tetrafluoride at —10° there was no diminution in pressure. The same negative result was found upon using barium fluoride.

Other attempts to prepare a fluocarbonate by the action of fluorine upon cesium carbonate and upon potassium bicarbonate resulted in the formation only of cesium fluoride and potassium acid fluoride.

It was thought that in spite of the theoretical considerations previously announced it might be worth while to determine whether hydrogen fluoride and carbon tetrafluoride would show any tendency to react. Mixtures of the two liquids were made in enclosed copper apparatus. The liquids were shaken together and then frozen. As the mixture was allowed to warm very slowly a time-temperature curve was taken. In every experiment the curves showed breaks only at the freezing points of the two liquids, indicating not only that there is no reaction between them, but that they are not appreciably soluble in each other.

The negative results of all these attempts to prepare fluocarbonic acid or a fluocarbonate render the possibility very remote of obtaining a carbon compound in which the carbon would show a greater coördination number than four.

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THE DOUBLE BOND

BY WALLACE H. CAROTHERS

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In his paper, "The Atom and the Molecule," Lewis[1] pointed out that the double bond represents, because of the mutual repulsion of the nuclei, a point of weakness in the molecule; and he showed how dissociation might be supposed to occur at non-polar linkages producing parts more or less polar and reactive.

In the present paper it is proposed to show how this idea together with other specific assumptions of the octet theory may be used to account for the reactions of the double bond.

Discussion will be limited for the sake of brevity to double bonds between any pairs of the following atoms: carbon, nitrogen and oxygen. This can be done without much loss of generality because most important addition reactions occur at such double bonds.

It has been found convenient to represent the more or less cubical structures assumed in the Lewis theory by means of a plane projection. Since

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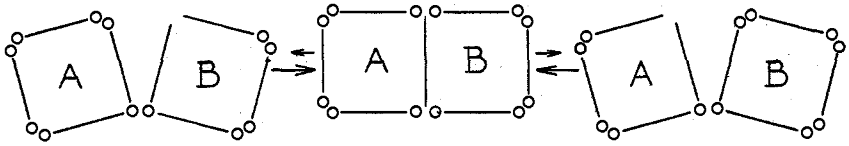
[1] Lewis, THIS JOURNAL, **38**, 762 (1916).

the electrons are shared in pairs, the third dimension is not needed to make the diagrams intelligible.



II I III

In the figure I represents any compound containing a double bond, II and III each represents one of the phases of the effect of the mutual repulsions of the nuclei. The figures are symbols, not pictures, and are intended to convey the idea that in the vibrations of the electrons, one pair has been displaced considerably from its mean position.

In discussing the effects of such displacements of electrons the results are similar and the treatment simpler if it be assumed that any double bond is capable of existing in two forms, an inactive form I, and an active form II and III in which one of the atoms has retained one of the pairs of electrons formerly shared with the neighboring atom so that the latter is left with only six electrons in its shell.[2] The latter atom will be called the deficient atom. The forms II and III are assumed to be capable of only momentary existence so that the actual concentration of the active forms is always small; the dissociations are assumed to be reversible so that there is equilibrium between the active forms and the inactive.

1. The extent of the dissociation under any given set of conditions is assumed to be determined by the effective nuclear charges of A and B, and for any given compound by the temperature, concentration, nature of the medium, etc. This permits an explanation of the difference in reactivity of different double bonds under the same conditions and of the same double bond under different conditions.

2. If A and B are different atoms, then in the dissociation assumed above, that atom which has the higher effective nuclear charge will retain the extra electron, and the atom having the smaller nuclear charge will, in the dissociated form, be the deficient atom.

3. If A and B are the same atom, both possible active forms (II and III) may result, but in general that atom will retain the extra electron which has attached to it groups or atoms having the higher effective nuclear charge. The attached groups are thought of as enhancing or exalting the nuclear charges of the groups to which they are attached.

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[2] (a) Lowry [*J. Chem. Soc.*, **123**, 822 (1923)] has made use of the idea that a double bond exists or is capable of existing in the form II or III. Thus he writes ethylene as $CH_2^+ - CH_2^-$, and refers the reactivity of such bonds to their polarity. See also (b) Noyes, This Journal, **45**, 2959 (1923), and (c) Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., **1923**, p. 124.

