finally reached from these data and also from an exhaustive study of the behavior of the various alkylhalides, nitrates, sulphates, alkylpotassium sulphates towards heat, sodium ethylate, caustic potash, quicklime and other salts are that ethylene can not possibly be a primary product of dissociation of the ethylhalides, sulphates and nitrates, and of free ethyl alcohol.

The ethylene, when obtained, is formed from ethylidene by an intramolecular addition reaction,

$$\overset{H}{\underset{|}{CH_2}}\!\!-\!CH= \ \longrightarrow\ \overset{|}{CH_2}\!\!-\!\overset{|}{CH_3} \rightleftarrows CH_2\!\!=\!\!CH_2,$$
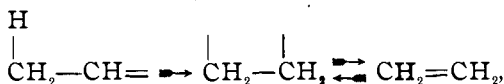
which is not reversible. A similar intramolecular change always, in fact, takes place whenever an olefine is formed, whether from a primary or secondary alcohol, or from a corresponding alkyl halide sulphate or nitrate. This transformation is perfectly analogous to the conversion, discussed above, of trimethylene and of propylenoxide into propylene, propionaldehyde and acetone.

When ethyl alcohol or ethyl ether is heated to its dissociation point the ethylidene interacts at once in great part with the other dissociation product, water, to give hydrogen and acetaldehyde,

$$CH_3CH= +O=H_2 \longrightarrow CH_3CH : O + 2H \cdots.$$
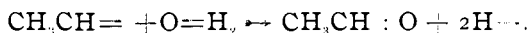
In the case of ether, since there are two ethylidene molecules to one of water, the atomic hydrogen is, in part, absorbed by ethylidene to give ethane. Finally, a portion of ethylidene, 20 and 37 per cent. respectively, is transformed, by intramolecular addition, into ethylene. The most striking proof that ether is dissociated into water and $2C_2H_4$ particles is the following: On passing ether vapor over phosphorus pentoxide at temperatures varying from 200° to 400° ethylene is formed quantitatively.

The primary and secondary alcohols and their corresponding ethers being in a state of very slight dissociation at ordinary temperatures we are able to understand perfectly their behavior towards oxidizing agents. The alkylidenes are all spontaneously combustible substances possessing a great affinity for oxygen. Absolutely pure dry ethyl ether, dissociation point 550°, contains a sufficient per cent. of ethylidene particles at ordinary temperatures to burn very slowly in dry oxygen; sodium ethylate, dissociation point 250 , on the other hand, being dissociated to a far greater extent, burns with great violence in dry air. Ethyl alcohol, dissociation point 650°, is not capable of burning in the air; if, however, we increase the per cent. of ethylidene particles by means of catalytic agents, enzymes, platinum sponge, etc., it, too, oxidizes readily, with incandescence with platinum sponge, giving acetic acid.

The aldehydes, $R—CH : O$, as has long been known, reduce Fehling's solution and silver solutions with great ease. This is due to the presence of oxyalkylidene particles, $\begin{smallmatrix} R \\ HO \end{smallmatrix} \hspace{-0.3em} \Big\rangle C=$, which

burn at the expense of the oxygen in the water.

The discovery that all primary and secondary alcohols reduce silver oxide to metallic silver in aqueous solution in the presence of caustic alkalies has only very recently been made. The function of the alkali is obviously to form first the metallic alcoholate,

$$\underset{R'}{\overset{R}{>}}C\underset{OH}{\overset{H}{<}} + MOH \rightleftharpoons \underset{R'}{\overset{R}{>}}C\underset{OM}{\overset{H}{<}} + H_2O,$$
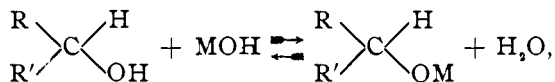
which, having a far lower dissociation point than the free alcohol, causes a great increase in the per cent. of alkylidene particles present; consequently, the following reaction can take place:

$$\underset{R'}{\overset{R}{>}}C= +2H-OH + Ag_2O \rightarrow$$

$$\underset{R'}{\overset{R}{>}}C=(OH)_2 + Ag_2 + H_2O, \text{ etc.,}$$
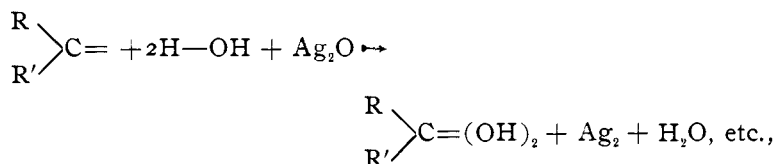
giving, as the end result, a fatty acid in the case of primary alcohols.

