CATALYSIS FROM THE VIEWPOINT OF THE ELECTRONIC THEORY OF ACIDS AND BASES[1]

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I. INTRODUCTION

One of the primary questions that theoretical chemistry has always concerned itself with is: How do reactions take place? The answer to this question has been sought with renewed vigor during the last two decades. Stimulated by the Lewis theory of the covalent bond, chemists have gone far toward answering the question for many reactions.

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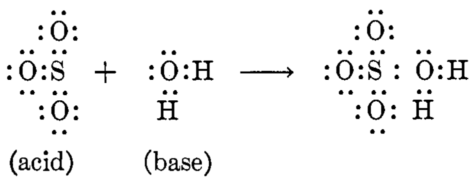
The point now seems to be reached, however, at which the lack of a comprehensive understanding of the terms "acid" and "base" may be a handicap to further progress. An adequate terminology is essential to the progress of any science. Not only is such a terminology necessary to deal with knowledge as it is gained, but it often suggests new interrelationships with other branches of the science which may in turn lead to new discoveries.

Fortunately the basis of this terminology has already been provided by the electronic theory of acids and bases (43, 44, 51), which although proposed twenty years ago has been largely ignored until recently (45–49, 51). This theory systematizes a widespread range of chemical phenomena. It fits a large number of apparently isolated data into a more complete and clear picture which, like a jig-saw puzzle, appears simple once the scattered pieces have been fitted together.

The one-element theory in various forms has been a persistent idea throughout the history of chemistry. Some of us can remember when the chemical behavior which we call oxidation was supposed to depend upon one element. We no longer hold to the one-element theory of oxidation–reduction, but we all know how difficult it is to give up the one-element theory of acids and bases. Of course at one time that element was oxygen, but it seems that when chemists changed from oxygen to hydrogen they decided never to change again. However, the experimental facts are compelling us to realize that the presence of a particular element in a substance is not essential for acid properties.

The electronic theory of acids and bases follows from Lewis' definitions based on these experimental facts (43, 44, 51). According to this theory a substance is acting as an acid when it accepts a share in a lone electron-pair from a base to form a coördinate bond. Any substance capable of donating a share in a pair of electrons may act as a base toward a sufficiently strong acid. The formation of the coördinate bond is neutralization. One example will be given here; others have been cited previously (44, 51).



Subsequent ionization depends upon several factors, including the dielectric constant and solvating power of the solvent—if a solvent is present.

We conclude that almost any substance may behave as an acid or a base. The majority of reagents, under properly chosen conditions, may react in either way, i.e., are amphoteric. There are a few exceptions such as the "inert" gases, which so far as we know can act only as extremely weak bases (10). But as a rule, most substances can be made to act as bases if reacted with a sufficiently strong acid (stannic chloride or sulfur trioxide will compel even hydrogen chloride to act as a base (51)), and many substances can be made to act as acids if reacted with a sufficiently strong base. Perhaps we should give up the terms "acid" and "base" and instead use "acidity" and "basicity" as referring to a particular reaction. But probably the convenience of using the nouns makes their retention worth while if we are careful to remember the importance of two other nouns—relativity and amphoterism.

The use of the terms "electrophilic" and "nucleophilic" is already well known. By changing nucleophilic to electrodotic (52) and using the Lewis theory of acids and bases we have the basis of a new terminology which includes both oxidation–reduction and acid–base phenomena as manifestations of the electrophilic and electrodotic properties of substances in general (52). Depending upon the conditions of the particular reaction, a large number of substances may act either as oxidizing agents or as acids (electrophilic reagents). Another large group of substances may act either as reducing agents or as bases (electrodotic reagents). Many in each group may react in all four ways. Water acts as an acid toward ammonia, as an oxidizing agent toward sodium, as a base toward sulfur trioxide, and as a reducing agent toward fluorine (table 1).

TABLE 1

Examples of electrophilic and electrodotic reactions of water

Electrophilic
$H_2O + NH_3 \longrightarrow NH_4^{+1} + OH^{-1}$ (acid)
$2H_2O + 2Na \longrightarrow 2Na^{+1} + 2OH^{-1} + H_2$ (oxidant)
Electrodotic
$H_2O + SO_3 \longrightarrow H^{+1} + HSO_4^{-1}$ (base)
$2H_2O + 2F_2 \longrightarrow 4H^{+1} + 4F^{-1} + O_2$ (reductant)

Many examples showing how the Lewis theory conforms to the experimental data have already been given (44, 51), but catalysis is one aspect of the subject which has not been dealt with systematically. This paper represents an attempt to do that. Familiar examples of acid–base catalysis are discussed from the Lewis viewpoint in order to show that there is no essential difference in catalytic behavior whether or not protons are involved.

"Catalysis" as usually defined has implied that the catalyst is recovered unchanged. Recently, there seems to be a tendency to broaden the definition. For example, Hammett (25) points out that there is no important distinction between catalysis in the older sense and the kind of acceleration produced by a base which appears as its "conjugate acid" at the end of the reaction. A few of our examples are of the latter type, but most of them conform to the older definition.

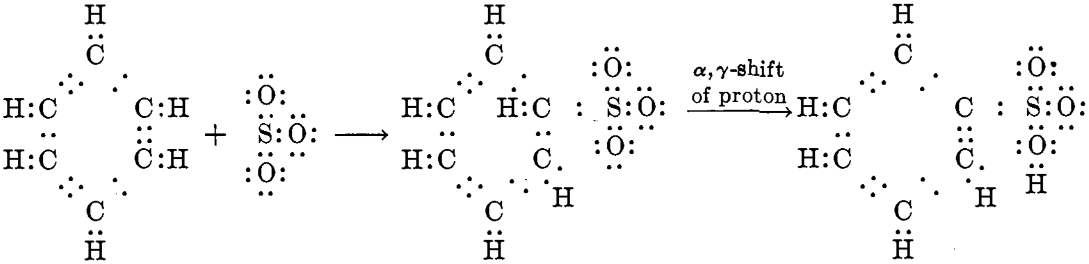
Since it is already generally recognized that basic behavior is displayed by a very large number of substances, only enough examples of base-catalyzed reactions are included in this paper to show that when a base acts as a catalyst the substance attacked by the base is behaving as an acid.

Many examples of typically acidic properties displayed by substances which do not contain protons have already been listed (44, 51), but the idea that acidic behavior does not depend upon protons and, in fact, is as widespread as basic behavior is not yet widely accepted. So, although a few more such examples are mentioned in this paper, the principal emphasis is upon systematic application of the new theory to acid catalysis.

II. ACID CATALYSIS

Evidence has been cited previously to show that the common Friedel–Crafts type catalysts such as aluminum chloride, ferric chloride, stannic chloride, and zinc chloride are acids (51). Their catalytic activity is well known in connection with organic reactions, but it is not usually recognized that they also catalyze such common reactions as those of metals with water. The reaction of iron with pure water to give hydrogen is a very slow one because the concentration of hydrogen ions (hydrated, of course) is so low. Any acid sufficiently strong to increase the hydrogen-ion concentration substantially will accelerate the reaction. It is immaterial whether the acid is molecular hydrogen chloride, acetic acid, sulfur trioxide, carbon dioxide, stannic chloride or ionic zinc chloride or cupric sulfate. The rate of reaction depends upon increasing the hydrogen-ion concentration, which in turn depends upon the concentration and strength of the acid which is displacing protons from the water. We shall see that this increase in positive-ion concentration is typical of acid catalysis. Obviously these ideas may have a far-reaching effect on the study of corrosion. Corrosion of metals is a complex subject, but it would seem that application of the electronic theory of acids and bases might be helpful in its investigation.

The Friedel–Crafts catalysts are usually thought of as halides of a few metals, so a natural question to raise might be: If these halides are really acids differing in no fundamental manner from H-acids in their behavior, why do not H-acids catalyze reactions of the Friedel–Crafts type also? The answer is that they do. Hydrogen fluoride (78), phosphoric acid, and sulfuric acid (14, 32) have been established as catalysts for Friedel–Crafts and similar reactions.



The catalytic activity of sulfuric acid seems especially interesting. Depending on the concentration of water or of sulfur trioxide, either sulfur trioxide or the

H-acid or both may be responsible for the catalysis. Lewis and Bigeleisen[2] have shown (10) that the very rapid increase in the acidity function of Hammett and Deyrup as 100 per cent sulfuric acid is approached is probably due to sulfur trioxide. This might indicate that in the sulfonation of benzene the sulfur trioxide is the principal agent in a direct electrophilic attack.

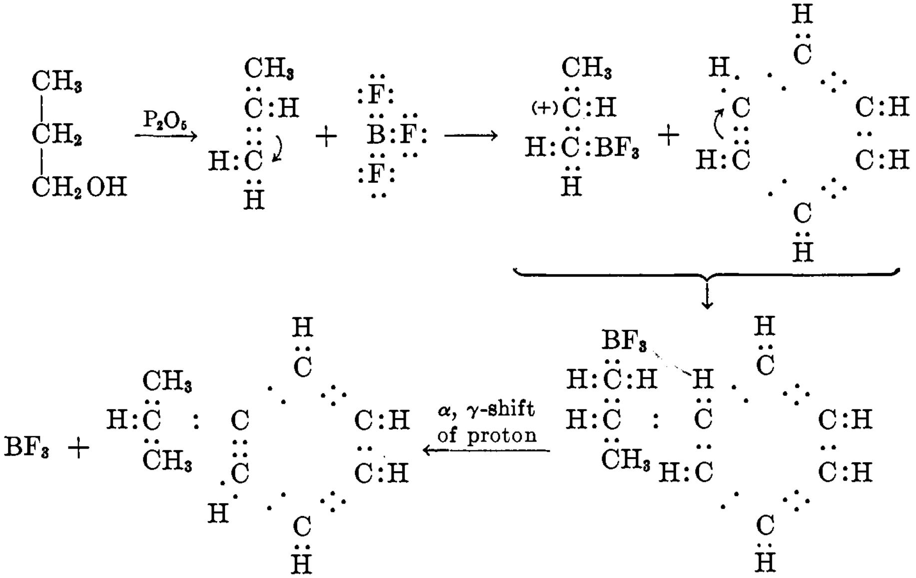
The examples listed below have been chosen because of their familiarity to most chemists. The application of a new terminology to well-known facts is always helpful in acquiring facility in its use.

