SURVEY ON CONDITIONS CATALYSIS OF CHEMICAL REACTIONS

NAGHAM MAHMOOD ALJAMALI
Organic Chemistry, Chemistry Department, College of Education, Iraq

ABSTRACT

The addition of catalysis affects in rate of a reaction. It assumes that you are already familiar with basic ideas about the collision theory of reaction rates. Note that this is only a preliminary look at catalysis as far as it affects rates of reaction.

KEYWORDS: Catalysis, Oxidize, Reagent, Reduce, Condition, Rate

INTRODUCTION

A catalyst is a substance which speeds up a reaction, but is chemically unchanged at the end of the reaction. When the reaction has finished, you would have exactly the same mass of catalyst as you had at the beginning.

Some examples: Some common examples which you may need for other parts of your syllabus include

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decomposition of hydrogen peroxide</td>
<td>manganese(IV) oxide, MnO₂</td>
</tr>
<tr>
<td>Nitration of benzene</td>
<td>concentrated sulphuric acid</td>
</tr>
<tr>
<td>Manufacture of ammonia by the Haber Process</td>
<td>iron</td>
</tr>
<tr>
<td>Conversion of SO₂ into SO₃ during the Contact Process to make sulphuric acid</td>
<td>vanadium(V) oxide, V₂O₅</td>
</tr>
<tr>
<td>Hydrogenation of a C=C double bond</td>
<td>nickel</td>
</tr>
</tbody>
</table>

The Explanation

The Key Importance of Activation Energy

Collisions only result in a reaction if the particles collide with a certain minimum energy called the activation energy for the reaction.

You can mark the position of activation energy on a Maxwell-Boltzmann distribution to get a diagram like this:
Only those particles represented by the area to the right of the activation energy will react when they collide. The great majority don't have enough energy, and will simply bounce apart.

**Catalysts and Activation Energy**

To increase the rate of a reaction you need to increase the number of successful collisions. One possible way of doing this is to provide an alternative way for the reaction to happen which has a lower activation energy.

In other words, to move the activation energy on the graph likes this:

![Figure 2](image)

**Figure 2**

Adding a catalyst has exactly this effect on activation energy. A catalyst provides an alternative route for the reaction. That alternative route has a lower activation energy. Showing this on an energy profile:

![Figure 3](image)

**Figure 3**
Be very careful if you are asked about this in an exam. The correct form of words is "A catalyst provides an alternative route for the reaction with a lower activation energy."

It does not "lower the activation energy of the reaction". There is a subtle difference between the two statements that is easily illustrated with a simple analogy.

Suppose you have a mountain between two valleys so that the only way for people to get from one valley to the other is over the mountain. Only the most active people will manage to get from one valley to the other.

Now suppose a tunnel is cut through the mountain. Many more people will now manage to get from one valley to the other by this easier route. You could say that the tunnel route has a lower activation energy than going over the mountain.

But you haven't lowered the mountain! The tunnel has provided an alternative route but hasn't lowered the original one. The original mountain is still there, and some people will still choose to climb it.

In the chemistry case, if particles collide with enough energy they can still react in exactly the same way as if the catalyst wasn't there. It is simply that the majority of particles will react via the easier catalysed route.

FACTORS AFFECTING RATE OF A CHEMICAL REACTION (Catalysis and Conditions)

Following are the main factors that influence the rate of a chemical reaction.

- **NATURE OF REACTANTS**

  Different reactants have different energies of activation. Reaction between polar or ionic molecules is very fast. Oxidation-Reduction reactions are slower than ionic reactions because they involve transfer of electrons and bond rearrangement. The physical states of reacting substances are important in determining their reactivities. The reaction in which ionic solutions are involved also take place at high speed

- **CONCENTRATION OF REACTANTS**

  The concentration of reactants plays an important role in chemical kinetics. It is usually true that by increasing the
amount of reactants, the rate of reaction is increased. As we know that an increase in concentration of reactants increases the number of molecules. According to collision theory, the greater the number of molecules the higher is the collision ratio, consequently faster is the rate of reaction.

