Chapter-I

Section A
Chemical kinetics

The subject of chemical kinetics is concerned with the quantitative study of the rates of chemical reactions and of the factors upon which they depend.

History:

The first kinetic measurements, was carried out by Wilhelmy[1], who in 1850 measured the rate of inversion of sucrose and investigated the influence of concentration upon the rate. The important result at which he arrived was that the rate of reaction at any instant was proportional to the concentration of sucrose remaining at that time. A similar conclusion was reached in 1862 by Berthelot and St.Gilles[2], their investigations concerned mainly the equilibrium between ethanol, acetic acid, ethyl acetate and water, but they obtained some data on the rate of combination of acid and alcohol and concluded that the rate in this case was proportional to the product of the two concentrations.

In the years 1865 to 1867 Harcourt and Esson[3] published the results of their investigations on the reaction between potassium permanganate and oxalic acid. Very detailed experimental studies of rate of its variation with the concentrations of the reacting substances were carried out by Harcourt, and the results were analyzed mathematically by Esson in the manner in which this is still frequently done today.

At about the same time it was pointed out by Gulberg and Waage[4] that the laws of chemical equilibrium can be derived from the kinetic laws by assuming that at equilibrium the rates of forward and reverse reactions are the same.

In 1889 an important advance was made by Arrhenius, who explained the large increase in velocity[5] that are very often brought about by a rise in temperature.

Introduction:

The energy relations between the reactants and the products are considered in thermodynamics. An important question, which is not, touched by thermodynamics is the rate of reaction and the mechanism of reaction i.e. the stage through which the reactants pass to reach the final products, are not indicated by thermodynamics. It makes no attempts to consider the rate, at which the equilibrium is attained. Thus, chemical kinetics compliments thermodynamics by supplying information about the rate of reaction and the mechanism, by which reactants are converted to products.

When a chemical reaction takes place there is a change in concentration of the reacting substances. These concentration changes would decrease with passage of time and after a particular period of time the concentration becomes time independent. This state of the system when the properties of the system become time independent is referred to as the equilibrium state.

Chemical kinetics is the study of the rates of reactions and the factors that affect those rates. It offers technique for examining the manner in which molecules, ions etc.take part in chemical reactions. It helps us to understand the mechanism of chemical reaction, it is said that, "Mechanism is to chemistry as a grammar is to a language; there is no branch of chemistry which can be satisfactorily studied without clear grasp of the principles of mechanism."

Rate or velocity of reaction:

The rate of reaction is defined as the rate of change of concentration of the reactants or products at a given temperature.

It may be expressed as the rate of decrease of the concentration of a reactant, or as the rate of increase of a product of the reaction.

$$\text{Rate} = -\frac{d[\text{Reactant}]}{dt} \quad \text{———} \quad [a]$$

or

$$\text{Rate} = +\frac{d[\text{Product}]}{dt} \quad \text{———} \quad [b]$$

Where [reactant] and [product] refer to the concentration of reactant and product respectively.

In equation [a] the minus sign in the time derivative of concentration is required to make the rate a positive quantity. It indicates the decrease in concentration and is always associated with the reactant.

In equation [b] plus sign is always associated with product because its concentration increases.

Rate law:

At constant temperature, the rate of reaction is a function of the concentration of reactants or products. The functional relation between rate of reaction and the concentration of reactants is called the rate law or the rate expression.

Rate constant or Velocity constant:

The rate constant of a chemical reaction is measure of the rate of reaction, when all the reactants are at unit concentrations.

Rate of reaction = k x (function of concentration of reactants)

If concentrations are equal to unity then,

Rate of reaction = k

Where k = rate constant.

This is known as specific rate or rate coefficient.

The unit of rate constant depends on the unit of concentration of the substance used.

Importance of chemical kinetics in reaction mechanism:

During the course of chemical reaction, molecules come closer, atoms change their positions, electron shift takes place and as a result new compounds are formed. A sequence of steps by which the reaction occurs is known as 'reaction mechanism'. The mechanism of reaction gives a detailed picture of the activated complex[6].

The importance of the chemical kinetics lies in the fact that its usefulness in giving the information not only about the reaction rate but also of,

1) The factors that determine the reaction rate.
2) Favourable condition necessary for the production of desired product qualitatively and quantitatively.
3) The reaction intermediates governing the overall reaction.
4) Extent of reaction on time.

Thus chemical kinetics plays an important role in elucidation of reaction mechanism.

For the reaction in solution, the mechanism is formed on the basis of different kinetic parameters in which order of the reaction with respect to the different reactant is most important. Apart from order of reaction, the factors, which affect the rate of reaction are, nature of the reactants, physical state, concentration, temperature, catalyst (if any), ionic strength, solvent etc. and provide valuable information so as to suggest the most probable mechanism of the reaction.

a] Concentration:

Concentration plays an important role in reaction. According to the collision theory of chemical reaction, this is due to the fact that the molecules must collide in order to react together. As the concentration of the reactant increases, the frequency of the molecules colliding increases, striking each other faster by being in closer contact of any given point in time. Thus the increase in the concentration of the reactant increases the number of particles in a given volume, thereby increasing the effective collision rate of the molecule. The higher frequency of collisions results in a higher rate of reaction.

If the concentration of product affects the rate, this effect is called autoinhibition or autocatalysis. If a substance, neither a reactant nor a product, affect the rate it is called as inhibitor, retarder, sensitizer, or a catalyst.

The order of reaction can change according to experimental condition. Thus a reaction is said to be zero order when its rate is independent on the concentration of the reactant.

It is represented as,

$$A \longrightarrow B$$

Where A and B denote the reactant and product respectively.

$$\text{Rate} = \text{constant}$$

$$-\frac{d[A]}{dt} = k_o [A_o] = k_o$$

Where k_o is the zero order rate constant.

b] Temperature:

It is well known fact that a velocity of a chemical reaction increases with rise in temperature. In homogeneous reactions, the rate becomes doubled or tripled for each 10°C rise in temperature.

J.J.Hood [7] was the first, investigated the enhancement of reaction with the rise in temperature. He was Arrehenius[5] who successfully applied his ideas to the experimental data for a number of and for various types of reactions. He suggested an equation to show the variation of rate constant (k) of reaction with absolute temperature (T).

The equation is,

$$k = A\,e^{-Ea/RT}$$

Where

A= Frequency factor

Ea = Energy of activation

R = molar gas constant

Thus, to account for the marked increase in reaction rate with rise in temperature, Arrehenius suggested that, molecules absorb heat energy and get activated, according to his hypothesis in every system equilibrium exists between normal reactant molecules and activated molecules; and only activated molecules cause the chemical change. Thus molecule acquires the additional energy required for a reaction to occur, which is known as the energy of activation. The magnitude of activation energy will depend on the nature of the process so that, the proportion of activated molecules will vary from reaction to reaction and hence they proceed with the different rates. Thus Arrehenius attributed influence of temperature on reaction rate to the concentration of activated molecules.

1] Thermodynamic formulation of reaction rate:

As stated earlier, 'mechanism of reaction is a series of elementary reactions, which account for overall reaction. When the numerical values of rate constant are studied the first striking feature that is noticed is the large variation of rate constant with temperature. This temperature dependence of reaction rate furnishes the most important clue to understand the molecular basis of the rate constant of elementary reaction steps.

An important approach to explain the mechanism of chemical reaction known as "Activated complex theory" or "Transition state theory" focuses attention on the species in the reaction process. This theory was first outlined by A.Marcelin[8] in 1915 and put forward in its developed present form by H.Eyring[9]. M.G.Evans and M.Polani[10].The theory states that reactant molecules possessing necessary energy of activation come together to form an "activated complex" or "Transition state" which is in equilibrium with the reactants and decomposes to yield the products of reaction. Thus according to this theory reactants exist in intermediate unstable combination (intermediate) before they pass on to the product of reaction. This intermediate has higher energy and complex structure than either the reactants or the products therefore, it has been referred to "activated complex". Since activated complex has transient existence and it is capable of slipping back to reactant or going further on the product it is also called "transition state". Thus the theory reveals that the rate of reaction is governed by two factors 1) the concentration of activated complex and 2) the rate at which activated complex decomposes into products.