A. FRIEDEL–CRAFTS REACTIONS

The mechanisms of Friedel–Crafts reactions have been studied extensively. The alkylations involve the use of olefins, alkyl halides, alcohols, ethers, and esters. The acylations make use of acids, esters, acid halides, and acid anhydrides. This type of reaction is *acid-catalyzed,* using such compounds as boron, aluminum, iron, tin, and other metallic halides, as well as sulfuric acid, phosphorus pentoxide, orthophosphoric acid, and hydrogen fluoride. These act as acids in the catalytic activity described because they all have a strong tendency to accept a share in an electron-pair as the first step in the reaction.

1. Alkylations

(*a*) *Alcohols:* Toussaint and Hennion (91) alkylated benzene with alcohols, using boron trifluoride as the acid catalyst and phosphorus pentoxide, sulfuric acid, and benzenesulfonic acid as assistants. They explained the mechanism on the basis of a dehydration of the alcohol to an olefin:



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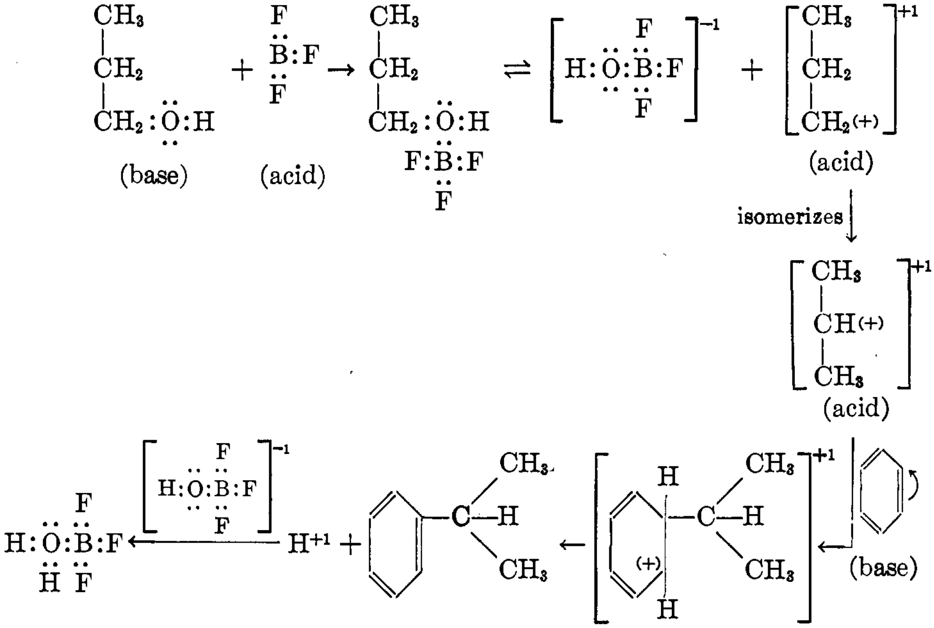
[2] The similarity of the absorption curves for methylene blue in stannic chloride and in sulfuric acid, given by the same authors, is a striking demonstration of the essential likeness in the behavior of these two acids toward indicators.

The fact that benzyl alcohol can be used to give diphenylmethane (80), however, seems to indicate that the mechanism involving olefin formation as a prlieminary step is not likely.

A preferable mechanism (56, 59, 95) would seem to be as follows:

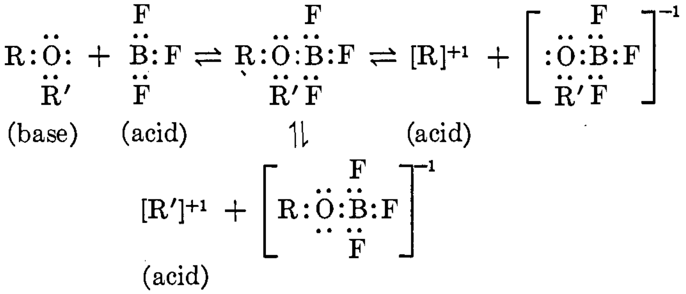


The first step involves the typically acidic behavior of boron trifluoride in accepting a share in a pair of electrons from the alcohol oxygen to form a coördinate bond. The alcohol is then behaving as a base just as it does according to the Brönsted theory when hydrogen chloride is added to it. The ionization which occurs produces a "positive fragment" (69) which is itself acidic, since it has a great tendency to accept a share in an electron-pair. The formation of this acid is exactly analogous to any acid–base displacement in which one acid displaces another from combination with a base. The catalytic effect of boron trifluoride in producing this positive fragment is also analogous to the catalytic effect of similar acids in increasing the "positive fragment" concentration in water, i.e., the hydrogen-ion concentration. As pointed out above, the acceleration of the reaction between iron and water in the presence of hydrogen chloride, sulfur trioxide, aluminum chloride, zinc chloride, etc., depends upon the increase in the concentration of hydrogen ions or "positive fragments" in the water. This seems to be typical of acid catalysis. The acid catalyst increases the speed of the reaction by increasing by displacement the concentration of the acid group involved in the reaction.

The use of hydrogen fluoride as an acid catalyst in the alkylation of benzene and phenol with alcohols has also been reported (80, 82, 84). This again indicates the similarity between boron trifluoride and H-acids. It is interesting to note that hydrogen fluoride does not effect methylations, although aluminum chloride does (84). This seems to indicate that aluminum chloride is a stronger acid than hydrogen fluoride.

(*b*) *Ethers:* The catalytic effect of boron trifluoride on alkylations with ethers (59, 63, 73) involves an acid–base reaction between boron trifluoride and ether. That this is a true acid–base reaction can be readily demonstrated by titrations in different solvents and with various indicators (54). The positive fragment that results from the ionization then reacts with the benzene, as previously described.

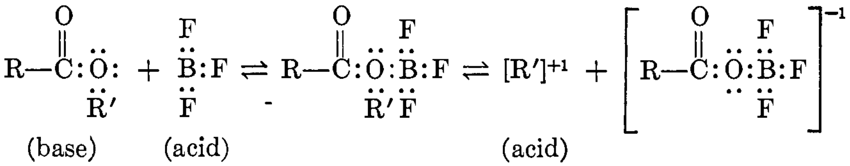
Hydrogen fluoride (80) has also been used to catalyze these reactions. Whether or not the acid contains hydrogen, the behavior is essentially the same. The acid accepts a share in a pair of electrons from the base to form a coördinate bond. Ionization into single ions may then occur if the dielectric constant is high enough and the ions can be solvated. In media of very low dielectric constant considerable association into higher ionic multiples is to be expected (22, 23, 53, 93), but this usually does not have to be indicated in the equations.



$$\underset{\text{(base)}}{R:\underset{R'}{\ddot{\underset{..}{O}}}:} + \underset{\text{(acid)}}{\overset{F}{\underset{F}{B}}:F} \rightleftharpoons R:\underset{R'}{O}:\overset{F}{\underset{F}{B}}:F \rightleftharpoons \underset{\text{(acid)}}{[R]^{+1}} + \left[:\underset{R'}{O}:\overset{F}{\underset{F}{B}}:F\right]^{-1}$$

$$\rightleftharpoons \underset{\text{(acid)}}{[R']^{+1}} + \left[R:O:\overset{F}{\underset{F}{B}}:F\right]^{-1}$$

(*c*) *Esters:* The behavior of esters toward acids may result in an alkylation or an acylation depending on the relative tendencies of acyl, alkyl, and aryl groups to become acidic ions in the presence of aluminum chloride, boron trifluoride, metallic halides, or H-acids. The alkylation mechanism (11, 57, 62) can be represented as:

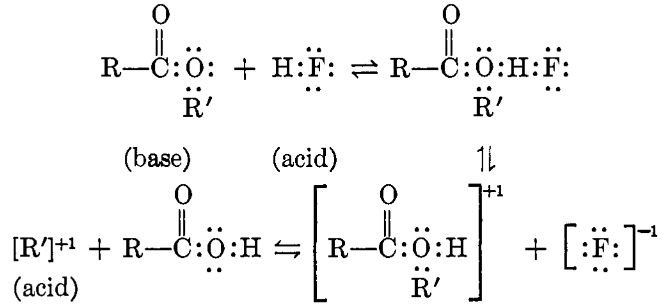


$$\underset{\text{(base)}}{R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}:\underset{R'}{O}:} + \underset{\text{(acid)}}{\overset{F}{\underset{F}{B}}:F} \rightleftharpoons R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}:\underset{R'}{O}:\overset{F}{\underset{F}{B}}:F \rightleftharpoons \underset{\text{(acid)}}{[R']^{+1}} + \left[R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}:O:\overset{F}{\underset{F}{B}}:F\right]^{-1}$$

The acyl group, being more electrophilic than the alkyl (R′) group, will not be released and, therefore, in the presence of an aromatic compound an alkylation will result.

However, if R′ is an aryl group which is more strongly electrophilic, then the acyl group will be released as a carbonium ion and acylation will result. This reaction is discussed further under the section on acylation.

The following mechanism has been suggested (83) for the hydrofluoric acid-catalyzed alkylation:

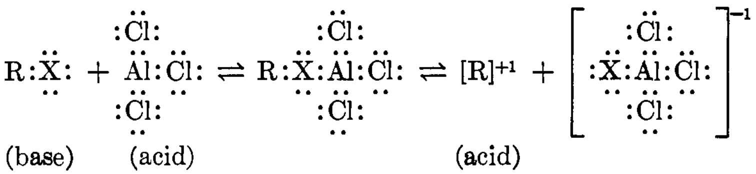


$$\underset{\text{(base)}}{\mathrm{R{-}\underset{R'}{\overset{O}{\overset{\|}{C}}}{:}\ddot{O}{:}}} + \underset{\text{(acid)}}{\mathrm{H{:}\ddot{F}{:}}} \rightleftharpoons \mathrm{R{-}\underset{R'}{\overset{O}{\overset{\|}{C}}}{:}\ddot{O}{:}H{:}\ddot{F}{:}}$$

$$\underset{\text{(acid)}}{[\mathrm{R'}]^{+1}} + \mathrm{R{-}\overset{O}{\overset{\|}{C}}{:}\ddot{O}{:}H} \leftrightharpoons \left[\mathrm{R{-}\underset{R'}{\overset{O}{\overset{\|}{C}}}{:}\ddot{O}{:}H}\right]^{+1} + [{:}\ddot{F}{:}]^{-1}$$

Again the action of the catalyst is essentially the same whether hydrogen is present or not.