- **SURFACE AREA OF REACTANTS**

  In heterogeneous reactions, the rate of reaction depends upon the surface area of solid reactant. Greater the surface area, higher is the rate of reaction. For example finely divided calcium carbonate (marble) reacts more quickly with hydrochloric acid than calcium carbonate chips. It is due to the fact that powered calcium carbonate offers larger surface area to the reacting acid. In other words, by increasing the surface area of reactant, rate of reaction increases due to greater contact between individual particles and also due to the fact that the surface molecules reacts more quickly.

- **TEMPERATURE**

  The rate of reaction increases with the rise of temperature. It can be explain by the fact that at higher temperature, a greater fraction of colliding molecules posse the necessary energy of activation

  Generally an increase of every $10^9K$ in temperature doubles the rate.

  As the temperature increases the velocity of molecules also increases which results in the increase in the frequency of collision.

  The rise in temperature rises the kinetic energy of each molecule. It has been found that by raising the temperature by 10k, the fraction of molecule possessing threshold or activation energy becomes double. As a result the no of effective collision is also double, hence rate is doubled

![Figure 5](image-url)

**PRESENCE OF CATALYST (Conditions of Reaction)**

A catalyst is a substance, which controls the rate of reaction without itself undergoing a permanent chemical change. Catalysts are of two types
POSITIVE CATALYST

A positive catalyst increases the rate of reaction by lowering the energy of activation. Thus in the presence of a positive catalyst, the greater fraction of the total molecule will possess lower energy of activation and collided successfully in a short period of time, thereby increasing the rate of reaction.

NEGATIVE CATALYST OR INHIBITOR

A negative catalyst retards the rate of reaction. Negative catalyst do not lower the energy of activation rather they are combined with reactant molecule thus decreasing the number of colliding reactant molecules. This decreases the effective collisions, hence rate of reaction.

ROLE OF POSITIVE CATALYST

A positive catalyst functions by providing an alternate path to the reaction or by the formation of a transition (intermediate) compound having low energy of activation. The activation energy of this path is lower. As a result rate of reaction is increased.

ROLE OF NEGATIVE CATALYST

A negative catalyst does not lower the energy of activation rather it combines with the reactant molecules, thus decreasing the number of colliding reactant molecules. This decreases the effective collisions, hence rate of reaction.

Oxidative Catalysis

Condition of Reaction

Catalytic oxidations are processes that oxidize compounds using catalysts. Common applications involve oxidation of organic compounds by the oxygen in air. Such processes are conducted on a large scale for the remediation of pollutants, production of valuable chemicals, and the production of energy.[1]

An illustrative catalytic oxidation is the conversion of methanol to the more valuable compound formaldehyde using oxygen in air:

\[ 2\text{CH}_3\text{OH} + \text{O}_2 \rightarrow 2\text{CH}_2\text{O} + 2\text{H}_2\text{O} \]

This conversion is very slow in the absence of catalysts. Typical oxidation catalysts are metal oxides and metal carboxylates.

Examples

Industrially important examples include both inorganic and organic substrates.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Process</th>
<th>Catalyst (Homogeneous or Heterogeneous)</th>
<th>Product</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>sulfur dioxide</td>
<td>contact process</td>
<td>vanadium pentoxide (heterogeneous)</td>
<td>sulfuric acid</td>
<td>fertilizer production</td>
</tr>
<tr>
<td>ammonia</td>
<td>Ostwald</td>
<td>platinum</td>
<td>nitric acid</td>
<td>basic chemicals, TNT</td>
</tr>
</tbody>
</table>
Applied Catalysis

Oxidation catalysis is conducted by both heterogeneous catalysis and homogeneous catalysis. In the heterogeneous processes, gaseous substrate and oxygen (or air) are passed over solid catalysts. Typical catalysts are platinum and redox-active oxides of iron, vanadium, and molybdenum. In many cases, catalysts are modified with a host of additives or promoters that enhance rates or selectivities.