The equation [c] is fundamental relation of transition state theory.

$$k_r = (KT/h)\, e^{\Delta S\#/R}\, e^{-\Delta H\#/RT} \quad \text{------------}[c]$$

Where k_r = Rate constant of the reaction

K = Boltzmann constant

h = Plank's constant

$\Delta S^{\#}$ = Entropy of activation

$\Delta H^{\#}$ = Enthalpy of activation

T = Absolute temperature

R = Gas constant

The relation between rate constant of reaction and free energy of activation ($\Delta G^{\#}$) is:

$$k_r = (KT/h)e^{-\Delta G\#/RT} \quad \text{--------}[d]$$

As an activated complex has got transient existence, it is not possible to determine its thermodynamic properties ($\Delta G^{\#}$, $\Delta H^{\#}$, $\Delta S^{\#}$) by direct measurement. However some useful information can be obtained from equation [c] and [d].

The experimental energy of activation ($E_{exp.}$) is related to enthalpy of activation by the expression.

$$E_{exp.} = \Delta H^{\#} - P\Delta V^{\#} + RT \text{ --------- [e]}$$

Where $\Delta V^{\#}$ is the increase in volume in going from the initial State to activated state.

For unimolecular reactions or for reactions in solution $\Delta V^{\#} = 0$

Therefore equation [e] becomes,

$$E_{exp.} = \Delta H^{\#} + RT$$

Then equation [c] becomes,

$$k_r = e\,(KT/h)\, e^{\Delta S\#/R}\, e^{-Eexp./RT} \text{ --------[f]}$$

In the case of bimolecular reaction in solution.

$$E_{exp.} = \Delta H^{\#} + 2RT$$

Therefore equation[c] becomes,

$$k_r = e^2\,(KT/h)\, e^{\Delta S\#/R}\, e^{-Eexp./RT} \text{ -----------[g]}$$

2] Significance of Thermodynamic Parameters:

The various thermodynamic parameters like Ea, A, $\Delta G^{\#}$, $\Delta H^{\#}$, and $\Delta S^{\#}$ are concerned with the reaction rate; hence their magnitudes give wealth of information which helps in suggesting the reaction mechanism.

The specific rate of any reaction at a particular temperature is governed by the factor $e^{-\Delta G\#/RT}$. The higher the value of $\Delta G^{\#}$ the slower is the reaction rate and vice versa. The equation [f] and [g) find use in evaluation of energy of activation for a reaction in solution by the study of effect of temperature on the reaction rate. Here factor $e^{-Eexp./RT}$ represents the fraction of activated molecules at a particular temperature. Hence it is evident that the reaction rate is controlled by the energy of activation. The greater the energy of activation the smaller the fraction of activated molecules and slower the reaction rate or vice versa.

The frequency factor (A) is concerned with frequency of collision in collision theory, where as it is a measure of the entropy of activation in the transition state theory.

Entropy is a measure of randomness of a system and entropy of activation is the entropy change in going from the reactants to the activated complex. The determination of the entropy of activation and its utilization in prediction of reaction mechanism has been explained by Moelwyn[11], Frost and Pearson[12].

Reaction is said to be normal if $\Delta S = 0$ otherwise it is termed as fast or slow according to whether ΔS value is positive or negative respectively.

c] Catalysts:

A catalyst is a substance that accelerates the rate of a chemical reaction but remains chemically unchanged afterwords. The Catalyst increases rate of reaction by providing a different reaction mechanism to occur with lower activation energy. In autocatalysis a reaction product itself is a catalyst for that reaction leading to positive feedback. Proteins that act a catalyst in biochemical reactions are called enzymes. Michaelis-Menten[13] kinetics describes the rate of enzyme-mediated reactions.

d] Dielectric constant:

The role of dielectric constant of solvent is important in reactions involving the electrostatic forces between solvent and solute molecules; Amis[14] has explained the subject systematically. To explain the effect of dielectric constant of solvent (D) on rate of reaction between two ions having valance Z_A & Z_B, Scatchard[15] derived an expression,

$$\ln k = \ln k_o = Z_A Z_B\, e^2/DrKT$$

Where k_o is the specific rate constant in the hypothetical medium having indefinite dielectric constant $\mu = 0$ and e, k, T, r are the electronic charge, Boltzmann constant, absolute temperature and radius of activated complex respectively. The above equation implies that logarithm of the rate constant of ionic reaction vary linearly with the reciprocal of dielectric constant by solvent and plot of a graph of log k Vs 1/D enables one to gain the information regarding the nature of reacting ions.

e] Salt effect:

In the case of ionic reaction, the reaction rate not only depends upon the nature of the reacting ion but also on the ionic strength of the reaction medium. A very satisfactory treatment of this matter was made by Bronsted[16], Bjerrum[17] and Christiansen[18], the reviewed later on by Lamer[19].
These effects of electrolytes are of two types.

1] Primary salt effect :- It deals with the influence of electrolyte concentration on activity coefficient of reacting ions and transition state.

2] Secondary salt effect :- It concerned with actual change in the concentration of the reacting ions resulting from the addition of electrolytes.

Primary salt effect is involved in non-catalytic reactions and is sub-divided into the two categories.
1] Primary exponential salt effect.
2] Primary linear salt effect.

The former primary salt effect for the reactions in dilute solution is represented by the Bronsted-Bjerrum equation.

$$\ln k = \ln k_o + \frac{2\alpha Z_A Z_B \ \mu}{1 - \beta r \ \mu} \quad \text{----------[h]}$$

For very dilute solution, where μ is small it gets reduced to,

$$\ln k = \ln k_o + 2\alpha Z_A Z_B \ \mu \ \text{------[i]}$$

Where k_o is the rate constant in a solution of ionic strength zero, Z_A and Z_B are the charges of the reacting ions with the distance of closest approach, while α and β are the Debye-Huckel constants. The equation[i] leads to the prediction that logarithm of the rate constant of ionic reaction should vary linearly with the square root of the ionic strength of the reaction medium. It also guides one to gain information regarding the nature of the charges on the reacting ions from plot of log k Vs μ.

Bronsted-Bjerrum equation[i] predicts that, a rate of reaction between an ion and a neutral molecule should not be affected by the ionic strength of the reaction medium, but this is true only for very dilute solutions. The activity coefficient of ions as well as neutral molecules are affected at higher ionic strength which cause the variation of reaction rates with ionic strength. In such cases for a reaction between an univalent ion A and neutral molecules B the influence of ionic strength on rate constant is given by equation.

$$\ln k = \ln k_o + (bA + bB - b^*)\mu \quad \text{--------[j]}$$

$$\sim \ln k_o + b'\mu$$

Where b is constant introduced by Huckel.

Equation [j] shows that, logarithm of the rate constant varies with first power of ionic strength and nature of slope of linear plots, logk Vs μ depend on the resultant magnitude with sign of b'.

Equation [j] can be rearranged to,

$$k = k_o e^{b'\mu} \quad \text{-----------[k]}$$

If b' is small it is possible to write equation [k] as,

$$k \sim k_o(1+b')\ \mu \text{ -------------[l]}$$

Thus as a result of the primary salt effect, the rate constant of ion dipole reaction should be a linear function of the ionic strength and the actual variation of rate constant with change in ionic strength depends on the magnitude as well as sign on b'.

Method of studying reaction kinetics:

The various experimental procedures are used to study the kinetics of slow as well as fast reaction in both gas and solution phase. In kinetic studies an experimental requirement is a suitable analytical procedure which would enable us to determine the rate of a chemical reaction.

Two types of analytical procedure are generally employed; they are chemical and physical method.