The following well-known assumptions of the octet theory will also be used.

4. The proton has a higher effective nuclear charge than other atoms.[3]

5. The stable form to which the atoms under consideration tend to revert is the octet. The octet may be completed either by (a) sharing electrons with other atoms or (b) taking up electrons.

6. The residual atomic charge on any atom or group of atoms tends to a minimum. The approximate residual atomic charge is given by the formula[4] $e-(s-v_c)$ where, for the atoms here considered, e is the number of electrons in the shell of the atom in the free state, s is the number of electrons in its shell in the compound, and v_c is its valence (that is, the number of bonds attached to it) in the compound. Application of this formula shows that if, in the undissociated form, each of the atoms A and B has a valence equal to $8-e$, then in the dissociated form the atom which retains the extra electron will have a residual atomic charge of —1 and the deficient atom a charge of +1. Otherwise this will not be true. Thus in ethylene in the inactive form $e = 4$, $s = 8$ and $v_c = 4$ for each carbon atom, and the residual atomic charge is 0. In the active form for the deficient atom, $e = 4$, $s = 6$ and $v_c = 3$, and the residual atomic charge is + 1; for the other atom $e = 4$, $s = 8$ and $v_c = 3$, and the residual atomic charge is —1. In this connection it will be observed that no attempt was made to indicate how extensive the electron displacement must be to result in a configuration which may be regarded as active; but since the two atoms are, in the active form, still attached to each other by one non-polar linkage, the nucleus of the deficient atom never gets far from the pair of electrons which has been lost. Hence the residual atomic charges on the atoms of the active forms may be, and probably are, always less than unity, and the magnitude of the charge as calculated by the formula must be regarded as a limiting maximum. The formula will, however, always tell whether charges exist, and if they exist what their sign is.

Addition.—The atoms carbon, nitrogen and oxygen are stable only when eight electrons are present in their shells. The deficient atom has only six electrons. The seat of the unsaturation in the active form of the double bond is, then, what may be called a vacant space in the octet of the deficient atom. Any atom which has an unshared pair in its shell may complete the deficient atom by sharing that pair with the deficient atom. If the resulting compound is stable, or if it can rearrange into a compound which is more stable under the conditions of the experiment than the original compound, then equilibrium is displaced with the formation of the new compound. Thus in the addition of hydrobromic acid to the car-

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[3] Or as Latimer and Rodebush state [THIS JOURNAL, 42, 1425 (1920)], "In one sense hydrogen is the most electronegative of elements."

[4] Langmuir, *Science*, **54**, 59 (1921).

bon-carbon double bond:[5] $R_2C{=}CR_2 \longrightarrow \underset{+}{R_2C^*}{-}\underset{-}{CR_2} \xrightarrow{HBr} R_2\overset{+\,BrH}{C}{-}\underset{-}{CR_2} \longrightarrow R_2CBr{-}CHR_2$.

The first step is the completion of the deficient atom by means of an unshared pair of the bromine atom in accordance with Paragraph 5. In the resulting compound the bromine has a residual atomic charge of +1 and the carbon atom of —1. By migration of a proton (hydrogen ion) to carbon, the tendency expressed by Postulate 6 is satisfied—all the residual atomic charges are reduced to zero. This general mechanism for addition reactions at the double bond emerges as the direct expression of the postulates, and the application of these to other cases such as the addition of halogens is sufficiently obvious to need no further illustration. A necessary condition for addition by this mechanism is the presence of an unshared pair in the shell of the addendum. A substance like methane does not satisfy this condition.

Selective Addition.—The active form of compounds containing the carbonyl group is $R_2C^*{-}O$. The active form $R_2C{-}{}^*O$ does not occur because oxygen has the higher nuclear charge (2). The direction of the addition of addenda of which the two halves are dissimilar is thus absolutely determined; and similarly for other double bonds between two different atoms. Addition at such bonds is completely selective and exclusively in the direction required by the theory.