Important homogeneous catalysts for the oxidation of organic compounds are carboxylates of cobalt, iron, and manganese. To confer good solubility in the organic solvent, these catalysts are often derived from ethylhexanoic acid, which are highly lipophilic. These catalysts initiate radical chain reactions, autoxidation that produce organic radicals that combine with oxygen to give from naphthenic acids hydroperoxide intermediates. Generally the selectivity of oxidation is determined by bond energies. For example benzylic C-H bonds are replaced by oxygen faster than aromatic C-H bonds.[2]

Examples of Oxidative Catalyst (As Condition of Reaction)

This page looks at the oxidation of alcohols using acidified sodium or potassium dichromate(VI) solution. This reaction is used to make aldehydes, ketones and carboxylic acids, and as a way of distinguishing between primary, secondary and tertiary alcohols.

Oxidising the Different Types of Alcohols

The oxidising agent used in these reactions is normally a solution of sodium or potassium dichromate (VI) acidified with dilute sulphuric acid. If oxidation occurs, the orange solution containing the dichromate (VI) ions is reduced to a green solution containing chromium (III) ions.
The electron-half-equation for this reaction is

\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\]

**Partial Oxidation to Aldehydes**

\[
8\text{CH}_3\text{CH}_2\text{OH} + \text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ \rightarrow 8\text{CH}_3\text{CHO} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\]

In organic chemistry, simplified versions are often used which concentrate on what is happening to the organic substances. To do that, oxygen from an oxidising agent is represented as [O]. That would produce the much simpler equation:

\[
\text{CH}_3\text{CH}_2\text{OH} + [\text{O}] \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O}
\]

It also helps in remembering what happens. You can draw simple structures to show the relationship between the primary alcohol and the aldehyde formed.

**Oxidation Reactions of Alcohols**

Simple 1 and 2 alcohols in the gaseous state lose hydrogen when exposed to a hot copper surface. This catalytic dehydrogenation reaction produces aldehydes (as shown below) and ketones, and since the carbon atom bonded to the oxygen is oxidized, such alcohol to carbonyl conversions are generally referred to as oxidation reactions. Gas phase dehydrogenations of this kind are important in chemical manufacturing, but see little use in the research laboratory.

Instead, alcohol oxidations are carried out in solution, using reactions in which the hydroxyl hydrogen is replaced by an atom or group that is readily eliminated together with the alpha-hydrogen. The decomposition of 1 and 2 alkyl hypochlorites, referred to earlier, is an example of such a reaction.

\[
\text{RCH}_2\text{OH} + \text{hot Cu} \rightarrow \text{RCH} = \text{O} + \text{H}_2
\]

\[
\text{RCH}_2\text{O}^-\text{Cl} + \text{base} \rightarrow \text{RCH} = \text{O} + \text{H}^-\text{Cl}
\]

The most generally useful reagents for oxidizing 1º and 2º-alcohols are chromic acid derivatives. Two such
oxidants are Jones reagent (a solution of sodium dichromate in aqueous sulfuric acid) and pyridiniumchlorochromate, 
\( \text{C}_5\text{H}_5\text{NH}^+\text{CrO}_3\text{Cl}^- \), commonly named by the acronym PCC and used in methylene chloride solution. In each case a chromate ester of the alcohol substrate is believed to be an intermediate, which undergoes an E2-like elimination to the carbonyl product. The oxidation state of carbon increases by 2, while the chromium decreases by 3 (it is reduced). Since chromate reagents are a dark orange-red color (VI oxidation state) and chromium III compounds are normally green, the progress of these oxidations is easily observed. Indeed, this is the chemical transformation on which the Breathalyzer test is based. The following equations illustrate some oxidations of alcohols, using the two reagents defined here. Both reagents effect the oxidation of 2alcohols to ketones, but the outcome of 1º-alcohol oxidations is different. Oxidation with the PCC reagent converts 1alcohols to aldehydes; whereas Jones reagent continues the oxidation to the carboxylic acid product, as shown in the second reaction. Reaction mechanisms for these transformations are displayed on clicking the "Show Mechanism" button. For the first two reactions the mechanism diagram also shows the oxidation states of carbon (blue Arabic numbers) and chromium (Roman numbers). The general base (B-) used in these mechanisms may be anything from water to pyridine, depending on the specific reaction.
Reduction is defined in chemistry as loss of oxygen, gain of hydrogen or gain of electrons; the gain of electrons enables you to calculate an oxidation state.