(*d*) *Alkyl halides:* Conductance studies (8, 96) indicate the formation of ionic complexes between the catalyst and the alkyl halide:

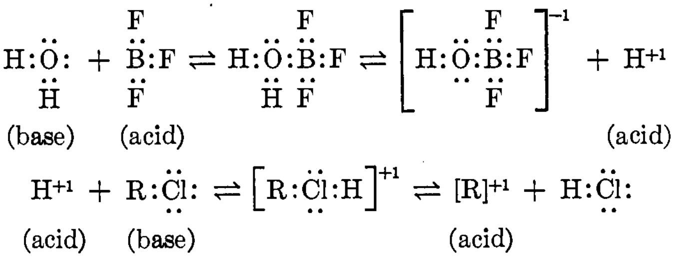


$$\underset{\text{(base)}}{\mathrm{R{:}\ddot{X}{:}}} + \underset{\text{(acid)}}{\mathrm{\underset{:\ddot{Cl}:}{\overset{:\ddot{Cl}:}{\ddot{Al}}}{:}\ddot{Cl}{:}}} \rightleftharpoons \mathrm{R{:}\ddot{X}{:}\underset{:\ddot{Cl}:}{\overset{:\ddot{Cl}:}{\ddot{Al}}}{:}\ddot{Cl}{:}} \rightleftharpoons \underset{\text{(acid)}}{[\mathrm{R}]^{+1}} + \left[\mathrm{{:}\ddot{X}{:}\underset{:\ddot{Cl}:}{\overset{:\ddot{Cl}:}{\ddot{Al}}}{:}\ddot{Cl}{:}}\right]^{-1}$$

According to the Lewis concept of acids and bases the catalyst in this reaction behaves as an acid, while the halide reacts as a base. Many other metallic halides will catalyze this reaction in a similar manner. All of them can be shown to be acids by titrating with indicators in the proper solvent (44).

Simons and Archer (79) report the use of hydrogen fluoride as the catalyzing agent. They (78) found that the tertiary halides react readily at 0°C., the secondary halides require a temperature of 25°C., but the primary halides react only at higher temperatures (80°C.), thereby affording an approximation of the relative acid characteristics of these alkyl groups. These facts are in agreement with other data on the electrophilic properties of these groups (19, 20).

Wohl and Wertyporoch (102) have reported that boron trifluoride will not catalyze the alkylation of benzene by alkyl chlorides. Recently Hennion and Kurtz (29) have found that the presence of water or alcohol helps the reaction as follows:

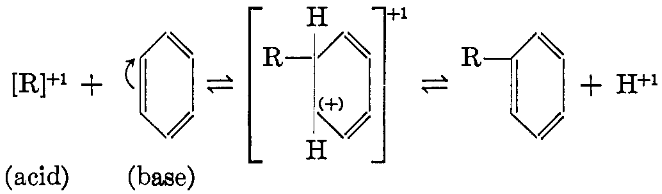


$$\underset{\text{(base)}}{\mathrm{H{:}\underset{H}{\ddot{O}}{:}}} + \underset{\text{(acid)}}{\mathrm{\underset{F}{\overset{F}{\ddot{B}}}{:}F}} \rightleftharpoons \mathrm{H{:}\underset{H}{\ddot{O}}{:}\underset{F}{\overset{F}{\ddot{B}}}{:}F} \rightleftharpoons \left[\mathrm{H{:}\ddot{O}{:}\underset{F}{\overset{F}{\ddot{B}}}{:}F}\right]^{-1} + \underset{\text{(acid)}}{\mathrm{H}^{+1}}$$

$$\underset{\text{(acid)}}{\mathrm{H}^{+1}} + \underset{\text{(base)}}{\mathrm{R{:}\ddot{Cl}{:}}} \rightleftharpoons \left[\mathrm{R{:}\ddot{Cl}{:}H}\right]^{+1} \rightleftharpoons [\mathrm{R}]^{+1} + \underset{\text{(acid)}}{\mathrm{H{:}\ddot{Cl}{:}}}$$

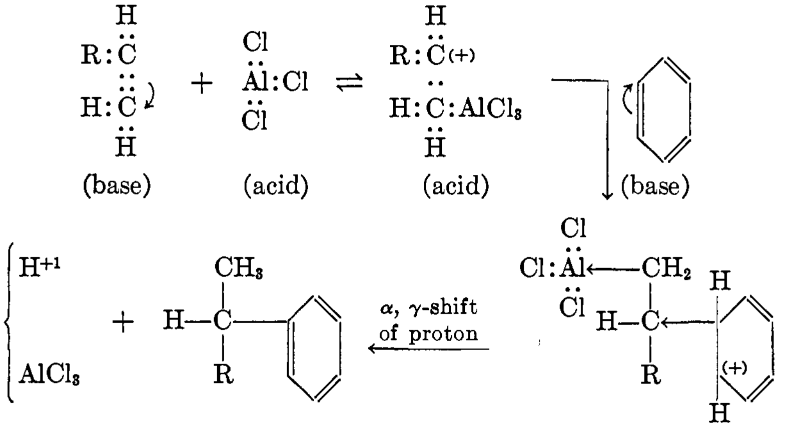
Burwell and Archer (14) report that although the alkyl chlorides and bromides are not catalyzed by boron trifluoride, the alkyl fluorides will react vigorously. They attribute this to the greater stability of the BF_4^{-1} ion as contrasted with the BF_3Br^{-1} ion or the BF_3Cl^{-1} ion.

The "positive fragments" formed as a result of these acid–base reactions alkylate or acylate aromatic compounds through an electrophilic mechanism involving the electron-deficient carbonium ion (R^+) (69).



(*e*) *Olefins:* Olefins can be employed for the alkylations of aromatic compounds by using acid catalysts such as hydrogen fluoride (77), sulfuric acid (32), phosphoric acid (34), phosphorus pentoxide (92), boron trifluoride (33, 87, 103), and aluminum chloride (31, 72).

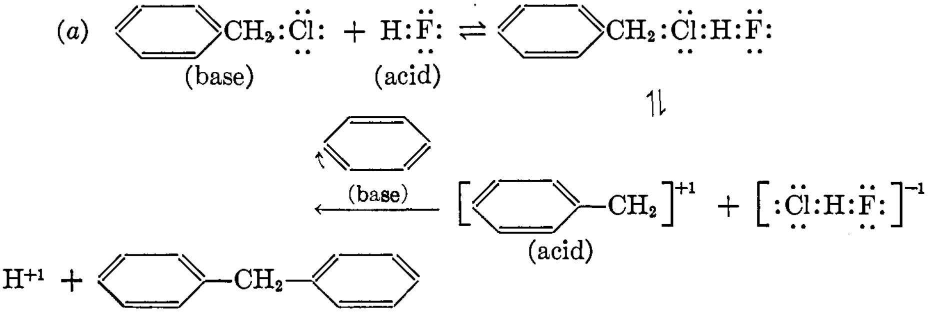
The condensation of olefins with aromatic compounds has been explained through an electrophilic mechanism involving the acid–base concept. The electrophilic (acidic) catalyst reacts with the electrodotic (basic) olefin to form an acidic intermediate which can react with the aromatic compound which is electrodotic. The reactions seem to be (69):



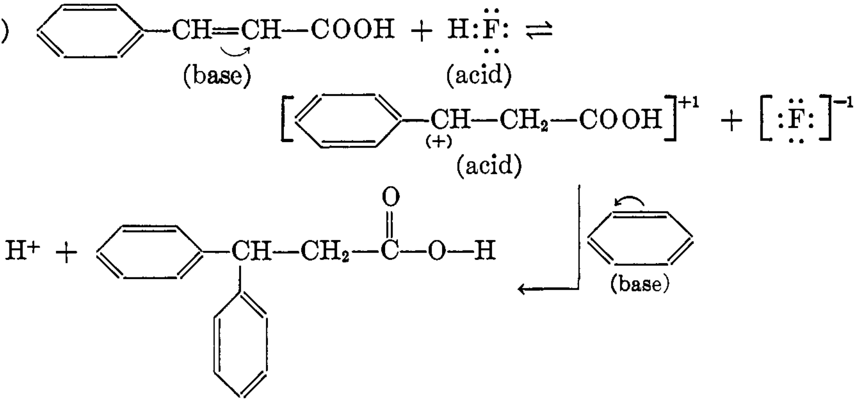
(*f*) *Allylic groups:* Simons and Archer (81) investigated the alkylations of benzene using benzyl chloride, cinnamic acid, and allyl alcohol as the alkylating agents and hydrogen fluoride as the acid catalyst. The products they obtained are in agreement with those that might be predicted on the basis of the polarization or polarizability of the alkylating agents. Boron trifluoride, stannic chloride, and other acid catalysts also will catalyze these alkylations.