Chemical method involves the measurements of concentration of one of the reactants or products as a function of time by volumetric or gravimetric techniques. Here it is important that the method employed is relatively slow, it must be possible to stop or freeze the reaction, and this may be done by rapid cooling in ice water, addition of an inhibitor or removal of reactant. This method gives the absolute value of concentration.

Physical method of analysis is based on the measurement of some physical property of reactant which changes as the reaction proceeds. Some of the methods used in kinetics studies is pressure measurements in gaseous reactions, dilatometry, optical, electrical, thermal methods etc.

Physical methods of analysis have the following advantages over the chemical method.

1]] They are rapid.

2] Since the reaction is carried out in a reaction vessel, the sampling error is eliminated.

3] The system has less disturbances.

The disadvantages of the method are

1] They do not give absolute value of concentration.

2] Side reactions may cause an appreciable error.

In the present work, the specrophotometric method for kinetic study is used.

References

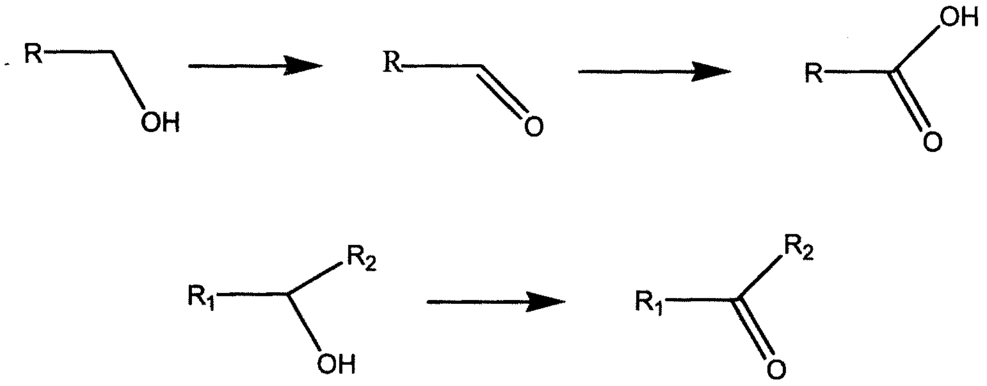
1. L .Wilhelmy, Pogg *.Ann.*,**81**,413(1850) 4999 .
2. M. Berthlot and L.P.St.Gilles ,*Ann.Chim.et.Phys.*, **63**,385; Berthlot, *ibid.*,**66** (1862) 110,and several later papers.
3. A.V.Harcourt and W.Esson, *Proc,Roy Soc.(London)* **14**(1865) 470 ; *Phil .Trans* .,**156**(1866) 193;**157**(1867) 117.
4. C.M.Gulberg and P.Waage, 'Etudes sur less affinities chimques' Brogger and Christie, *Christiania (Oslo)* (1867).
5. S.Arrhenius ,*Z.Physik. Chem.*, **4**(1889) 226.
6. S.Glassstone, K.J. Laidler, and H.Erying,*The theory of rate processes* (*MC.Graw Hill Book Co.New York*) (1941).
7. J.J.Hood, *Phil.Mag.*, **6**(1878) 371; **20**(1885)323.
8. A. Marcelin; *Ann.Phys.*,**3**(1915);*Physik Z.***18**(1917)53.
9. H. Eyring, *J.Chem.Phys.*,**3**(1935)107.
10. M.G.Evans and M. Polayni;*Trans.Faraday Soc.,* **31**(1935)875; *ibid*, **33**(1937) 448.
11. E.A. Moelwyan;*The kinetics of reactions in solution (The clarendom press Oxford) Second Edn.*(1947).
12. A.A.Frost and R.G.Pearson, *Kinetics and mechanism (John Wiley and Sons, Inc.New York)* (1963).
13. L.Michaelis and M.L.Menten,*Biochem.Z.*,**49**(1913)333.
14. E.S.Amis, *Solvent effect on reaction rates and mechanism* (Academic *Press .New York),* (1966).
15. G. Scatchard; *Chem.Revs.*,**10**(1932) 229 .
16. J.N. Bronsted;*Z.Physik chem.*,**102**(1922) 169;*ibid.*,**118**(1925) 251.
17. N. Bjerrum;*Z.Physik chem.*,**108**(1924)82;ibid,**118**(1925)251.
18. J.A.Christenansan;*Physik Chem.*,**113**(1925)35.
19. V.K Lamer; *Chem.Rev.*, **10**(1932)185.

Chapter-I

Section B
Chromium based oxidizing agents

Chromium (VI) compounds are widely used and very powerful oxidizing agents[1] for several functional groups.

Their most common application is the selective oxidation of primary and secondary alcohols to aldehydes, ketones, [2,3] or carboxylic acids. Aldehydes derived from primary alcohols can only be isolated under certain reaction condition or by using specialized oxidation reagents.

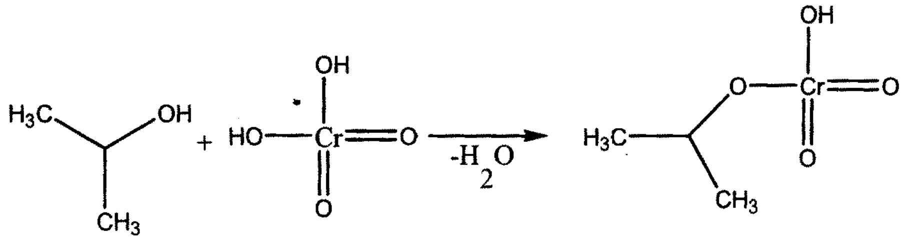


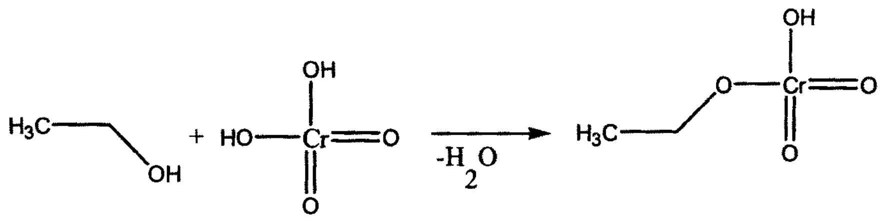
The mechanism of this reaction is known to proceed via chromyl-ester [4], which is cleaved to their product through base – catalysis.

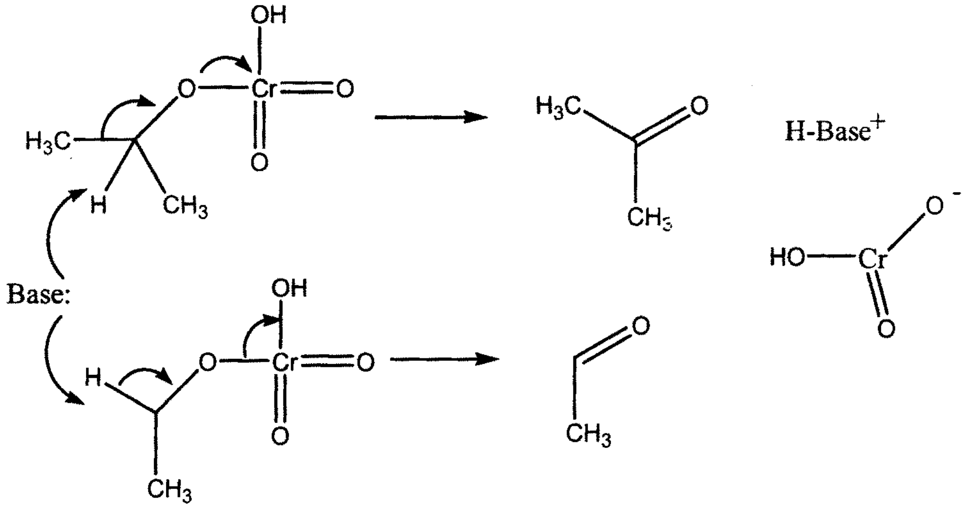
During reaction chromium species of lower oxidation states (IV and V) are also involved[5,6].