Hydride Reagents and Dihydrogen

Lithium Aluminum Hydride

LiAlH₄ is a strong, unselective reducing agent for polar double bonds, most easily thought of as a source of H⁺. It will reduce aldehydes, ketones, esters, carboxylic acid chlorides, carboxylic acids and even carboxylate salts to alcohols. Amides and nitriles are reduced to amines. In each case the partially negative hydrogen reacts with the partially positive carbon of the substrate. It can also be used to reduce nitro groups and even as a nucleophile to displace halide from an sp³ carbon or open an epoxide.

Why does it work? Remember that aluminum is a metal with a low electronegativity; thus, the Al-H bond is strongly polarized with Al positive and H negative. The abnormal polarization (and oxidation state of -1) for hydrogen, which is normally positive, results in a high reactivity, especially with atoms that can accept electrons (be reduced), allowing the hydrogen to become positive again (normal oxidation state of +1).

Precautions: It reacts with other positive centers as well, especially any slightly acidic hydrogens, like those of alcohols, water, carboxylic acids or alkynes to produce hydrogen gas, which is highly flammable and can readily explode (e.g. the Hindenberg). LiAlH₄ requires anhydrous conditions for the reaction and usually an excess of the reagent (to soak up any water that was missed in the glassware or reagents); the most common solvent for the reactions is diethyl ether. "Workup" at the end of the reaction is usually done by careful addition of aqueous acid (remember the flammable hydrogen gas and ether), followed by extraction of the organic products from the water-soluble salts.
To LiAlH₄ make less reactive and more selective, the hydride is made more hindered, e.g., in the compound LiAl(OtBu)₃H. It can reduce acid chlorides (and some esters) quickly, but is slow to react with aldehydes; therefore LiAl(OtBu)₃H provides a convenient way to synthesize aldehydes by reduction of acid chlorides, something that can’t be done with LiAlH₄ or NaBH₄.

**Boron Hydrides**

**Sodium Borohydride**

NaBH₄ is less reactive than LiAlH₄ but is otherwise similar. It is only powerful enough to reduce aldehydes, ketones and acid chlorides to alcohols: esters, amides, acids and nitriles are largely untouched. It can also behave as a nucleophile toward halides and epoxides. It is also convenient that, although LiAlH₄ is strong enough to reduce the C=C of a conjugated carbonyl compound, NaBH₄

Is not; thus the carbonyl group can be reduced without the alkene.

**Precautions:** NaBH₄ is unreactive enough that the reductions can be done in alcohol solution, or even water (as long as they don’t take too long); this can be advantageous for polar compounds which can be pretty insoluble in ether. Hydrolysis with acid and water followed by extraction is used to isolate the product (hydrogen gas is produced).

**Diborane and 9-BBN**

B₂H₆ is the actual molecular formula for a reagent whose simplest formula is BH₃. The boron would have only 6 electrons in BH₃; its attempt to get 8 electrons results in its sharing hydrogens and their electrons in a bridged structure shown below.

![Figure 9](image-url)

You will often find this reagent referred to as just BH₃, since it is commonly sold in solution as a complex with a base such as methylamine or in solution of a moderately high boiling ether such as THF(tetrahydrofuran) with which it also forms a complex, shown above.

B₂H₆ does not behave as a source of hydride; instead it adds to carbon-carbon double bonds in a concerted manner to place the boron (somewhat positive) on the less substituted carbon and the hydrogen (somewhat negative) on the more substituted carbon (better able to support a slight positive charge as the electrons are being reshuffled in the transition state). This addition results in an addition to (a reduction of) the double bond which puts the heteroatom on the less substituted carbon.

![Figure 10](image-url)
Since boron is less electronegative than carbon, the B is somewhat positive, and can only be replaced by other slightly positive things. Useful things like halides and hydroxides are negative and won't work; instead sources are needed which can produce positive halogen or oxygen-oxidizing agents! Reaction with bromine or chlorine (Br₂, Cl₂) produces the less substituted halide from the alkene, reaction with hydrogen peroxide (HOOH) the alcohol and chloramine (NH₂Cl) the amine. See the essays on halogens and peroxides as oxidizing agents.