The action of hydrazine on the active form $R_2C^*{-}O$ by the mechanism described above would lead[6] to $R_2C\langle\begin{matrix}NHNH_2\\OH\end{matrix}$. By the elimination of water the hydrazone is formed; by the elimination of NH_2NH_2, the original aldehyde or ketone. In either case the mechanism is thought of as precisely the reverse of the addition; for example, hydrogen ion (which is always mobile when attached to nitrogen, oxygen or halogen) migrates to the oxygen, and water splits out with the formation of the active form of the hydrazone.

The carbonyl bond is very reactive because of the proximity of the carbon and oxygen nuclei. But many possible addition products of carbonyl are unstable because, while the opposed nuclei are not so close together, the total opposed nuclear charges are much greater. Hence when fission of the type described above is possible it frequently occurs. And when two products may be the results of such reaction, the tendency is to form that one which involves the opposition of the smaller nuclear charges. Thus, hydrazones and N-alkyl imines are formed readily from aldehydes

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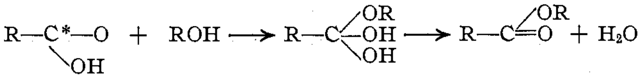
[5] The symbol A*— is used to indicate the deficient atom. The signs + and — indicate the residual atomic charges.

[6] Ref. 2 c, p. 136.

even in the presence of a large excess of water (nitrogen has a smaller nuclear charge than oxygen). Again, comparing the compounds of the type $R_2C{=}N{-}R'$: the simple imines in which R' is H are in general very unstable compared with the alkyl imines in which R' is alkyl. In the former the proton is attached directly to the doubly bound nitrogen; in the latter this is absent; hence, this relative instability of the simple imines is that required by Postulates 3 and 4.

The assumption of the mechanism described above will be found to interpret the behavior of a large number of types of compounds which may be represented by the general formula $R_2C\begin{matrix}\diagup X\\ \diagdown Y\end{matrix}$. Suppose X and Y to be methyl. This mechanism does not permit methane to split out with the formation of $R_2C{=}CH_2$, because neither X nor Y has a free pair to which the wandering hydrogen ion might attach. Suppose Y to be any alkyl radical and X to be NH_2, OH or halogen. Then this mechanism permits the splitting out of NH_3, H_2O or HX with the formation of the unsaturated hydrocarbon, but the reaction will not be expected to proceed spontaneously because, due to the small nuclear charge of the carbon atom, the hydrogen nuclei attached to it are held very firmly, and there is little tendency for them to wander. On the other hand, the elimination of H_2O where X and Y are OH would be expected to be spontaneous and rapid.

Esterification.—Since in so far as primary alcohols are ionized at all they are exclusively acidic,[7] esterification cannot be regarded as a neutralization reaction without violence to experimental facts. The following mechanism for esterification is deduced from the above postulates:



$$R{-}\underset{\diagdown OH}{C^*}{-}O + ROH \longrightarrow R{-}C\begin{matrix}\diagup OR\\ {-}OH\\ \diagdown OH\end{matrix} \longrightarrow R{-}C\begin{matrix}\diagup OR\\ {=}O\end{matrix} + H_2O$$

The deficient carbon atom of the active form of the carbonyl group is completed by sharing a free pair with the oxygen atom of the alcohol in accordance with Postulate 5, and the hydrogen ion from the alcohol wanders to the adjacent oxygen atom in accordance with Postulate 6. Water then splits out by the mechanism and for the reasons suggested above in connection with the discussion of the addition products of the carbonyl group. It is even possible to suggest a definite mechanism for the catalytic effect of hydrogen ion. Hydrogen ion would add at the oxygen atom bearing the residual negative charge, the equilibrium between the active and inactive forms of the acid would thus be displaced and the momentary concentration of the former increased.

The Polarity of the Double Bond.—In terms of the dualistic theory, double bonds were said to be polar, and the assumption of polarity was supposed to account for the reactivity of double bonds, and for such

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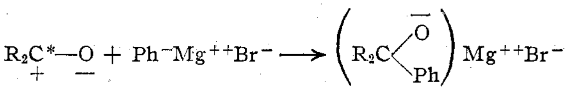
[7] See for example, Williams and Truesdail, THIS JOURNAL, **45**, 1348 (1923).

facts as selective addition. In terms of the view developed here there is a certain (precisely defined) sense in which polarities may exist or may be developed at double bonds. In the mechanism of addition reactions described above it has been assumed that the force which is of chief importance in bringing about addition reactions is the tendency to complete the octet. Polarity is of secondary importance and operates only through the weaker tendency expressed by Postulate 6.