Possible mechanisms might be as follows:

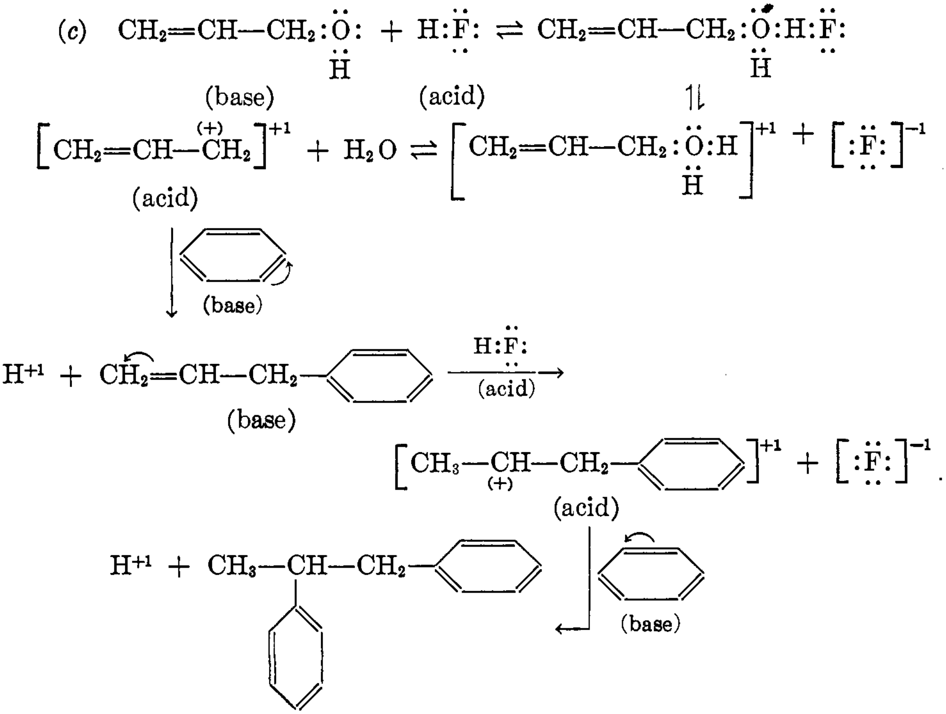
(a)



(b)



(c)

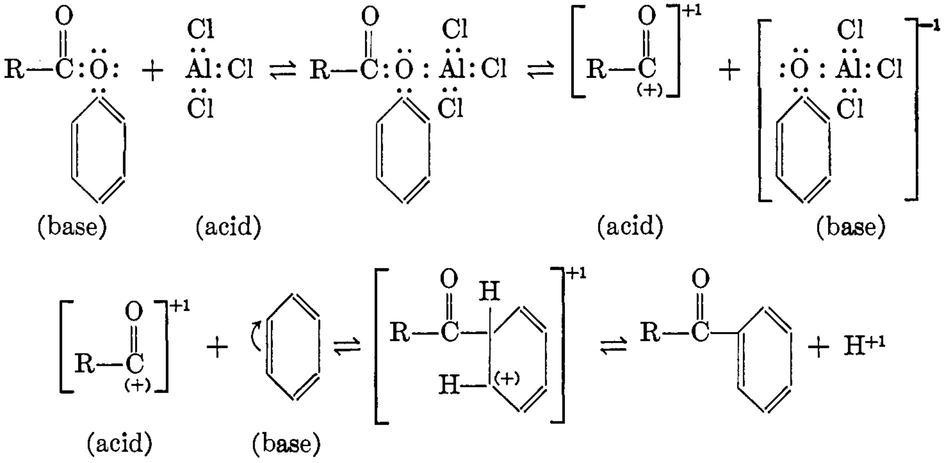


With allyl alcohol the first point of electrophilic attack is at the carbon–oxygen bond, thus producing an allyl carbonium ion which will attack a benzene molecule to produce the 3-phenyl-1-propene. This product is very susceptible to electrophilic attack by the catalyst because of the polarization of the molecule. Thus a carbonium ion would be produced that on reaction with benzene would produce the 1,2-diphenylpropane. The polarization indicated is supported by the fact that practically no 1,3-diphenylpropane is formed in the reaction.

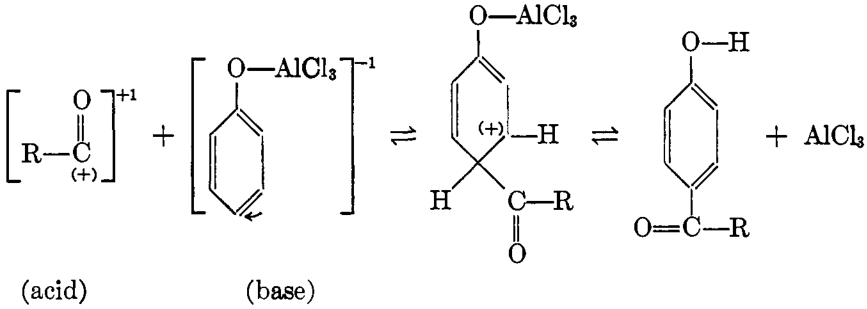
The use of sulfuric acid as an electrophilic catalyst produces much larger amounts of the 1,2-diphenylpropane and less of the 3-phenyl-1-propene.

2. Acylations

(*a*) *Esters:* Acylation by esters (11, 13, 17, 36, 57, 98), mentioned in a preceding section, can be catalyzed by aluminum chloride, boron trifluoride, metallic halides, and H-acids as catalysts. The possible mechanism is represented by the following equations:

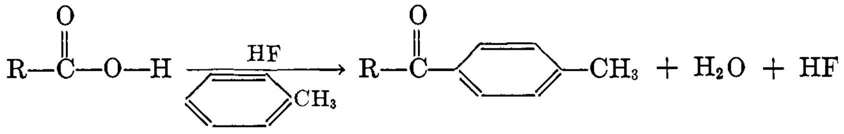


The Fries reaction (7) may be explained on the same basis, i.e.,

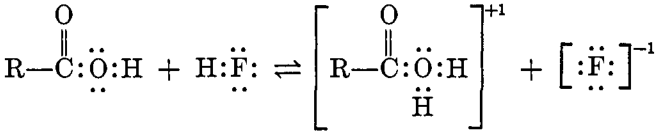


In this special case of an acylation there is an intramolecular reaction between the acidic acyl group and the electrodotic aromatic nucleus. The fact that ortho and para derivatives are obtained can readily be explained on the basis of increased electron density at these positions, an increase which facilitates the electrophilic attack of the carbonium ion.

(*b*) *Acids:* Acids (86) have been employed for acylations using hydrogen fluoride as a catalyst:



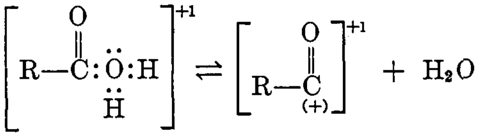
Simons (76) reports that carboxylic acids dissolved in liquid hydrogen fluoride produce conducting solutions:



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{:}\ddot{\underset{\cdot\cdot}{O}}{:}H + H{:}\ddot{\underset{\cdot\cdot}{F}}{:} \rightleftharpoons \left[R{-}\overset{\overset{\displaystyle O}{\|}}{C}{:}\ddot{\underset{\cdot\cdot}{O}}{:}H \atop \quad\;\; H\right]^{+1} + \left[{:}\ddot{\underset{\cdot\cdot}{F}}{:}\right]^{-1}$$

(base) (acid)

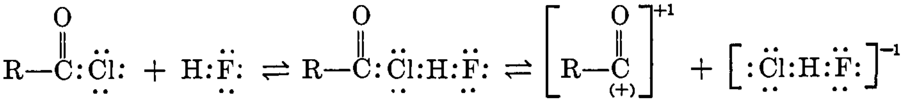
The resulting cation will then dissociate to form water and the acyl carbonium ion, which will acylate an aromatic compound through an electrophilic attack.



$$\left[R{-}\overset{\overset{\displaystyle O}{\|}}{C}{:}\ddot{\underset{\cdot\cdot}{O}}{:}H \atop \quad\;\; H\right]^{+1} \rightleftharpoons \left[R{-}\underset{(+)}{\overset{\overset{\displaystyle O}{\|}}{C}}\right]^{+1} + H_2O$$

It will be noted that these weak carboxylic acids are being forced to act as bases by the much stronger acids used as catalysts.

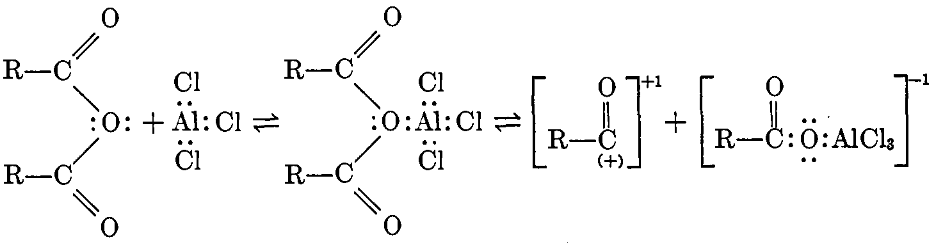
(*c*) *Acyl halides:* The mechanism of the acylation reaction of the acid halides (76, 86) could also be explained on the basis of the following equation:



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{:}\ddot{\underset{\cdot\cdot}{Cl}}{:} + H{:}\ddot{\underset{\cdot\cdot}{F}}{:} \rightleftharpoons R{-}\overset{\overset{\displaystyle O}{\|}}{C}{:}\ddot{\underset{\cdot\cdot}{Cl}}{:}H{:}\ddot{\underset{\cdot\cdot}{F}}{:} \rightleftharpoons \left[R{-}\underset{(+)}{\overset{\overset{\displaystyle O}{\|}}{C}}\right]^{+1} + \left[{:}\ddot{\underset{\cdot\cdot}{Cl}}{:}H{:}\ddot{\underset{\cdot\cdot}{F}}{:}\right]^{-1}$$

(base) (acid) (acid)