In aqueous solutions primary alcohols are usually oxidized to carboxylic acids[7,8]., while in absence of water the oxidation will stop at the aldehyde .The complete oxidation to carboxylic acid can also be avoided if the intermediately–formed aldehyde are removed from the reaction mixture by distillation or other means[7].

Common reagents for the selective oxidation of alcohol to aldehydes and ketones are pyridinium chlorochromate, known as Corey's reagent[9], and a mixture of chromium (VI) oxide and pyridine [10,11] in dichloromethane, known as Collin's reagent. [12]







In addition to the oxidation of alcohol, several other reactions can use chromium (VI) compounds such as:

- The oxidation and the oxidative cleavage [13] of double bonds,
- The oxidation of allylic[14] or benzylic compounds to aryl ketones [15], benzoic acids[16] and aromatic aldehydes.[17]
- The oxidation of polyaromatic hydrocarbons to quinones.

- Recovery of carboxyl compounds from their oxime derivatives.[18]
- The mild and selective oxidative deprotection of trimethylsilyl[19] or THP-ethers.[20]
- Oxidation of aromatic thioester to sulfoxides [21] and sulfones.
- Synthesis of (dichloroiodo) arenes. [22]

In past years numerous similar reagents with special properties, such as ease of preparation, selectivity and stability have been developed. Solid supported reagents have been also recently gained interest.[20,23,24,25]

Chromium based oxidation reagents:

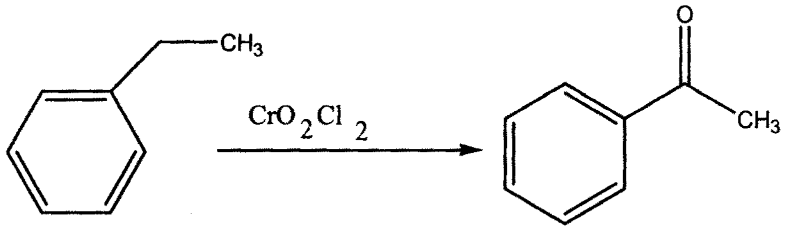
Chromosulfuric acid:

Chromosulfuric acid is a very powerful oxidizing agent. It can used for the cleaning of glassware, because it destroys organic substances by oxidation, but has often been replaced by less toxic alternatives.

Chromyl chloride:

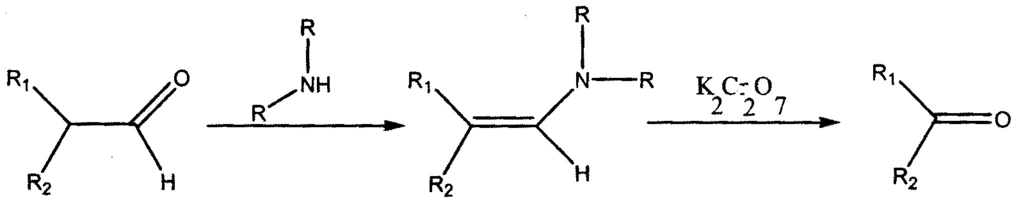
Chromyl chloride[26] has been used in the Etard[27]-reaction, the oxidation of methylarenes to benzaldehyde[28]. It has also been used in the oxidation of olefins[29] to epoxides,[30,31] chlorocarbonyl compounds[32], chloroacetal[33], and carbonyl compounds[34].

A complex of chromyl chloride with pyridine is a very powerful oxidation reagent for alcohols compared to the Collins reagent[35].



Potassium Dichromate:

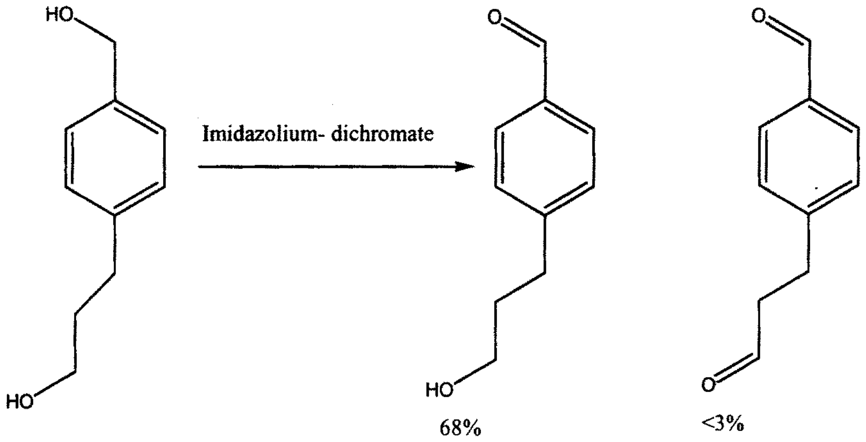
Potassium dichromate is widely used as strong oxidizing reagent. It has been used for the oxidation of alcohol and for oxidative cleavage of oxime, trimethylsilyl-and THP ethers under solvent free conditions[36].A solution of potassium dichromate and sulfuric acid can be used for the oxidative cleavage of enanmine double bonds[13], a method to de-homologize aldehydes.



Imidazolium Dichromate:

A selective and mild reagent for the selective oxidation of allylic and benzylic alcohols to carbonyl compounds[37].

Oxime, hydrazones and semicarbazones are converted to the corresponding carbonyl compound using imidazolium dichromate adsorbed on alumina[38].



Potassium chlorochromate:

Reagent for the oxidation of allylic, benzylic and secondary alcohols to aldehydes and ketones.

Benzyltriethylammonium chlorochromate:

The mechanism and kinetics of the oxidation of formic acid and oxalic acids with benzyltriethylammonium chlorochromate[39] has been determined.

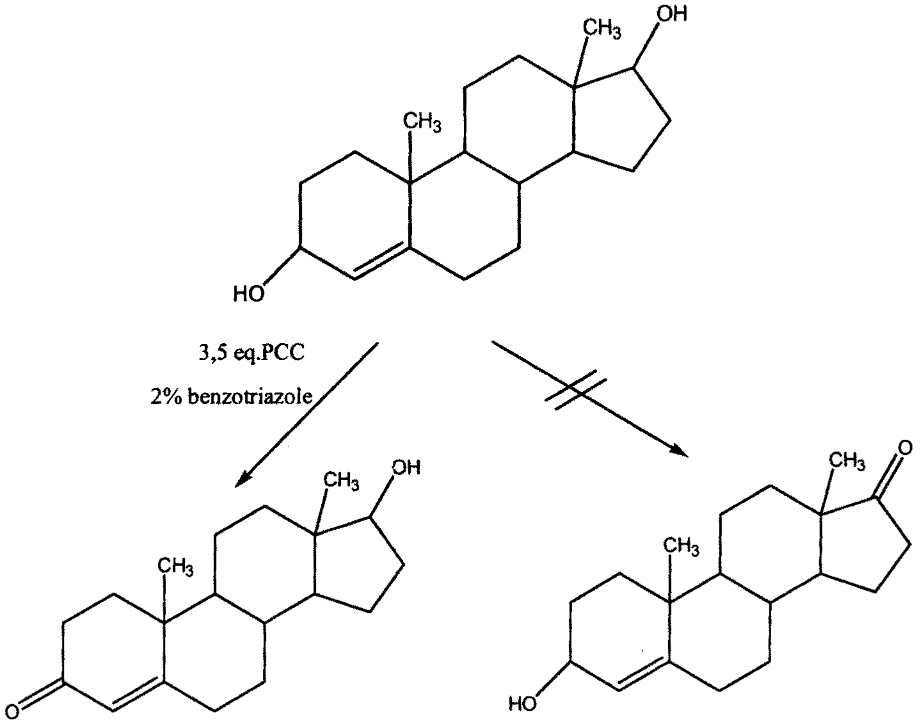
Pyridinium chlorochromate, silicagel, Functionalise with pyridinium chlorochromate:

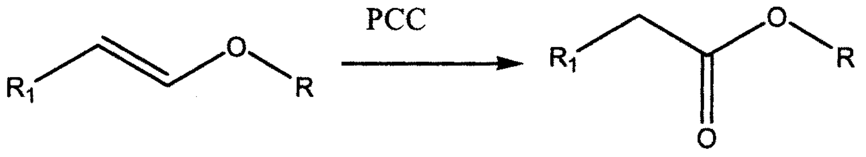
Pyridinium chlorochromate (Corey's reagent).