That the order of the strength of the two tendencies involved is that which has been assigned to them is evident from a number of considerations. Thus, in the formation of sodium chloride from its elements, each atom completes its group of eight and each develops residual atomic charges which were not previously present. Obviously in general in the formation of any completely polar compound from its elements, the two tendencies are in opposition and the tendency to complete the group of eight is the stronger.

Postulate 6 admits the existence of double bonds which are non-polar in the active form. Diazobenzene-imide[8] furnishes an example of such a bond, and examination of its reactions confirms the relative unimportance adduced above of purely polar effects: $Ph—N{=}N{=}N \rightleftarrows Ph—N{=}N—N^*$. There are no residual atomic charges on the atoms of the active form of this compound; nevertheless the Grignard reagent would be expected on the basis of the above assumptions to react as follows: $Ph—N{=}N—N^* + Ph^-Mg^{++}Br^- \longrightarrow (Ph—N{=}N—\bar{N}—Ph)Mg^{++}Br^-$. This may be compared with the addition of the Grignard reagent at a polar double bond, such as the carbonyl.

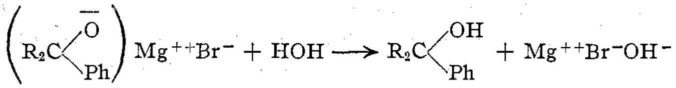


$$\underset{+}{R_2C^*}—\underset{-}{O} + Ph^-Mg^{++}Br^- \longrightarrow \left(R_2C\begin{smallmatrix}\diagup \bar{O}\\ \diagdown Ph\end{smallmatrix}\right)Mg^{++}Br^-$$

On the addition of water

$$(Ph—N{=}N—\bar{N}—Ph)\,Mg^{++}Br^- + HOH \longrightarrow Ph—N{=}N—NHPh + Mg^{++}Br^-OH^-$$

and



$$\left(R_2C\begin{smallmatrix}\diagup \bar{O}\\ \diagdown Ph\end{smallmatrix}\right)Mg^{++}Br^- + HOH \longrightarrow R_2C\begin{smallmatrix}\diagup OH\\ \diagdown Ph\end{smallmatrix} + Mg^{++}Br^-OH^-$$

In both cases the phenyl ion adds at the deficient atom in accordance with Postulate 5 regardless of whether the atom happens to be polar or not. In the decomposition of the addition products there are no octets to be completed, and the hydrogen ion places itself in accordance with Postulate 6.

What it is desired to emphasize is, that according to the view here developed, the double bond though usually polar is not necessarily so,

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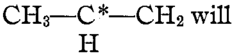
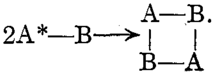
[8] For specific evidence for this structure see Carothers, THIS JOURNAL, **45**, 1734 (1923). For the action of the Grignard reagent on azo-imides see Dimroth, *Ber.*, **38**, 670 (1905); **39**, 3905 (1916).

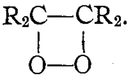
and its reactivity is not chiefly due to polarity. What it is desired to avoid is the tendency to regard reactivity as exclusively the attribute of polarity and polarity as in some nebulous manner the ultimate cause of typically organic reactions. The most reactive organic compounds are perhaps some of the metal-carbon compounds which are probably completely polar, but the reactions of these compounds with other organic compounds bear no resemblance to the typical reactions of completely polar inorganic compounds. The most characteristic reaction of the latter is metathesis, and in so far as chemical reaction involves the formation or rupture of valence bonds, is not chemical reaction at all. On the other hand, the above postulates assign to such polarities as are assumed to exist at the double bond a definite significance and a definite function.