Because the reaction of the B-H bond with the C=C bond is concerned, it is also stereospecific. Moreover, the subsequent reaction of the oxidizing agent retains that stereochemistry. Thus, B₂H₆ provides a method for producing not only the less substituted alcohol, etc., but only one diastereomer thereof. This control of both the regiochemistry and stereochemistry is important in the synthesis of natural products such as pheromones and antibiotics.

To improve the selectivity of the boron for the less substituted carbon, a bulky group can be added; the most common reagent of this type is 9-borabicyclo[3.3.1]nonane, 9-BBN, below. B₂H₆ can also be used to reduce carbonyl groups, but it is less convenient to use than NaBH₄.

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B₂H₆

Figure 11

Precautions for B₂H₆: Similar to NaBH₄ and LiAlH₄, with extra care since B₂H₆ is a gas. The ether solutions are of course flammable.

Dihydrogen

Since reduction is defined as addition of hydrogen, dihydrogen (H₂) would seem to be the ideal reducing agent. However, the strength of the H-H bond and the lack of polarizability of the molecule makes it extremely unreactive. Fortunately some precious metals - platinum, palladium, nickel - "react" with dihydrogen in a rather unusual way. The metals dissolve dihydrogen and partially bond to it, effectively breaking the H-H bond; platinum will dissolve more than a mole of hydrogen and swells visibly in the process - it is like a sponge. Thus these metals serve as catalysts for reactions of dihydrogen. Typically dihydrogen adds to multiple bonds - alkenes, alkynes, carbonyl compounds - in the presence of these catalysts. Since the hydrogenation reaction takes place on the surface, it is stereospecific syn.

By careful control of the reaction conditions and the exact nature of the catalyst, it is possible to reduce one kind of multiple bond without some others that are present reacting. An alkyne can be reduced to a Z (cis) alkene by "poisoning" the Pt catalyst so that the addition stops at the alkene; reagents that have been used are sulfur compounds such as barium sulfate, organic amines such as quinoline. A weakened palladium catalyst called Lindlar's catalyst (Pd with CaCO₃ and Pb(OAc)₂) is very popular too. With a weaker catalyst or much milder conditions, it is possible to reduce an alkene without reducing a carbonyl in the same molecule, even if they are conjugated.
Metals and Organometallic Reagents

The Grignard Reagent ((Mg as Catalysis)

Reaction of an alkyl halide with magnesium metal in diethyl ether results in the formation of an organo metallic compound with the magnesium replacing the halide; the second valence of the magnesium (II) is satisfied by the halide removed from the carbon.

Figure 12

The carbon has been changed from positive to negative and has been reduced; magnesium, the reducing agent, has been oxidized. This reaction changes the normal polarity of carbon in organic compounds, and that negative carbon produced is very reactive toward positive sites. The most useful reaction of the negative carbon of the Grignard is addition to carbonyl groups. It reduces aldehydes, ketones, esters, carboxylic acid chlorides to alcohols and nitriles to amines. It is unselective, adding twice to esters and carboxylic acid chlorides. Thus aldehydes give secondary alcohols, and ketones, esters, and carboxylic acid chlorides give tertiary alcohols. Nitriles give primary amines with a tertiary carbon (see amine nomenclature).

Precautions: The negative carbon of the Grignard reagent will react with almost anything that is positive; for example: the OH's of water, alcohols, carboxylic or other acids, the NH's of amines or amides, the N of nitro groups. It is essential that glassware and reagents be completely dry; the complex mechanism of Grignard formation can be completely halted by traces of water. There are also severe restrictions on the functional groups that can be in the molecule the Grignard is made from or reacting with (no polar double bonds or slightly acidic hydrogens). In addition, ether (diethyl ether or tetrahydrofuran, THF) is essential to stabilizing the Grignard reagent; if the solution becomes too concentrated the Grignard will react with the somewhat positive carbon of the starting halide as a nucleophile.