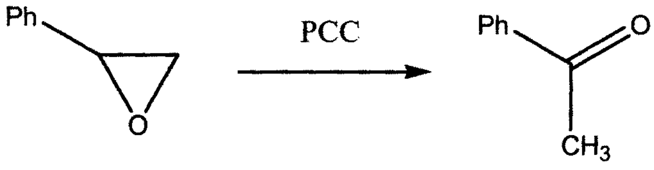
A air-stable yellow solid, is the reagent of choice for many types of oxidation reactions.[3,40] This reagent oxidizes 1° and 2° alcohols selectively to aldehyde and ketones.

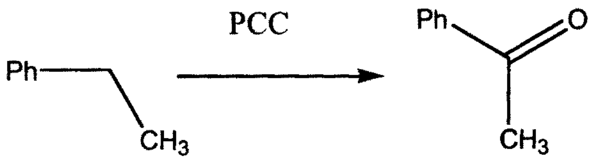
Addition of other aromatic amines like benzotriazole[41] increases the selectivity of this reagent toward allylic alcohols rather than non-allylic alcohols.

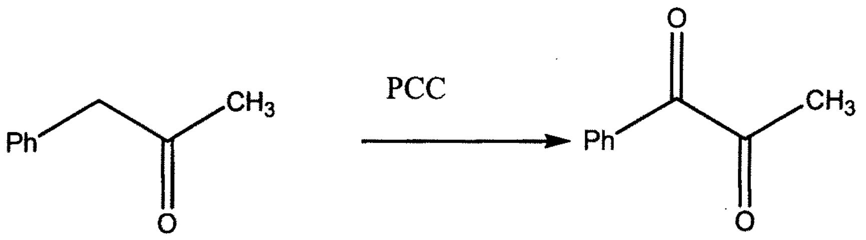
PCC can be used for the oxidative cleavage of boranes and oximes[18], to aldehydes and ketones.The oxidation of 5,6-Dihydropyranes with PCC leads to α,β unsaturated δ-Lactones[42].



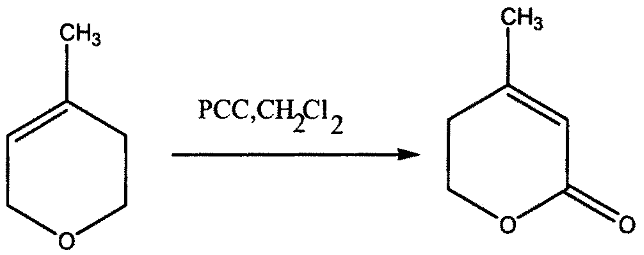


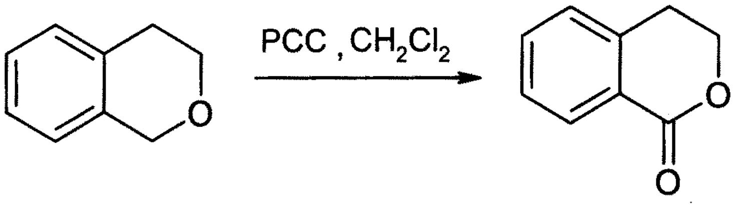






PCC can be used for several other oxidation reactions, which are summarized in the following scheme.





A higher reactivity and an easier work-up can be achieved using reagent adsorbed on alumina[43] and in the presence of molecular sieves[1].

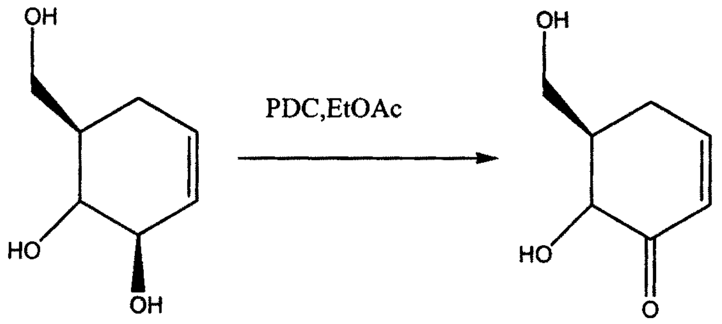
Pyridinium Dichromate, silicagel, Functionalise with 20%pyridinium Dichromate

Poly (4-Vinylpyridinium dichromate), cross linked with 2% DVB; 2.2mmol Cr/gm resin

Pyridinium dichromate, or Corey Schmidt[44] reagent, is a stable orange solid used for the selective oxidation of allylic alcohol to α,β unsaturated aldehydes in presence of other primary and secondary alcohols.

Depending on the solvent, the reagent oxidizes non-allylic primary alcohols to aldehydes in dichloromethane or to the carboxylic acids in dimethylformamide.

Another application of PDC is in aromatization of 1,4-dihydropyridines.[45]



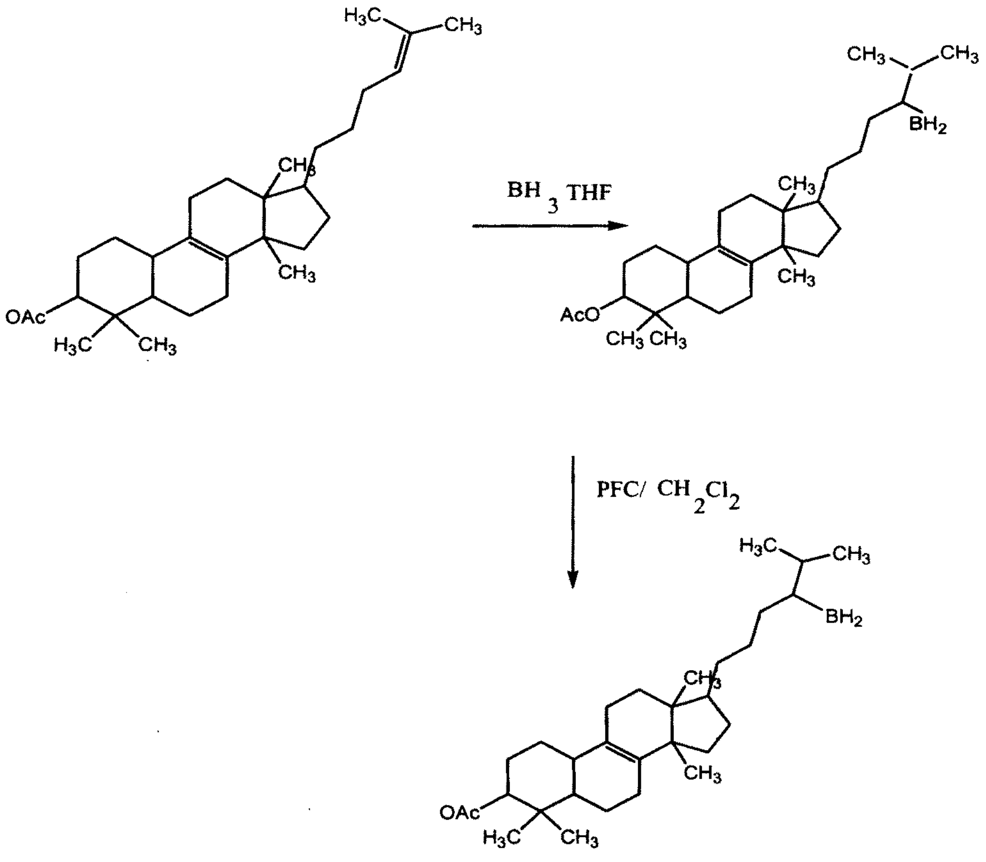
2, 2-Bipyridinium chlorochromate:

2, 2-Bipyridinium chlorochromate is a mild, air stable and non-hygroscopic oxidation reagent[46].It is somewhat weaker than pyridinium chlorochromate, and a higher excess of reagent (usually 2-4 fold) is necessary for complete reaction[1].It is used mostly for the oxidation of alcohols to carbonyl compounds but the reagent has been used together with m-Chloroperbenzoic acid for the oxidative cleavage of cyclic acetals[47] and for the oxidation of sulfides to sulfoxides and sulfones.