Markownikoff's Rule.—Where the atoms A and B are different and the two halves of the addendum are dissimilar, addition is completely selective; its direction is determined by Postulate 2. This has already been illustrated for the reactions of the carbonyl group. If A and B are the same atoms, but have different groups attached to them, then addition may be more or less selective. Since hydrogen has a higher effective nuclear charge than other atoms (4), that atom which has attached to it more hydrogen atoms will usually in the dissociation retain the extra electron, and addition of the new octet will occur at the other atom. Thus in $CH_3—CH═CH_2$ the active form  $CH_3—\underset{H}{C^*}—CH_2$ will usually predominate, and in the addition of hydrogen bromide *iso*propyl bromide will be the chief product. Markownikoff's rule is thus seen to be an implication of Postulate 3. Since the influence of (especially singly bound) groups on the nuclear charge of atoms to which they are attached is secondary and weak, the rule obviously admits of exceptions, which are actually numerous.

Conjugated Systems and 1,4 Addition.—The compound A═B—B═B may on dissociation give rise to various active forms. Suppose that the conditions of Postulates 2 or 3 cause the dissociation at A═B to take place so that A retains the extra electron. Then A—*B—B═B will be formed. Now the deficient atom B will usually have a residual atomic charge of +1 so that on further dissociation the adjacent atom will retain the extra electron (3). A—*B—B—*B will be formed. This may be in equilibrium with A—B═B—*B. Only 1,4 addition can occur with the last active structure, only 1,2 addition with the first, either 1,2, 3,4 or 1,4 with the second. By making use of the ideas developed above it is frequently possible to anticipate which type of addition will occur.

Reactions of the Active Form of the Double Bond with Itself and with Other Active Forms.—The active form of A*—B obviously presents the possibility of reacting with itself:  $2A^*—B \longrightarrow \begin{array}{c}A—B.\\ |\quad\ \ |\\ B—A\end{array}$ In this way the tendencies expressed by Postulates 5 and 6 are in general both satisfied. By similar reactions trimers and higher polymers may be formed. One factor which will determine the ease of such reactions is the degree of dissociation, that is, the amount of active form present. Since this will be determined by the nuclear charges of the atoms A and B and attached groups, it is to be expected that formaldehyde will polymerize more readily than acetaldehyde, and this more readily than acetone (2, 3 and 4).

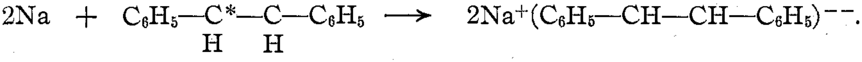
The reaction of one active form with another is precisely similar. It will be illustrated by the first stage of auto-oxidation: $R_2C^*\text{—}CR_2 + O^*\text{—}O \longrightarrow$



$$R_2\underset{\displaystyle \text{O—}}{\overset{}{C}}\text{—}\underset{\displaystyle \text{O}}{C}R_2.$$

Reduction of the Double Bond.—The idea of the double bond developed here is especially interesting in connection with reduction and hydrogenation. In the active form $A^*\text{—}B$ the atom A may complete its octet by taking up electrons (5b).[9] The anion $(A\text{—}B)^=$ is thus formed in which each atom usually has a residual charge of —1. If the reaction is carried out under suitable conditions, the anion may be isolated in polar combination with a cation as a salt; otherwise hydrolysis will frequently occur, and the product will be the compound H—A—B—H. When oxygen reacts with sodium, sodium peroxide is formed. The reaction is $2Na + O\text{—}^*O \longrightarrow 2Na^+, (O\text{—}O)^{--}$. On the addition of water, $2Na^+, (O\text{—}O)^{--} + HOH \longrightarrow 2Na^+OH^- + HOOH$.

The carbon-carbon double bond would be expected to react similarly, though the tendency would be smaller because the extent of the dissociation is smaller (the opposed nuclear charges are smaller). Stilbene treated in dry ether with powdered sodium forms a sodium salt of diphenylethane,[10]



$$2Na + C_6H_5\text{—}\underset{H}{C^*}\text{—}\underset{H}{C}\text{—}C_6H_5 \longrightarrow 2Na^+(C_6H_5\text{—}CH\text{—}CH\text{—}C_6H_5)^{--}.$$

On the addition of water, $2Na^+(C_6H_5\text{—}CH\text{—}CH\text{—}C_6H_5)^{--} + HOH \longrightarrow 2Na^+OH^- + C_6H_5\text{—}CH_2\text{—}CH_2\text{—}C_6H_5$. The reaction is precisely analogous to the formation of sodium peroxide. The relative tendency of oxygen and stilbene toward reaction of this type is shown to be that which the theory demands by the fact that when the sodium salt of diphenylethane is treated with oxygen metathesis occurs, with the formation