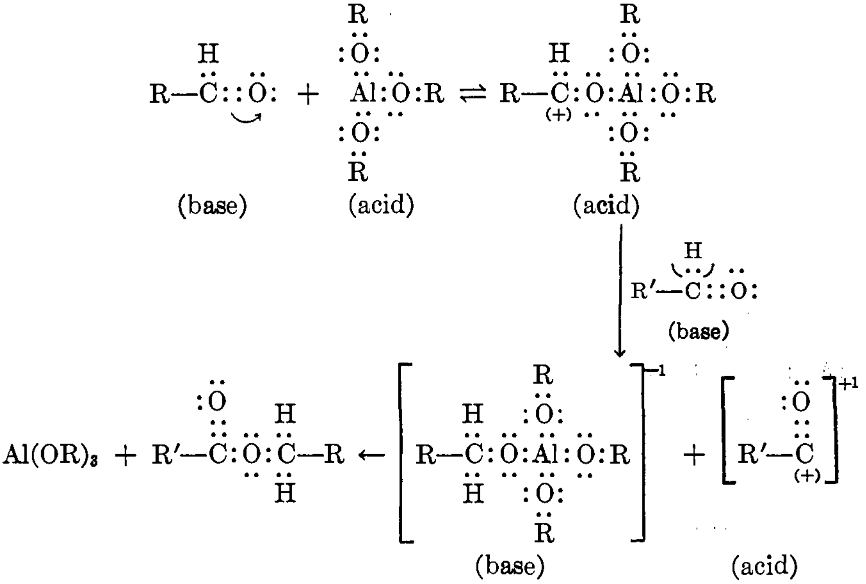
(*d*) *Acid anhydrides:* The mechanism of the acid-catalyzed acylations using an acid anhydride as the acylating agent could be written as follows:



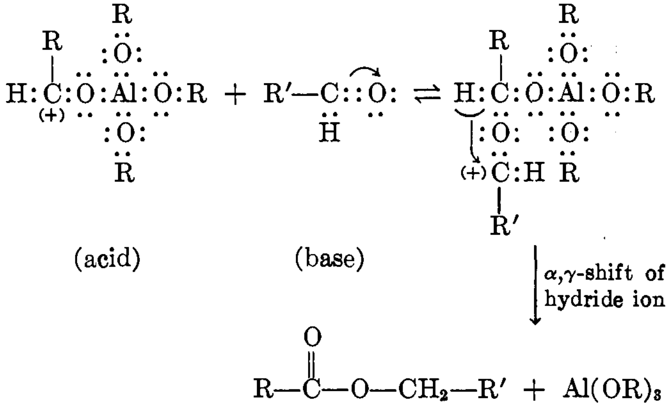
(base) (acid) (acid)

B. CANNIZZARO REACTION

A special case of the Cannizzaro reaction results in the direct formation of an ester from two molecules of an aldehyde (15, 90). The catalytic agent used here is a generalized acid. The aluminum ethylate coördinates with a molecule of the aldehyde, acting as a base, and produces an acidic intermediate. The next step has been considered as the removal of a hydride ion from a second molecule of aldehyde as follows:



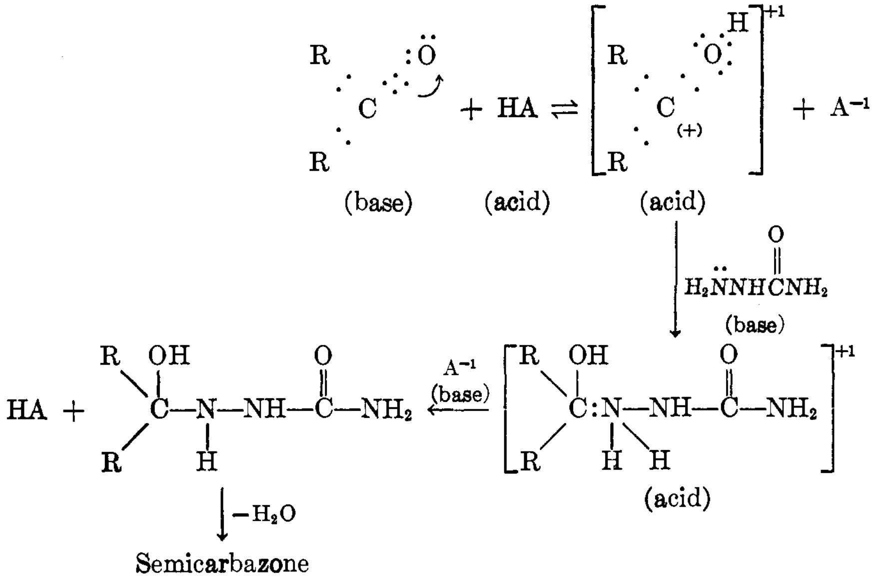
On the basis of the Lewis theory a more logical explanation would seem to be a typical acid–base reaction. The electron-deficient carbon atom of the aldehyde which is coördinated with the acidic aluminum ethylate shares a pair of electrons from another aldehyde oxygen atom acting as a base, followed by an α,γ-shift of the hydride ion:



This is a striking illustration of how the consistent application of the Lewis acid–base concepts leads to a more logical interpretation of reaction mechanisms.

C. SEMICARBAZONE REACTION

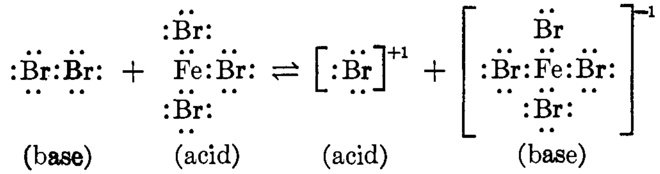
The formation of a semicarbazone of a carbonyl compound can be explained in terms of the new terminology. The acid catalyst coördinates with the carbonyl oxygen, which is electrodotic. The resulting carbonium ion behaves as an acid and thus coördinates with the semicarbazide nitrogen (16, 97).

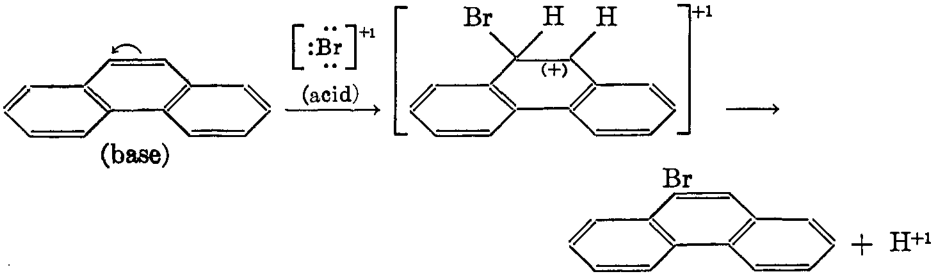


D. HALOGENATION

1. *Aromatic compounds*

The halogenation of aromatic compounds probably has a mechanism similar to that of the Friedel–Crafts reactions, which take place through the formation of an ionic complex (58, 64, 65, 70, 100, 101).





$$\underset{\text{(acid)}}{H^{+1}} + \underset{\text{(base)}}{FeBr_4^{-1}} \longrightarrow HBr + FeBr_3$$

Other acidic compounds such as antimony pentachloride, stannic chloride, and iodine can catalyze the reaction through the hetero-fission of the bromine molecule and the formation of the polar complex.

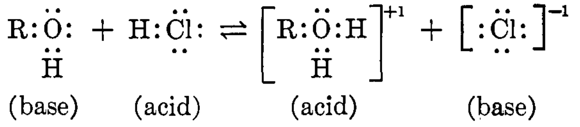
Benzene can be iodinated under anhydrous conditions by the use of silver perchlorate as a catalyst (4, 5, 6). One suggested mechanism is:

$$\underset{\text{(base)}}{:\underset{\cdot\cdot}{\ddot{\mathrm{I}}}:\underset{\cdot\cdot}{\ddot{\mathrm{I}}}:} + \underset{\text{(acid)}}{\mathrm{AgClO_4}} \longrightarrow \mathrm{Ag}:\underset{\cdot\cdot}{\ddot{\mathrm{I}}}: + \mathrm{ClO_4^{-1}} + \left[:\underset{\cdot\cdot}{\ddot{\mathrm{I}}}\right]^{+1}$$

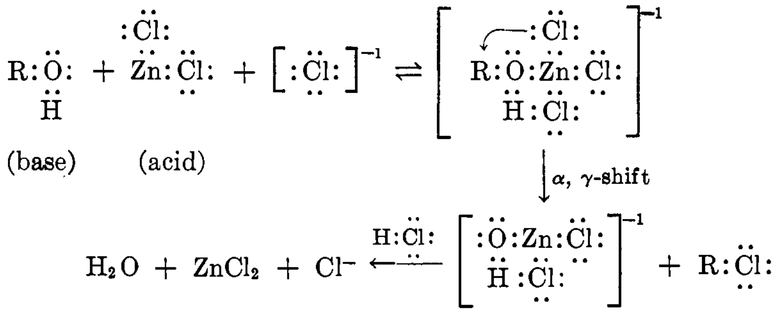
Such a simple ionic equation is probably inadequate because of the high ionic association observed in benzene (52, 92). However, there is no doubt that silver ion is acidic, as shown by its behavior in forming complexes in water and by its effect on indicators in other solvents (44).

2. Alcohols

The catalytic action of zinc chloride on the conversion of alcohols to halides is well known. The catalyst used is an acid which coördinates with the basic alcohol. An α,γ-shift of the chlorine atom accounts for the formation of the organic halide (50).