Pyridinium Fluorochromate:

Pyridinium fluorochromate is a stable solid and can be stored for prolonged period. It oxidizes primary alcohols to aldehydes and secondary alcohols to ketones in high yield, and can be used for the oxidation of polycyclic aromatic compounds to chinones[48]. Pyridinium fluorochromate has a comparable selectivity in oxidation reactions to pyridinium chlorochromate, but has a lower acidity. This makes pyridinium flluorochromate more suitable where acid selective alcohols have to be oxidized[49]. The tolerance of PFC against ter-Butyldimethylsilyl protecting groups allows the oxidation of secondary alcohol in presence of a (protected) primary alcohol[50].

The reagent also allowed the direct oxidation of organoboranes to ketones in the synthesis of 24-Ketolanosteryl acetate[51].



Sodium dichromate dihydrate:

Sodium dichromate in sulfuric acid or in acetic acid is a very powerful oxidizing reagent and was widely used before the development of milder and more selective alternatives[1].

Sodium dichromate and sulfuric acid in dimethyl sulfoxide oxidize primary and secondary alcohols to the aldehydes and ketones.[52] An aqueous solution of sodium dichromate oxidizes alkyl arenes to carboxylic acid[16].It can also oxidize primary alcohols to the carboxylic acids via the aldehydes, which can only be isolated under special reaction conditions[7].

Ammonium dichromate:

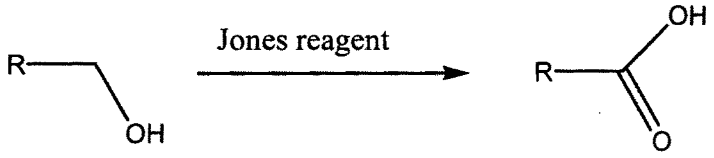
Ammonium dichromate on silica has been used in solvent free conditions for the oxidation of primary and secondary alcohols to aldehydes. [53]

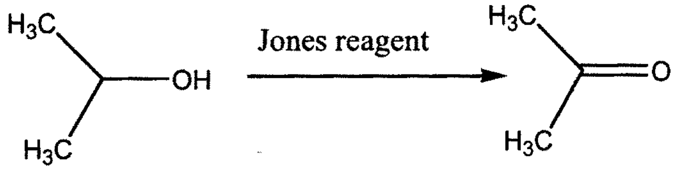
Chromium (VI) oxide:

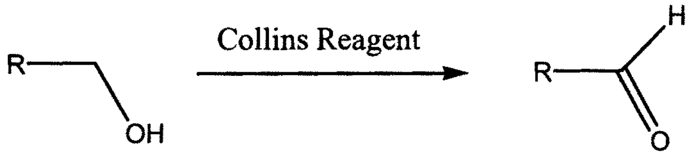
Chromium (Symbol Cr and atomic number 24)occurs in the oxidation state 0,+2,+3,+6 states, element (0) and divalent chromium,however,are unstable. Chromium (0) immediately produces a thin oxide layer. Divalent chromium is easily oxidized to the trivalent form in air. The trivalent and hexavalent oxidation state are important in industry, which exist in their divalent anions called chromate and dichromate respectively and a chromic anhydride form called chromium trioxide (CrO_3) and chromic oxide (Cr_2O_3).In industries, chromium trioxide is called chromic acid.

The structure of chromium trioxide has been determined[54] and may be described as a linear polymer of chromium and oxygen attached to the side of each chromium. The CrO_4 unit form distorted tetrahedral with Cr-O distance of 1.79-1.81A°.It is not appreciably soluble in acetic acid[55] or in most common non-hydroxylic solvents. It however dissolves in reagent such as water, acetic anhydride[56], t-butyl alcohol[57] and pyridine,[58] via a reaction which leads to depolymerisation

Chromium (VI) oxide is widely used for the preparation of other oxidation reagents such as the Jones and Collin's reagents. Chromium (VI) can be used for the oxidation of aromatic hydrocarbons to ketones[59]. The mixture of chromic acid and sulfuric acid in acetone, the Jones reagent[60] is widely used for oxidations.



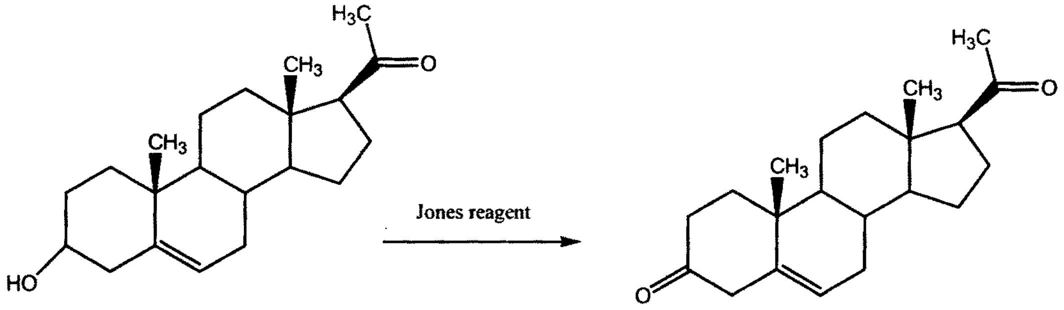




Secondary alcohols are oxidized to ketones while primary alcohols are oxidized to carboxylic acid. The oxidation of secondary alcohol to ketones can be performed in the presence of isolated double and triple bonds, where they will not be attached by the reagent. An example for the use of Jones reagent is the oxidation of Pregnenolone[61].

The complex of chromium (VI) oxide with pyridine[12] in dichloromethane is called the Collin's reagent[62]. The complex is difficult and dangerous to prepare[63], very hygroscopic, not very soluble in dichloromethane and usually requires a six-fold excess to complete the reaction. It does, through, oxidize primary alcohols selectively to the aldehydes and tolerates many functional groups.

The complex of chromium (VI) oxide with 3,5- dimethylpyrazole is very soluble in dichloromethane and generally requires a smaller excess of reagent(~2.5 fold).



Chromium (VI) oxide in different solvents has been used for the oxidation of secondary alcohols to ketones and the oxidation of aromatic side chain to benzaldehyde or benzoic acids. Examples include chromium (VI) oxide in:

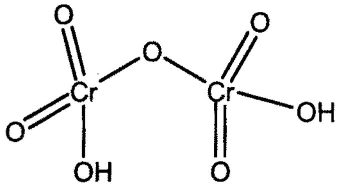
- Acetic acid (Fieser reagent),
- Pyridine (Sarett reagent[64]),
- Aqueous pyridine (Cornforth reagent[65]),

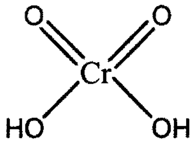
- Acetic anhydride and sulfuric acid (Thiele reagent[66]),
- Dimethylether in presence of Celite[67].

Chromium (VI) oxide has been used as a catalytic oxidant with ter-butylhydroperoxide as Co-oxidant[68].