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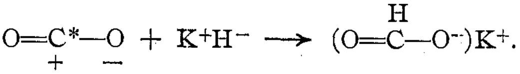
[9] In addition to the unsymmetrical dissociation of double bonds which has been assumed there might also be a symmetrical dissociation in which each atom of the active form has only seven electrons. Due to the odd electrons, such a form would probably be colored (Lewis, Ref. 2 c, p. 124). Evidence for the existence of equilibrium amounts of such a form may perhaps be found in the fact that double bonds are in general chromophoric. The symmetrical dissociation may also be useful in explaining reduction and hydrogenation, but it has no significance for ordinary addition reactions. The unsymmetrical dissociation accounts for all the phenomena discussed here, and so the other type has not been considered.

[10] Schlenk and others, *Ber.*, **47**, 473 (1914).

of stilbene and sodium peroxide. Other double bonds such as C=O, and N=N behave similarly.[10]

Another substance which is capable of furnishing electrons readily is the hydride ion. This ion consists of a hydrogen nucleus held between a pair of electrons. It furnishes a pair of electrons to the deficient atom thus completing its octet, together with one proton, so that the product of the addition is a univalent anion. An example is the action of potassium hydride on carbon dioxide:  $O=\underset{+}{C^*}-\underset{-}{O} + K^+H^- \longrightarrow (O=\overset{H}{C}-O^-)K^+$. Potassium formate is the product.[11] The possibilities of metallic hydrides as reducing agents in organic chemistry appear to have been little realized.

Catalytic Hydrogenation.—The view of the double bond which has now been developed permits the following interpretation of catalytic hydrogenation.

The ultimate surface of a metal consists of a layer of electrons. Compounds containing double bonds are adsorbed at such surfaces. The adsorption consists in a sharing of electrons between the deficient atom and the surface of the metal. The metals which act as catalysts for hydrogenation are all capable of existing in more than one state of valence and are all more or less readily oxidized and reduced, that is, they gain and lose electrons readily. The deficient atom tends to take up two electrons. In the desorption of the adsorbed compound, the deficient atom may retain the pair of electrons which the surface previously shared with it. The reaction here postulated is similar to that described above for the action of sodium on stilbene or on oxygen. Here, however, the reaction is restricted to the surface by the physical conditions (hardness, etc.) of the metal. The desorption cannot proceed very far because the surface of the metal is limited in area and because electrostatic forces are developed. In order that the reaction may proceed, hydrogen ions (protons) must be furnished to the adjacent phase and electrons to the surface of the metal. This is provided by the adsorption of hydrogen. The net result of the adsorption of one molecule of hydrogen is the addition of two electrons and two protons at the surface of the metal. Suppose now (after the adsorption of one molecule of hydrogen) that one molecule of the double-bonded compound is desorbed in the manner suggested above. Then the metal acquires a charge of +2. The desorbed ion takes up two protons from the adjacent phase, thus forming the hydrogenated compound, and two protons evaporate from the surface of the metal to replace those taken up by the desorbed ion. Both the metal and the adjacent phase are now in the same electrical state as at the beginning of the cycle and one molecule of the double-bonded compound has been hydrogenated.

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[11] Moisson, *Compt. rend.*, **136**, 723 (1903).

This idea, though purely speculative, does not appear to violate anything known experimentally about catalytic hydrogenation; it is logically consistent with the perfectly general view of the double bond which is developed in this paper; and although it is explicit where theories of catalysis are commonly vague, nevertheless it appears to include three theories which are widely accepted today, namely, the theory of intermediate compound formation, the theory of adsorption and the theory of the electrolytic circuit.