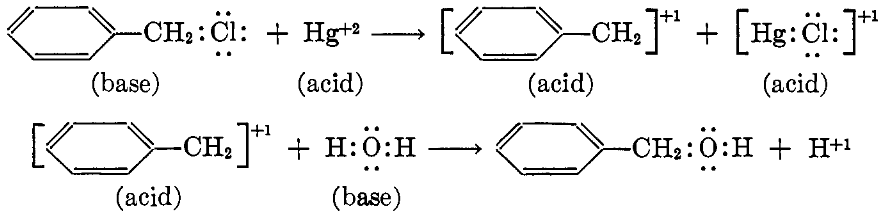


$$\underset{\text{(base)}}{\underset{\mathrm{H}}{\mathrm{R}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:}} + \underset{\text{(acid)}}{\mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:} \rightleftharpoons \underset{\text{(acid)}}{\left[\underset{\mathrm{H}}{\mathrm{R}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\mathrm{H}}\right]^{+1}} + \underset{\text{(base)}}{\left[:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:\right]^{-1}}$$



E. HYDROLYSIS

The hydrolysis of benzyl chloride is catalyzed by the presence of Hg^{+2} salts (74). The electrophilic Hg^{+2} salts are here behaving as acids and react with the organic halide to form a carbonium ion:



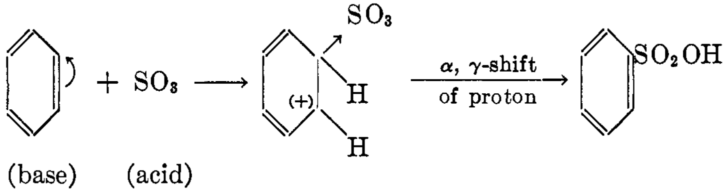
F. SULFONATION AND NITRATION

Boron trifluoride has been reported as an acid catalyst in sulfonation and nitration reactions (89). The amounts of catalyst required indicated that the reaction proceeds as follows:

$$RH + HOSO_2OH + BF_3 \longrightarrow RSO_2OH + [H_2O{\rightarrow}BF_3]$$

$$RH + HONO_2 + BF_3 \longrightarrow RNO_2 + [H_2O{\rightarrow}BF_3]$$

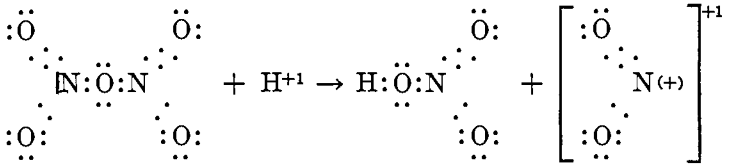
Since the rate of sulfonation increases with increasing acid concentration in sulfuric acid of less than 100 per cent concentration and with the concentration of sulfur trioxide in fuming acid (55, 66, 67), the sulfonation probably takes place largely through the typically acidic displacement of a proton by the acid SO_3.

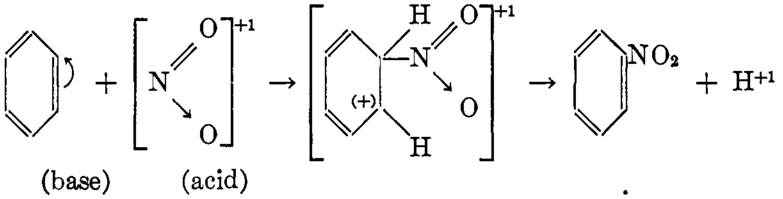


The catalytic function of the boron trifluoride seems to be to increase the concentration of the sulfur trioxide by combining with the water to form $[H_2O{\rightarrow}BF_3]$

$$H_2SO_4 + BF_3 \rightarrow SO_3 + [H_2O{\rightarrow}BF_3]$$

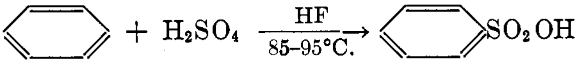
The actual nitrating mechanism is not known, but it may possibly involve nitrogen pentoxide, as suggested by Price (71).



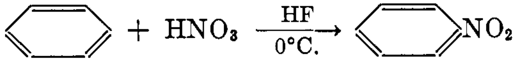


The catalytic effect of the boron trifluoride might be due to increasing the nitrogen pentoxide concentration by combining with the water to form the coördination compound.

Hydrogen fluoride has recently been reported as having a strong catalytic effect on sulfonation and nitration reactions (85).



(75 per cent yield)



(83 per cent yield)

G. SUMMARY

In all the examples of acid catalysis considered above the characteristic effect of the acid catalyst is the increase in concentration of the acid group involved in the reaction. In most cases this is accomplished by the familiar displacement of one acid by another. In a few cases displacement does not result, but the combination of the acid with the reacting substance merely localizes the electron deficiency on one atom, which can then act acidically. One example of this is alkylation by olefins.

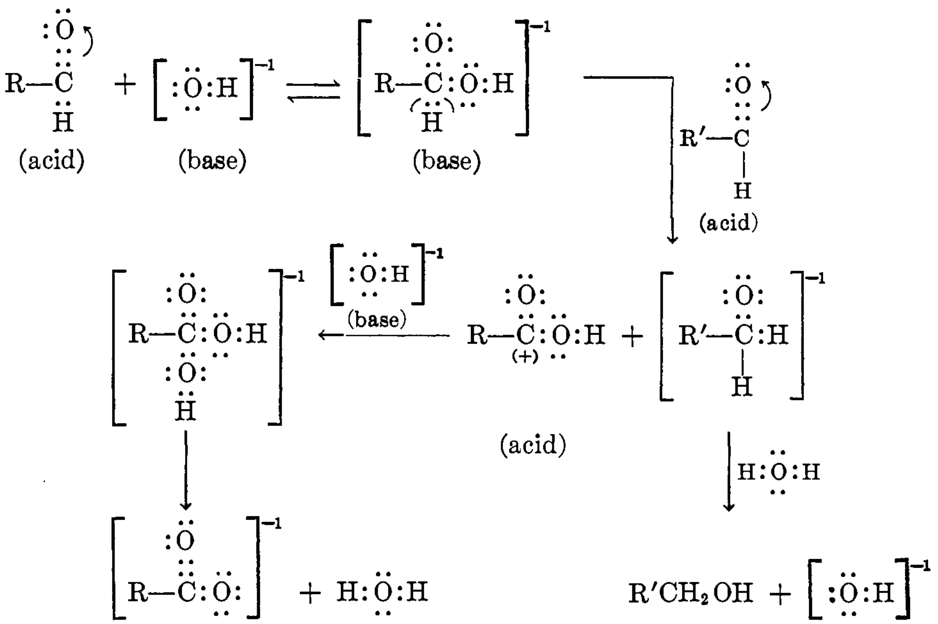
Either way, the net result is the characteristic increase in the concentration of the acid group. The effect is the same whether the catalyst is an H-acid or any other acid.

III. BASE CATALYSIS

The examples of basic substances used as catalysts in the following illustrations do not differ fundamentally from those considered as illustrations of the Brönsted concept of a base. Admittedly, these substances are proton acceptors, *but* they can and do react with acid substances other than protons. The proton is only one of many acid groups or compounds having similar electrophilic characteristics. Brönsted's bases are proton acceptors because they can furnish lone pairs of electrons to form a coördinate bond with an acid whether or not the acid is a proton, a hydronium ion, a neutral H-acid, or any other electron-pair acceptor.

A. CANNIZZARO REACTION

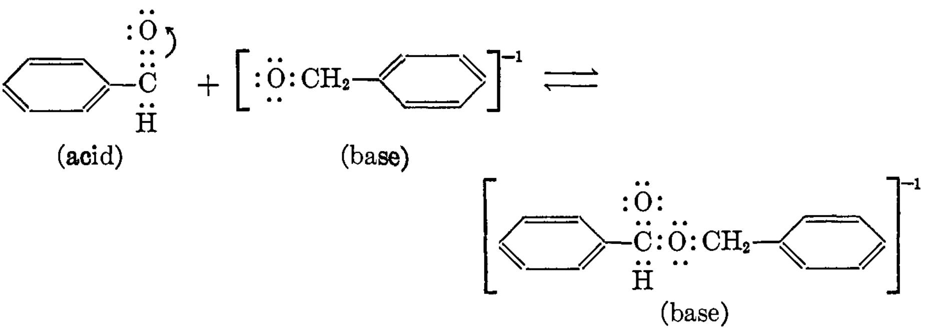
Fundamentally, the base-catalyzed Cannizzaro reaction involves the reaction between two molecules of an aldehyde containing no α-hydrogen atoms. The over-all result is the transfer of one aldehyde hydrogen to another aldehyde group, thus producing two radicals that could combine to form an ester. In most cases the presence of the basic catalyst prevents the ester formation and there results an alcohol and a metal carboxylate (19, 24, 68). The mechanism can be shown as follows:



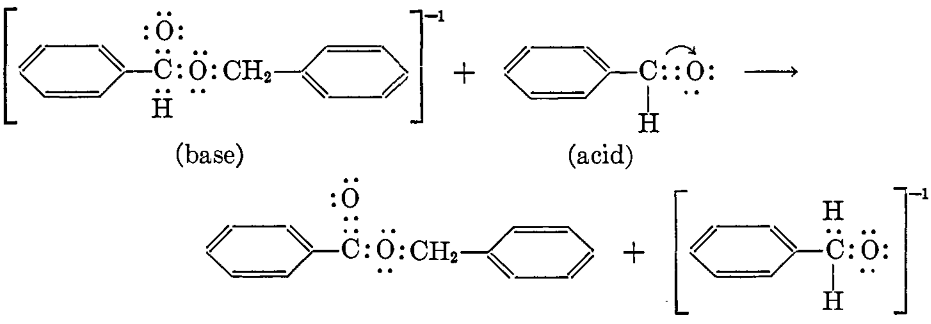
The amphoteric nature of benzaldehyde is shown by this base-catalyzed reaction and by the previously discussed acid-catalyzed reaction to form an ester. In the former the carbonyl oxygen offers a share in an electron-pair to the acid catalyst, and in the latter the carbonyl carbon accepts a share in an electron-pair from the basic catalyst. In the base-catalyzed reactions of aldehydes containing no α-hydrogen the effect of the entering basic catalyst is to shift the carbon-hydrogen electron-pair toward the hydrogen, thus favoring $\overset{+}{\mathrm{C}}\text{—}\overset{-}{\mathrm{H}}$ rather than $\overset{-}{\mathrm{C}}\text{—}\overset{+}{\mathrm{H}}$. This is true only with electron release groups such as OH^{-1} and $OC_2H_5^{-1}$ ions. This change enables a hydride ion to be split off more easily than would be the case if the basic catalyst were an electron-withdrawal group, such as the cyanide ion. This latter group would cause the carbon–hydrogen electron-pair to shift $\overset{-}{\mathrm{C}}\text{—}\overset{+}{\mathrm{H}}$ rather than $\overset{+}{\mathrm{C}}\text{—}\overset{-}{\mathrm{H}}$ and thus favor the removal of a proton rather than a hydride ion. This might explain the specificity of the cyanide ion as a basic catalyst in the benzoin condensation, which will be discussed later.