Chromic acid:

Chromic acid refers to a collection of compounds generated by the acidification of solutions containing chromate and dichromate anions or by dissolving Chromium trioxide in sulfuric acid, or dissolving chromium trioxide in water. Often the species are assigned the formula H_2CrO_4 and $H_2Cr_2O_7$.The anhydride of these 'Chromic acid' is Chromium trioxide, also called Chromium (VI) Oxide, Industrially Chromium oxide known as Chromic acid





Regardless of its exact formula, chromic acid features Chromium is in oxidation state +6 (Or VI) often referred to as hexavalent chromium. Chromium can existing number of oxidation states Cr(VI) ,Cr(V) ,Cr(IV), Cr(III), Cr(II),hexavalent state is the highest.

In aqueous solution and in the absence of other ions the following equilibrium obtain.[69]

$H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^-$ k_1= 1.21 moles/lit.

$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{--}$ k_2= 3.0 x10-7 moles/lit.

$2\ HCrO_4 \rightleftharpoons CrO_7^{2-} + H_2O$ kd = 35.5

- $HCr_2O_7 \rightleftharpoons H^+ + Cr_2O_7^-$ k_2 = 0.85 moles/lit.

$H_2Cr_2O_7 \rightleftharpoons H^+ + HCr_2O_7^-$ ki = large

At higher concentration polychromate are formed,[70] organic compounds often not soluble in water and therefore a mixed solvent is commonly used in effecting chromic acid oxidation .The majority of the of the work has employed acetic acid as the co-solvent. The monomer–dimer equilibrium constant in 91% acetic acid has been determined.[71]

Chromic acid is one of the most versatile oxidizing agents, reacting with almost all types of oxidizable groups .The reaction may be controlled to yield largely one product and this makes chromic acid oxidation a useful synthetic tool. The mechanism of these reactions is fairly well understood as a result of pioneering work of Westheimer and his collaborations.

Chromic acid is used for oxidation of aryl alkane, allylic oxidation, alkanes, carbon–carbon double bonds, aromatic ring, diols, aldehydes, ketones, carboxylic acid, and alcohols.

Oxidation of aryl alkanes: by chromic acid

Toluene gives benzoic acid[72], m and p-xylene gives the corresponding dicarboxylic acids.[73]Oxidation of secondary alkyl group occurs at the carbon-hydrogen bond adjacent to the aromatic ring i.e. isopropyl benzene gives some 2-phenyl-2-propanol along with acetophenone on oxidation with CrO_3 in acetic acid.[74,75]

Allylic oxidation: by chromic acid

In an investigation of oxidation of alkenes by chromic acid. Whitmore and Pedlow[76] observed that in some cases, allylic oxidation occurred. Allylic oxidation by chromic acid appears to be relatively minor reactions with straight chain alkenes.

Oxidation of alkanes: by chromic acid

The chromic acid oxidation of alkanes has not received wide use as synthetic method. The lower reactivity of the primary C-H bond makes it enable to complete with the secondary or tertiary C-H bonds. The oxidation of secondary C-H bond would leads to the formation of ketones.Ketones are readily oxidized by chromic acid; the yield of ketones depends on the relative rate of oxidation of hydrocarbons and ketones.

Thus in the oxidation of 1-Chloronorchamphene[77] and of bornyl acetate a reasonable yield of ketone may be obtained.

Oxidation of carbon-carbon double bonds: by chromic acid

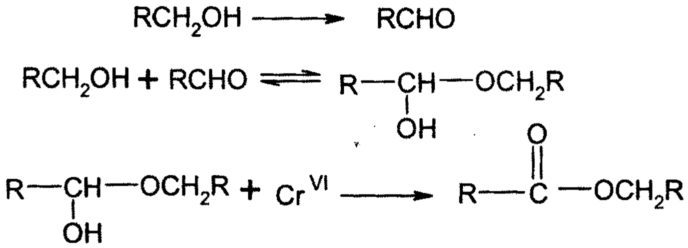
Chromic acid oxidation of alkenes is brought about by the use of acetic acid as solvent and the use of aqueous H_2SO_4.Although the reactions are same. The products are different, may leads to epoxide, a ketol, acids or ketones, having same number of carbon atoms as the alkenes via rearrangement.

Oxidation of aromatic ring: by chromic acid

The chromic acid oxidation of polynuclear aromatic compounds generally leads to nuclear oxidation rather than side chain oxidation. Thus methyl naphthalene gives 5-methyl -1,4-naphthaquinone[78] rather than 1-naphthoic acid.

Oxidation of alcohols: by chromic acid

The oxidation of primary alcohols leads to extra problem. The aldehydes, formed are fairly easily oxidized, and will be converted to the corresponding carboxylic acids. However, this does not account for low yield often obtained. The major side reaction involves, the equilibrium between the aldehyde and unreacted alcohol to give the hemiacetal, which may be further, oxidized to ester.[79]



$$RCH_2OH \longrightarrow RCHO$$

$$RCH_2OH + RCHO \rightleftharpoons R\text{—}\underset{\displaystyle OH}{\underset{|}{CH}}\text{—}OCH_2R$$

$$R\text{—}\underset{\displaystyle OH}{\underset{|}{CH}}\text{—}OCH_2R + Cr^{VI} \longrightarrow R\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}OCH_2R$$

The formation of an aldehyde is removed as it formed .This is often possible because of the lower boiling point of the aldehyde compared to the alcohol and in many cases a flow of carbon dioxide or nitrogen serve to sweep the aldehyde out of the reaction mixture.

In an investigation of the oxidation of primary alcohols, Bowmawan et.al observed that, chromic acid ester of primary or secondary alcohols are readily decomposed to the corresponding carbonyl compounds.[79]

Mechanism:

The first serious attempt to understand the mechanism of the chromic acid oxidation of alcohols was made by Westheimer and Novick[80], who found the rate law for the oxidation of isopropyl alcohol to be:

$$= Ka\left[HCrO_4^-\right][R_2CHOH]\left[H^+\right] + kb\left[HCrO_4^-\right][R_2CHOH]\left[H^+\right]^2$$

This rate law has been found to apply to the oxidation of all other primary or secondary alcohols which have been studied[81].

The most probable reaction sequence was:

$$R_2CHOH + Cr^{VI} \rightarrow R_2C=O + Cr^{IV}$$

$$Cr^{IV} + Cr^{VI} \rightarrow 2Cr^{V}$$

$$2\left(Cr^{V} + R_2CHOH \rightarrow R_2C=O + Cr^{III}\right)$$

Thus only one-third of the total oxidation is effected by chromium (VI) and two-third is effected by chromium (V).

Westheimer then proposed that the oxidation of primary and secondary alcohols proceeded via the acid chromate esters as intermediates.

$$R_2CHOH + HCrO_4^- + H^+ \rightarrow R_2CHOCrO_3H + H_2O$$

$$R_2CHOCrO_3H + H^+ \rightarrow R_2CHOCrO_3H_2^+$$

$$R_2CHOCrO_3H \xrightarrow{k_1} R_2C=O + Cr^{IV}$$

$$R_2CHOCrO_3H_2^+ \xrightarrow{k_2} R_2C=O + Cr^{IV}$$

Karunakaran et.al[82] have studied the oxidation of benzyl alcohol by dichromate and Cr (VI) complexes in aqueous HOAc in presence of $HClO_4$.

Yadav G.D.,Hadvanavekar B.V.[83] has studied the oxidation of Benzyl chloride to benzaldehyde with polymer supported reagents.

Oxidation of diols: by chromic acid

One of the first investigation of the chromic acid oxidation of diols was reported by Slack and Waters[84].They found that the oxidation of ethylene glycol led to only small amount of cleavage, and that 2,3-butylene glycol gave somewhat more cleavage (20-30%).The oxidation of pinacol has been studied in some details by Chang and Westheimer.[85]

Oxidation of aldehyde: by chromic acid

The first kinetic study of chromic acid oxidation of aldehydes was reported by Lucchi.[86a,b] He studied the oxidation of a series of aldehydes in acetic acid solution using sulfuric acid as a catalyst. The reaction was first order in the aldehyde and in Cr (VI).