The most striking proof that ethyl alcohol is dissociated only into ethylidene and water,

$$CH_3CH\underset{OH}{\overset{H}{<}} \rightleftharpoons CH_3CH= +H_2O,$$
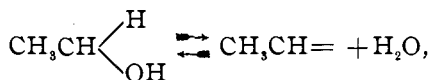
i. e., contains no ethylene particles, is the following: Ethyl alcohol, containing 1 molecule of aqueous sodium hydroxide, gives, in the cold, with potassium permanganate solution, practically acetic acid only. If any active ethylene particles were present,

$$CH_3CH_2OH \rightleftharpoons \overset{|}{C}H_2-\overset{|}{C}H_2 + H_2O,$$

these must necessarily, in view of the work of Wagner with olefines and permanganate, be first converted by oxidation to ethylene glycol,

$$3CH_2-CH_2 + 6H-OH + 2KMnO_4 \rightarrow$$

$$3CH_2-CH_2 + 2MnO_2 + 2KOH + 2H_2O.$$
$$\overset{|}{OH}\quad\overset{|}{OH}$$
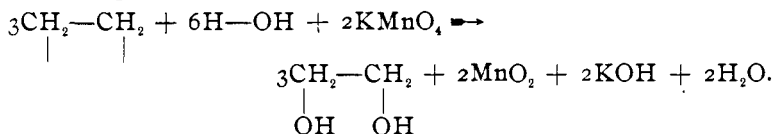
Analogous results would naturally be expected in the case of all the homologous primary and secondary alcohols. Now a

primary alcohol invariably first gives, by oxidation with potassium permanganate or other oxidizing agents, the corresponding fatty acid. Glycols or their oxidation products have never been observed in such cases.

The fact that ethyl alcohol gives glyoxal, glyoxylic and oxalic acids with nitric acid is no exception to this rule, because these substances result from the hydrolysis and oxidation of iso-nitrosoacetaldehyde, which is formed by the action of nitrous acid on acetaldehyde as follows:

$$H-CH_2CHO + O-NOH \longrightarrow HO-N-OH \longrightarrow$$

$$\begin{array}{c} CH_2.CH:O \\ HON \\ -H_2O. \\ CH-CH:O \end{array}$$

The behavior of aldehydes and of primary alcohols towards aqueous or solid caustic potash also leads to the conclusion that only alkylidene dissociation occurs. Ethyl alcohol gives, at 250°, with an excess of caustic potash, hydrogen and potassium acetate quantitatively,

$$CH_3CH\Big\langle \begin{array}{c} H \\ OK \end{array} + 2KO-H \longrightarrow CH_3CH =\; +3KO-H \longrightarrow$$

$$CH_3CH(OK)_2 + 2H + KOH \longrightarrow \begin{array}{c} CH_3 \\ KO \end{array}\Big\rangle C= \; + 2H-OK + H_2 \longrightarrow$$

$$\begin{array}{c} CH_3 \\ KO \end{array}\Big\rangle C(OK)_2 + 2H + H_2 \longrightarrow CH_3C(OK)_3 + 2H_2.$$

If any of the potassium ethylate, which is first formed, were dissociated into ethylene and caustic potash,

$$CH_3CH_2OK \rightleftarrows CH_2-CH_2 + HOK.$$

the olefine must naturally give, besides hydrogen, ethyleneglycol,

$$CH_2-CH_2 + 2H-OK \longrightarrow \begin{array}{c} CH_2-CH_2 \\ OK \quad OK \end{array} + H_2.$$

or its decomposition products; these are, however, not formed. The reaction with potash-lime and primary alcohols is so deli-
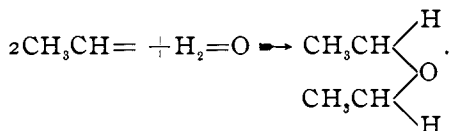
cate and accurate that it has been suggested by Hell as a means of determining the molecular weight of an unknown primary alcohol.

As mentioned above, ethyl ether is the chief product when ethyl halides are treated with alcoholic potash, or with dry sodium ethylate; this is also true when dry silver oxide and ethylhalides are used.

These reactions, which have been interpreted by Williamson and others on the basis of double decomposition or of minute ionization, must obviously be attributed to the absorption by the ethylidene of alcohol or of water, which is set free by the action of the halogen hydride particles on the sodium ethylate or silver oxide respectively,

$$CH_3CH= +H-OC_2H_5 \longrightarrow CH_3CH_2OC_2H_5,$$

or

$$2CH_3CH= +H_2=O \longrightarrow \begin{matrix} CH_3CH \diagup{}^H \\ \diagdown O \\ CH_3CH \diagdown{}_H \end{matrix}.$$