The reaction in deuterium water (21) results in an alcohol containing no deuterium hydrogen attached to the carbon. This indicates that the transfer of a hydrogen from one aldehyde molecule to another does not involve water in the transfer mechanism.

Another example of the acidic behavior of the amphoteric aldehyde and the basic action of a catalyst in this type of reaction is the formation of benzyl benzoate under anhydrous conditions.

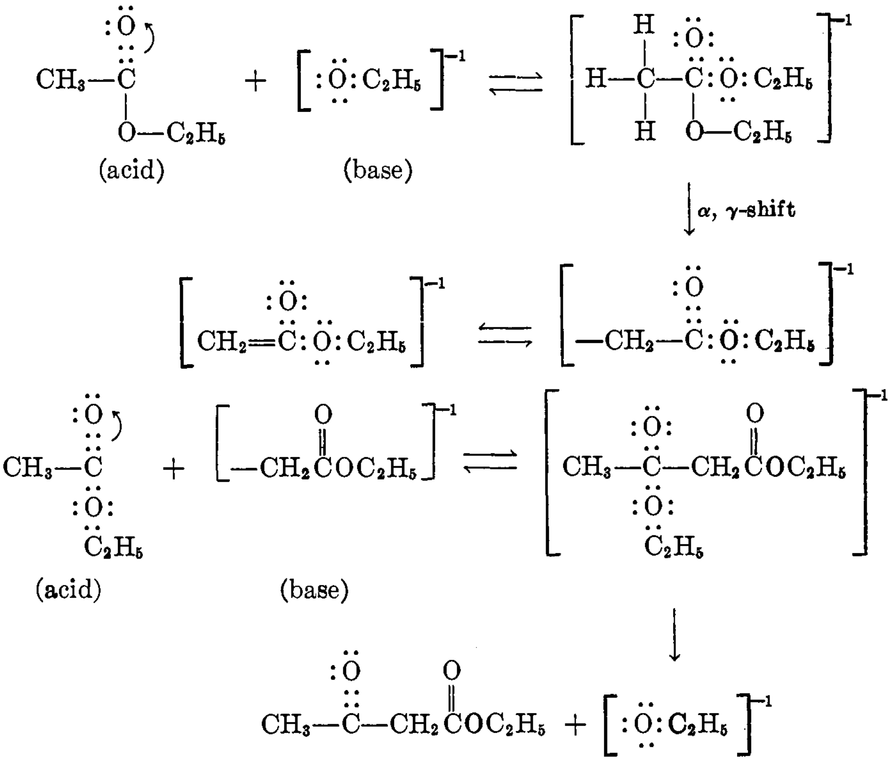


A second molecule of aldehyde reacts as an acid with this intermediate and removes a hydride ion, thus forming the neutral ester molecule and at the same time regenerating the basic catalyst, i.e., the benzylate ion:



B. THE CLAISEN REACTION

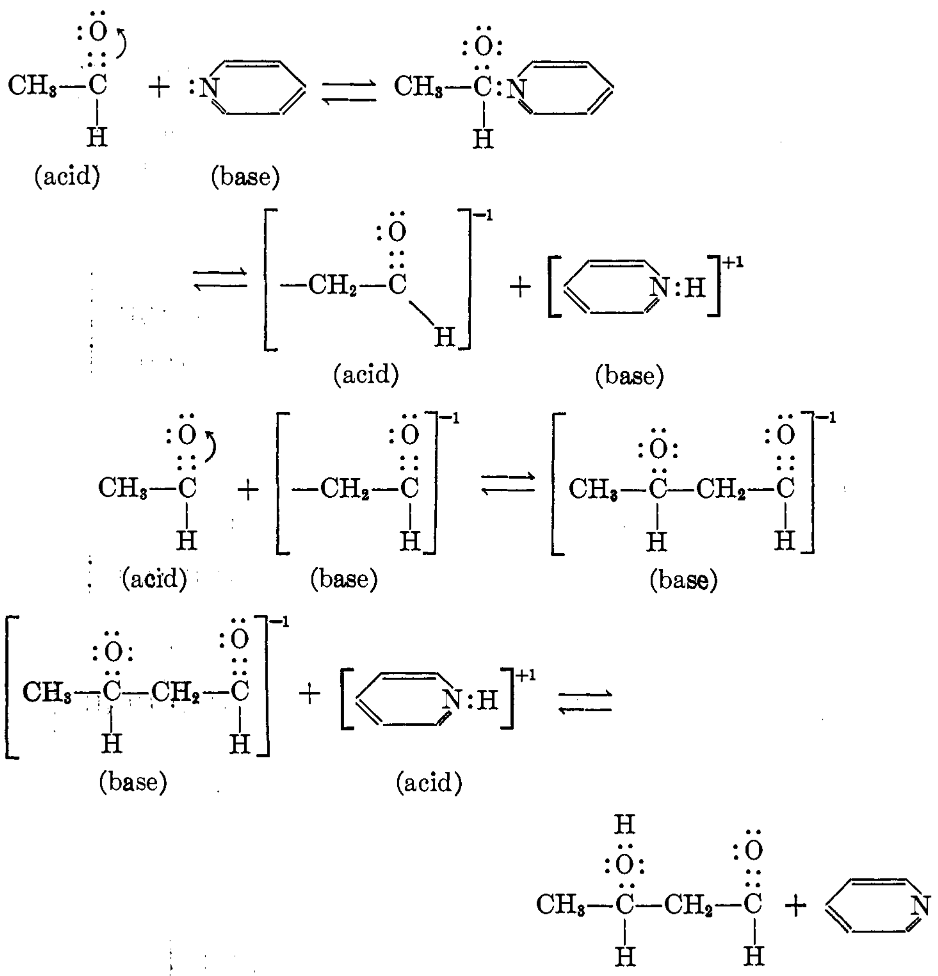
The Claisen reaction (1, 26, 27, 88) probably involves an ionic mechanism, the first step of which is an acid–base exchange in the presence of the basic ethylate ion. This exchange probably takes place through the formation of an intermediate coördinate complex, followed by an α,γ-shift and ionization to form the ester anion.



Evidence of anion ester formation according to the reactions given has been obtained (61, 75). Other bases can be used as catalysts in these condensations. The use of the triphenylmethyl carbanion has been reported in recent years (28, 30, 61, 75).

C. ALDOL CONDENSATIONS

The synthetic importance of these condensations is known to all organic chemists. A wide variety of compounds can be prepared through the condensation of two carbonyl compounds. The catalysts used are bases such as acetates, carbonates, pyridine, and amines (3). These catalytic agents are bases according to both the Lewis and the Brönsted theories. The mechanism of the reaction is represented as follows:



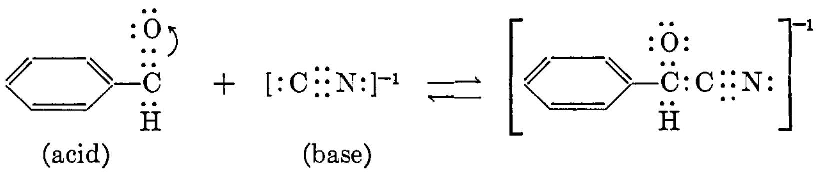
When the reaction is carried out in deuterium water (9) no deuterium hydrogen becomes attached to the carbon, indicating that water takes no direct part in the mechanism of the reaction.

The formation of diacetone alcohol has been carefully studied (38, 41). The reaction is catalyzed by ammonia, primary amines, and secondary amines (94).

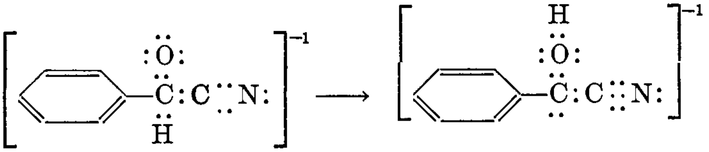
D. THE BENZOIN CONDENSATION

The specificity of the basic cyanide ion used as a catalyst in the formation of benzoin has been considered puzzling and apparently no adequate explanation has yet been suggested (25). Hydrogen cyanide, mercuric cyanide, and sodium hydroxide have no effect on the rate of benzoin formation, while sodium cyanide, potassium cyanide, and barium cyanide have a powerful catalytic effect (42).

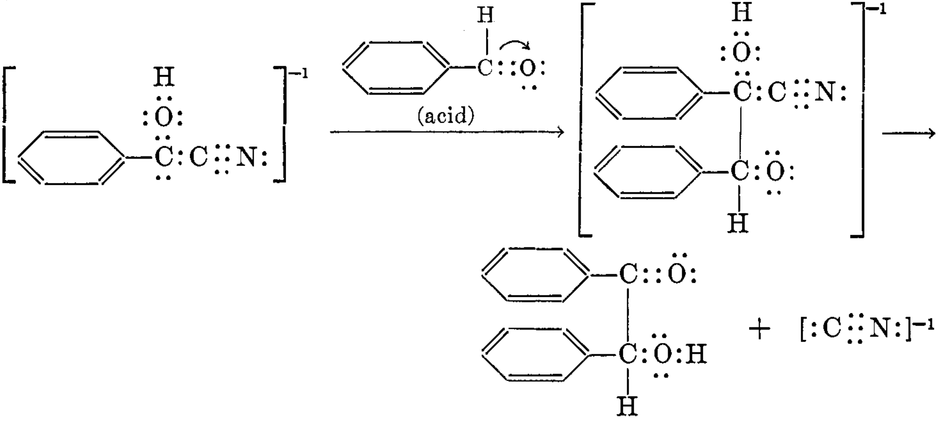
The kinetics of the reaction, however, leave little doubt that the following mechanism exists:



In the product formed the cyanide group, which is an electron-withdrawal group, greatly activates the α-hydrogen by causing an electron displacement in the C—H bond which results in $\overset{-}{C}$—$\overset{+}{H}$ rather than $\overset{+}{C}$—$\overset{-}{H}$. Therefore, instead of a hydride ion, a proton is split off by the oxygen of a similar molecule. The net result can be considered as a shift of a proton from the carbon to the oxygen of the carbonyl group. It seems reasonable to suspect that the specificity of the cyanide ion as a catalyst for this reaction is due to the fact that it has electron-withdrawal properties. The other common basic catalysts, such as OH^{-1}, $OC_2H_5^{-1}$, and the amines, all have electron-release properties, which would cause the electron shift to $\overset{+}{C}$—$\overset{-}{H}$ and thus produce a hydride ion rather than a proton.