Figure 13

Aryl (aromatic) halides may also be converted into Grignard reagents; bromobenzene generates phenylmagnesium bromide, which reacts just like butylmagnesium bromide. The only restriction is that chlorobenzene is too unreactive and can only be converted to the corresponding Grignard reagent at higher temperatures, e.g. using THF as a solvent. Alkyl Grignards are most easily prepared from primary halides, followed by secondary; tertiarys are difficult; the negative carbon is responsible for these differences (compare the order of stability of positive carbon in carbocations). Halide reactivity toward magnesium is in the order I>Br>Cl.

Dialkylcopper Lithium (Lithium Dialkylcuprate) Reagents

The dialkyl copper lithium reagents are often made from Grignard reagents. R₂CuLi reagents are less reactive and more selective than Grignard reagents. They react with aldehydes and ketones only slowly but with carboxylic acid chlorides very quickly. As a result they can be used to reduce carboxylic acid chlorides to ketones without further
reduction to the tertiary alcohol. Since they are often made from the Grignard reagent, the same precautions and restrictions on structure apply. Note that their selectivity is like that of LiAl(OtBu)3H, discussed above, but of course the variable R group gives them more versatility.

**Sodium, Alkyl Sodium and Alkyl Lithium**

Treatment of alkyl halides with sodium results in a rapid oxidation of the metal, but the negative carbon of the corresponding RNa reacts with the positive carbon of the remaining RX to give RR (like a Grignard does without the ether); this is called coupling, or sometimes the Wurtz reaction. RLi’s are more manageable and is used as nucleophilic reagents for addition to carbonyl groups. More often, they are just used as strong bases, e.g. to convert an alkyne to its conjugate base.

Treatment of compounds with even slightly acidic protons with sodium metal will result in the same reaction as occurs with the acidic hydrogen of water, namely reduction of that somewhat positive hydrogen to H₂ and oxidation of the sodium to Na⁺. Useful examples include: alcohol to alkoxide (base and nucleophile), and alkyne to alkynide (nucleophile).

**Acidic Reducing Agents**

If you look at the reducing agents above, you will note that they are all basic. But there is a family of reducing agents that are acidic - a moderately reactive metal with hydrochloric acid. The Tin (Sn) or iron (Fe) with HCl can be used to reduce nitro groups to amino groups; this reduction is especially useful for making anilines since the nitrobenzenes are easy to make.

**Boron Hydrides as Reducing Reagents**
What it’s Used for

For our purposes, zinc amalgam has one important use: in the Clemmensen reduction of ketones to alkanes.

Similar to

The reagent has essentially the same effect as the Wolf-Kishner reaction, although it is done under acidic conditions.

Examples

Zinc amalgam (Zn-Hg) is most commonly used in the Clemmensen reduction, which takes ketones adjacent to aromatic rings down to the alkane. This can be useful in, say, after the Friedel-Crafts acylation when you want to obtain a straight chain alkane that would otherwise rearrange.

![Example 1: The Clemmensen reduction](image)

Figure 16

Note that the Clemmensen isn’t as effective on ketones that aren’t adjacent to aromatic systems, a sign that the reaction is probably proceeding through a carbocation or other electron-deficient intermediate that is stabilized through resonance with the aromatic ring.

How it Works:

Amalgams are alloys of mercury and other metals. They are among the oldest of reducing agents, but their precise mode of action remains somewhat mysterious. I remember reading at some point that their mode of action is not unlike that of an electrochemical cell. In the Clemmensen, addition of acid protonates the ketone, and electrons from the Zn(Hg) are delivered to the carbon; the new hydrogens come from the acid, while the oxygen is eventually expelled as water.

Real Life Tips

Although I’ve never prepared zinc amalgam, for a good time, try makingsodium amalgamthrough dropping liquid Hg into a beaker of molten Na in mineral oil. Watch that you don’t get splattered. Shulgin uses aluminum amalgam as the reductant of choice for taking ketones and aldehydes to alcohols. In PIKHALI recall him describing the preparation of aluminum amalgam through cutting conventional aluminum foil into small squares and adding a solution of mercuric chloride in water.

REFERENCES

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