The debt of this picture of hydrogenation to the ideas of Langmuir on heterogeneous catalysis is obvious, but it may be observed that the view developed above does not require that the compound to be hydrogenated and the hydrogen be adsorbed at adjacent points on the crystal lattice. The two adsorption processes may even occur on the surfaces of different metals providing that these two metals are in continuous or very frequent electrical contact. Indeed, since in general for any two metals the first will take up electrons more readily than the second, and the second will lose electrons more readily than the first, while the accumulation of electrostatic differences is prevented by metallic conduction, it is quite possible that two metals together may be a very much more efficient catalyst than either alone. This offers a possible explanation of promotion or activation. These phenomena appear to have been little studied for catalytic hydrogenation, but it may be mentioned that Ipatiew[12] found that the ethylene linkage is only partially saturated by hydrogen at high temperature and pressure in a copper tube, but is completely hydrogenated if both iron and copper be present. Professor Adams and the writer have shown[13] that pure platinum black (in small amounts) is almost totally ineffective in the reduction of aldehydes, while the same platinum is extremely active when traces of iron salts are present. The study has been extended and the results will be made the matter of a future communication. It may, however, be mentioned that the power to exalt the catalytic activity of platinum in the catalytic reduction of aldehydes is common to a remarkably large number of substances, and that U. S. P. iron powder, not intimately mixed with the platinum, but merely thrown into the same bottle has such power.

Summary

In compounds containing a double bond, dynamic equilibrium is assumed to exist between an inactive form and an active form. In the former the double bond is supposed to consist of two typical non-polar unions, while in the latter dissociation of one of the bonds has occurred so that one atom has only six electrons. The amount of the active form present is always

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[12] Ipatiew, *Ber.*, **43**, 3387 (1910).

[13] Carothers with Adams, This Journal, **45**, 1071 (1923).

small and varies with the conditions. In the dissociation, that atom which has the higher effective nuclear charge retains the extra electron. These assumptions together with certain other (specific) assumptions of the octet theory are used to interpret the properties of the double bond. Simple addition, selective addition, 1,4 addition, Markownikoff's rule, reduction, catalytic hydrogenation, and promoter action are discussed.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE UTILIZATION OF CASSIA OIL FOR THE SYNTHESIS OF CINNAMYL ALCOHOL[1]

BY ARTHUR J. HILL AND EDITH H. NASON

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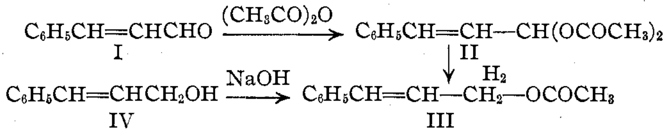
Cinnamyl alcohol has found fairly extensive use, either alone, or as a fixative, in the manufacture of perfumes.

The main source of this compound has been storax gum, in which it occurs as cinnamyl cinnamate, associated with other esters.

There is need, however, for a practical synthesis because of the many disadvantages attending the use of storax. Of the three[2] syntheses which have been recorded in the literature, that of Barbier appears to be the most practicable. This method involves first the reduction of cinnamyl diacetate (II) by means of iron and acetic acid, followed by saponification of the resulting acetate (III) with alcoholic sodium hydroxide.



$$\begin{tikzcd} \underset{\text{I}}{C_6H_5CH{=}CHCHO} \arrow[r, "(CH_3CO)_2O"] & \underset{\text{II}}{C_6H_5CH{=}CH{-}CH(OCOCH_3)_2} \arrow[d, "H_2"] \\ \underset{\text{IV}}{C_6H_5CH{=}CHCH_2OH} \arrow[r, "NaOH"] & \underset{\text{III}}{C_6H_5CH{=}CH{-}CH_2{-}OCOCH_3} \end{tikzcd}$$

The yield is stated to be 20%. Unfortunately, however, the directions given by Barbier and Leser are rather inadequate and, as a result, have but little practical value in their present form. Indeed, they state that the method could undoubtedly be greatly improved by a study of the conditions of the reaction.

Cassia oil affords a comparatively cheap and abundant source of cinnamic aldehyde. Indeed, there are no methods involving the synthesis of the cinnamyl residue which so far would appear to compete successfully with this natural product. It has seemed desirable, therefore, to utilize this naturally occurring aldehyde for the preparation of cinnamyl alcohol, in particular through the medium of the Barbier method.

[1] This paper is constructed from the dissertation presented by Edith H. Nason to the Faculty of the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Barbier and Leser, *Bull. soc. chim.*, [3] **33**, 858 (1905). Rona, *Biochem. Z.*, **67**, 137 (1914). Skita, *Ber.*, **48**, 1692 (1915).