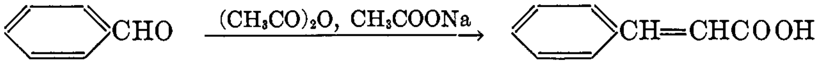
A second molecule of the benzaldehyde reacts acidically with this basic complex as follows:



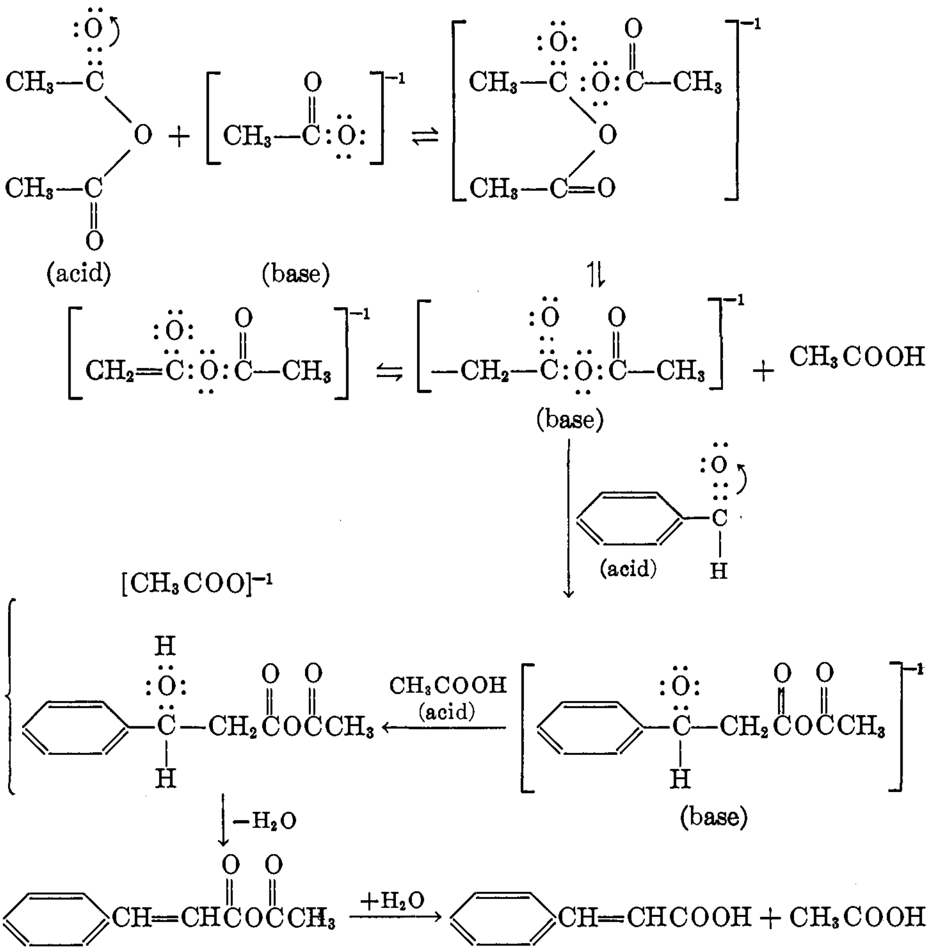
E. THE PERKIN REACTION

Fundamentally, this reaction involves an aldehyde, an acid anhydride, and the sodium salt of its acid. Although much controversy has existed in regard to the function of the anhydride and its salt, it is now generally accepted that the anion of the salt serves the function of a basic catalyst (35). Many other bases such as alkali-metal acetates, carbonates, sulfites, phosphates, pyridine, quinoline, and triethylamine (2, 40, 60) have been used for the condensation.

Although the over-all reaction is represented as:

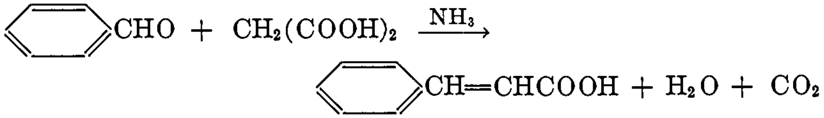


the mechanism of the reaction can be shown as follows:



F. THE KNOEVENAGEL REACTION

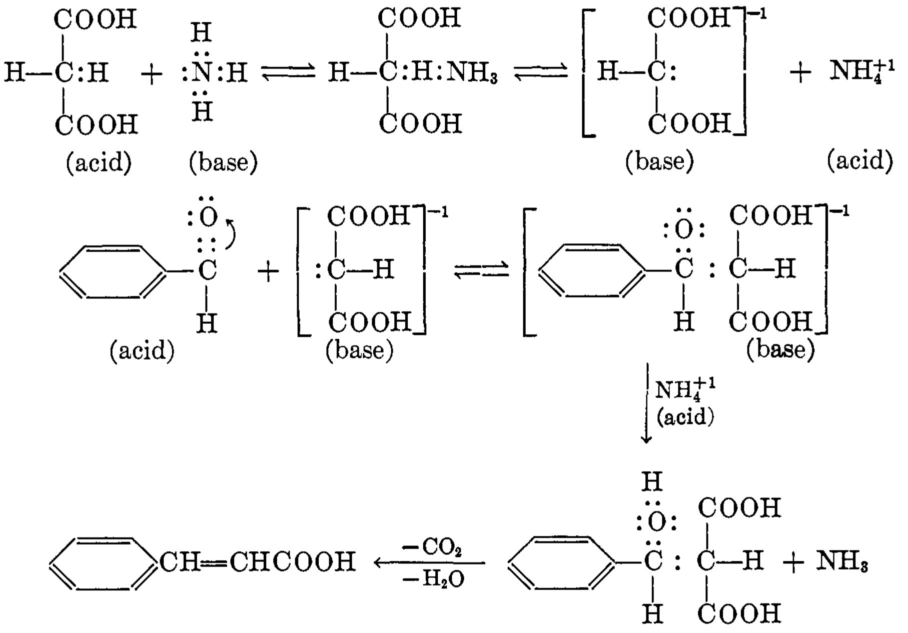
Aldehydes will condense readily with malonic acid (37) in the presence of basic catalysts:



$$CH_3CHO + CH_2(COOH)_2 \xrightarrow{C_6H_5N} CH_3CH{=}CHCOOH + H_2O + CO_2$$

Ammonia, pyridine, primary and secondary amines, and especially piperidine, all of which are basic compounds, have been used as catalysts (12, 18, 20, 39).

The mechanism can be explained as follows:



G. SUMMARY

In all the examples of basic catalysis considered above the characteristic effect of the basic catalyst is the increase in concentration of the basic group involved in the reaction. In most cases this is done by the familiar displacement of one base by another: for example, the displacement of the ester anion from ethyl acetate by the ethylate ion catalyst in the Claisen reaction. In some cases displacement apparently does not result, but the combination of the basic catalyst with the reacting substance merely localizes the electron excess on one atom, which can then act basically. An example of this is the shifting of the electron-pair of the C—H linkage toward the hydrogen in the base-catalyzed Cannizzaro reaction, thus enabling a second molecule of aldehyde to remove a hydride ion.

IV. CONCLUSION

In presenting these examples of acid–base catalysis, no attempt has been made to survey the literature for every possible case to which the new terminology might be applied. The reactions which have been discussed were chosen primarily to show how consistently this terminology can be applied to familiar chemical behavior. In many cases the reaction mechanisms obviously can be interpreted adequately as isolated phenomena without reference to the Lewis theory. It is only as these catalytic reactions are correlated with each other and with a large body of other phenomena that any great benefit is to be expected from the application of the theory. The insight gained from such a systematic use of the theory should do much to stimulate chemical thinking and research.

The four experimental criteria of acids and bases listed by Lewis (44) are: (I) neutralization, (II) displacement of an acid or base by a stronger acid or base, (III) titration with indicators, (IV) catalytic effects. Previous papers (44, 51) have given examples of the acid properties of many other substances besides H-acids according to the first three of these criteria. It has been shown in those papers that the behavior of substances like sulfur trioxide, boron trifluoride, aluminum chloride, stannic chloride, and silver perchlorate is analogous to the behavior of H-acids in neutralization, in displacement, and toward indicators.

The catalytic effect of these substances is well known. So in demonstrating their similarity to H-acids in this respect it is necessary to reverse the comparison made by means of the first three criteria. The behavior of H-acids must be shown to be analogous to the behavior of sulfur trioxide, boron trifluoride, aluminum chloride, stannic chloride, and silver perchlorate, rather than *vice versa*. It has been shown in the present paper that this is the case. Sulfuric acid, phosphoric acid, and hydrogen fluoride show catalytic activity similar to that of the strong non-hydrogen acids. It is apparent that the presence of a particular element is unnecessary for a substance to behave as an acid. Instead, whether hydrogen is present or not, acidity depends upon the electrophilic character of the reagent *and* upon the electrodotic character of the base.

The characteristic behavior of acids and bases toward amphoteric solvents has been discussed in a previous paper (51). If the acid is strong enough, it will increase the concentration of solvent cations. One acid displaces another. For example, sulfur trioxide displaces hydrogen ions from water. If a sufficiently strong base reacts with an amphoteric solvent, the concentration of solvent anions is increased. The base displaces the basic ion from the solvent. For example, piperidine displaces hydroxyl ions from water. In this paper it has been shown that analogous behavior is responsible for acidic and basic catalysis. Acidic catalysis is due to the increased concentration of the acidic group involved in the reaction—caused by the addition of the acid catalyst. Basic catalysis is due to a similarly increased concentration of the basic group involved in the reaction.

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