We are now able to consider an entirely new explanation of the function of sulphuric acid, or of phenyl sulphonic acid, in converting ethyl alcohol into ether. Sulphuric acid acts, first of all, with alcohol at ordinary temperatures to give both mono- and diethyl sulphate; the first stage in the reaction can not be ascribed to the union of ethylidene, formed by dissociation of alcohol, with free sulphuric acid since ethyl ether, which is relatively more dissociated than alcohol, acts *only very* slowly with concentrated sulphuric acid at ordinary temperatures to give monoethyl sulphate. Furthermore, since sulphuric acid itself is completely dissociated into its components, sulphur trioxide and water, at 400°, it is extremely probable that monoethyl sulphate is formed by the union of sulphur trioxide, present by dissociation,

$$H_2SO_4 \rightleftarrows SO_3 + H_2O, \text{ with alcohol,}$$

$$O_2S-O + H-OC_2H_5 \longrightarrow O_2S\diagup{}^{OH}_{OC_2H_5}.$$
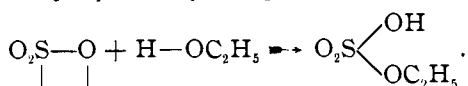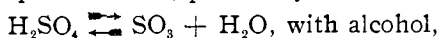
Now it is well known that ether formation in a mixture of sulphuric acid and alcohol begins perceptibly only at 95° and

proceeds *very* slowly at that temperature. The favorable temperature for ether manufacture is 140°. This is self-evident in view of the following considerations: Primary and secondary ethyl sulphate possess the dissociation points 160° and 200° respectively; consequently, these substances must be dissociated at 140° to a very great extent into sulphuric acid and one or two molecules of ethylidene respectively. Addition of alcohol at 140°, therefore, simply necessitates a combination with the ethylidene particles.

$$CH_3CH= + H-OC_2H_5 \rightarrow CH_3CH_2OC_2H_5.$$

to give ether, and this process can naturally go on indefinitely.

When ethyl alcohol is mixed with an excess of concentrated sulphuric acid and heated to 160°, no ether, but some ethylene, is formed; in fact, this method is still suggested and used as the best means of preparing ethylene.

The yield of olefine, however, can never be raised above 20 per cent. of the theory and the operation is extremely tedious because carbonization and formation of sulphur dioxide takes place to a very marked extent. These results are now easily understood. The ethylidene molecules, formed by dissociation of ethylated sulphuric acid, burn chiefly at the expense of the oxygen present in sulphuric acid,

$$CH_3CH= + O=SO_2 \rightarrow CH_3CH : O + SO_2.$$
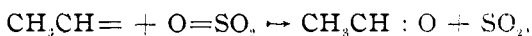
and the resulting acetaldehyde is then at once charred by the vitriol present. Only 20 per cent., at the utmost, of the ethylidene particles escape this oxidation by intramolecular conversion to ethylene.

Finally we may summarize the conclusions reached in the above discussion as follows:

The valence of carbon is not a constant. At definite temperatures, which vary remarkably with the nature of the groups bound to it, a carbon atom becomes spontaneously dyad. Below these limits there is dynamic equilibrium between bivalent and quadrivalent carbon. The existence of carbon compounds containing bivalent carbon has been definitely established; methylene chemistry plays a great rôle in many of the fundamental reactions of organic chemistry.

The conception of substitution or metalepsis, which has been

our guide in interpreting the reactions of carbon chemistry since 1833, is no longer tenable. It must be replaced by the conception of dissociation in its broadest sense. Fundamentally speaking, there are but two classes of carbon compounds—the saturated and the unsaturated. Excluding reactions called ionic, a chemical reaction between two substances always first takes place by their union to form an addition product. The one molecule being unsaturated and partially in an active molecular condition absorbs the second molecule because it is partially split or dissociated into two active portions. The resulting addition product then often dissociates spontaneously, giving two new molecules. The similarity of such reactions to those called ionic is at once apparent, but their relationship can not, in the present state of our knowledge, be clearly understood.

A REVISION OF THE ATOMIC WEIGHT OF IODINE.

By Gregory Paul Baxter.

THE atomic weight of iodine has been for some time considered one of the best determined of chemical constants, owing to the extremely concordant results of Stas and Marignac, who both deduced the value 126.85 (O = 16.000) from syntheses of silver iodide. Within the last two years, however, two series of determinations, one by Ladenburg and one by Scott, have yielded results over one-tenth of a unit higher than the above. Ladenburg's method consisted in heating silver iodide in a current of chlorine until all the iodine had been displaced, and gave the result 126.96, while Scott, like Stas and Marignac, synthesized silver iodide and obtained in two analyses the values 126.96 and 126.98.[1] The anomaly in the atomic weights of iodine and tellurium has always been of the greatest interest, and has led to a large number of investigations upon the atomic weight of tellurium during the last few years, which have shown conclusively that this value lies in the neighborhood of 127.6. The doubt thrown upon the

[1] Very recently, since the work described in this paper was completed, Köthner and Aeuer have published a preliminary notice of experiments involving syntheses of silver iodide as well as a repetition of Ladenburg's work, from which they conclude that the atomic weight of iodine cannot be lower than 126,963. Details of their work are not given. See *Ber. d. chem. Ges.*, **37**, 2536.