Further studies of benzaldehyde oxidation were reported by Grahum and Westheimer[87] and Wiberg and Mill.[88] In aqueous solution the reaction had the rate law

$$=ka\,[[RCHO]\,[HCrO_4^-]\,[H^+] + kb\,[RCHO]\,[HCrO_4^-]\,[H^+]^2$$

Where in aqueous acetic acid it was

$$= k\,[RCHO][HCrO_4^-]ho$$

Oxidation of ketones: by chromic acid

The chromic acid oxidation of ketones generally leads to carbon-carbon bond cleavage with the formation of two carboxylic acids. Thus diethyl ketones give propionic acid and acetic acid.[89]

Oxidation of carboxylic acid: by chromic acid

The oxidation of Oxalic acid by chromium (VI) has been studied by several investigators[90-92].The rate of reaction was proportional to the concentration of chromic acid and Oxalic acid.

References

1. S.V Ley, A.Madin, Oxidation Adjacent to oxygen by Chromium Reagents in Comprehensive Synthesis,*Pergamon Press, Oxford* (1991).
2. F.A.Luzzio.*Organic Reactions* (1998) 1.
3. G.Piancatelli, A.Scettri, M.D.Auria, *Synthesis,* (1982)245
4. F.Holloway,M.Cohen,F.H.Westheimer,*J.Am.Chem.Soc.*,**71**(1951) 65. 5. a]K.B.Wiberg,G.Szeimies,*J.Am.Chem.Soc.*,**96**(1974)1889: b]K .B.Wilberg,S.K.Mukherjee,*J.Am.Chem.Soc.*,**96**(1974) 1884
6. M.doyle,R.J.Rocek,*J.Am.Chem.Soc.*,**95**(1973) 8352.
7. D.G.Lee,U.A.Spitzer,*J.Org.Chem.*,**35**(1970)3589.
8. G.R.Robertson, *Organic Synthesis, Coll.,* 1p.138.
9. E.J.Corey, J.W.Sugges *Tetrahedron Lett.*, **31** (1975)2647.
10. G.I.Poos, G.E.Arth, R.E.Beyler, L.H.Sarett, *J.Am .Chem.Soc.*, **75** (1953) 422.
11. R.Racliffe, R.Rodehorst, *J.Org.Chem.*, **35** (1970) 4000.
12. J.C.Collins, W.W.Hess, J.F.Frank, *Tetrahedron Lett.*, **30** (1968) 3363 .
13. C.E.Harris, L.Y.Lee, H.dorr, B.Singaram, *Tetrahedron Lett.*,**365** (1995) 2921.
14. Marshall,Ley,leos,Rigel,*J.Am.Chem.soc.*, **79** (1957) 6308 ; Suga, Sugimoto, Fujita, Matsuura,*Bull.Soc.Chim.Jap.*,**39** (1966) 2546; Dauber,Lorber fullerton,*J.Org. Chem.*, **34**(1969) 3587.
15 .a]J.W.Burnham, W.P.Duncan, E.J.Eisenbraun, G.W.Keen, M.C. Hamming,*J.Org.Chem.*,(1974)1416; b]R.Rangarajan,E.J. Eisenbraun ,*J.Org.Chem.*,**50**(1985)2435.
16. L.Friedman, D.L.Fishel ,H.Shechter,*J.Org.Chem.*,**30**(1965)1453.
17. H.Maer, J.M.Smallheer, *J.Org.Chem.*, **46** (1981)1752.
18. J.Drabovicz, *Synthesis* (1980)125.
19. J.Muzard, *Synthesis* (1993)11.
20. M.M.Hervari, D.Ajami, M.Ghassemzadesh, *Synthesis*, **3**(1999) 393.

21. C.Karunakaran,V.Chidambaranathan, *Croatica Chemica Acta.*,**74** (2001) 113, 670.
22. N.Obeid,L.Skulski,*Molecule*,**6**(2001)869.
23. A.Kirschnigg,H.Monenschein,R.Wittenberg,*Angew.Chem.*,**113** (2001) 670.
24. M.Z.Kassaee,S.Z.Sayyed-Alangi,H-Sajjadi-Ghotbabadi,*Molecules*, **9**(2004)825.
25. N.Deirmenba.B.Ozgun,*Monatshefte fur.Chemie.*,**135**(2004)407.
26. F.A.Luzzio,W.J.Moore,*J.Org.Chem.*,**58**(1993)512.
27. A.L.Etard, *Compt.Rend.*, **90**(1880)534.
28. W.H.Hartford, M.Darrin, *Chem.Rev.*, **58** (1958)1-61.
29. M.Torrent,L.Deng,T.Ziegler,*Inorg.Chem.*,**37**(1998)1307;M.Torrent, L.Deng, M.Duran,M.Sola,T.Ziegler. *Can.J.Chem.*, **77**(1999)1476.
30. N.Miyaura, J.K.Kochi, *J.Am.Chem.Soc.,* **105**(1983)2368; F.W. Bachelor, U.O.Cheriyan, *Can.J. Chem.*, **54** (1976)3383; F.W. Bachelor , U.O.Cheriyan, *J.Chem.Soc.Chem.Commun.*, (1973) 95.
31. C.Limberg, R.Koppe, *Inorg.Chem.,* **38** (1999)2106.
32 K.B.Sharpless and A.Y.Teranishi, *J.Org.Chem.*, **38** (1973)185.
33. J-E.Backvall, M.W.Young, K.B. Sharpless, *Tetrahedron Lett.*, (1977)3523;K.B.Sharpless ,A.Y.Teranishi, and J-E Backvall *J.Am.Chem.Soc.*,**99**(1977)3120.
34. F.Freeman, P.J.Cameron, *J.Org.Chem.*, **33**(1968) 3970; F.Freeman ,R.H.DuBois,N.J.Yamachika,*Tetrahedron*,(1969)3441,Freeman, N.J. Yamachika,*J.Am.Chem.Soc.*,**94**(1972)1214.
35. K.B.Sharpless, K.Akashi, *J.Am.Chem.Soc.*, **97** (1975)5927.
36. I.Mohammadpoor.Baltork,M.M.Sadeghi,A-H.Adibi,*Molecules*,**6** (2001) 900.
37. S.Kim.D.C.Lhim.*Bull.Soc.Chim.Jap.*, **59** (1986)3297.
38. S.Kanta De,*Letters in Organic Chemistry*.**2/1**(2005).
39. K.Chuhan,P.K.Sharma ,*Ind.J.Chem.*,**43A**(2004)1434-1438.
40. R.A.Fernandez, *Synlett*, **5**(2003)741.

41. E.J.Parish, S.Chitrakorn, *Synth. Comm.*, **15**(1985)393.

42. F.Bonadies, R.DiFabio, C.Bonini, *J.Org.chem.,* **49** (1984)1647.

43. Y-S.cheng,W-L.Liu,S-H.Chen,*Synthesis*(1980)223.

44. E.J.Corey,G.Schmidt,*Tetrahedron Lett.*,(1979)399-402.

45. K.Y.Park,Bull.*Korean Chem,.Soc.*,**16**(1995)200-201.

46. F.S.Guziec, F.Luzzio, *Synthesis*, 9(1980)691.

47. F.A.Luzzio,R.A.Bobb,*Tetrahedron Lett.*,**38**(1997)1733.

48. M.N.Bhattacharjee, M.K.Chaudhari, H.S.Dasgupta, N.Roy, D.T. Khathing .*Synthesis,* (1982).

49. M.N,Bhattacharjee ,M.K.Chaudhari ,S.Purkayastha, *Tetrahedron*, **43**(1987)5389.

50. T.Nonaka,S.Kanemoto,K.Oshima,H.Nozaki,*Bull.Soc.Chim.Jap,.* **57**(1984)2019.

51. E.J.Parish,H.Sun,S.Kizito,T.L.Boss, *Molecule*, **5**(2000)114.

52. Y.S.Rao, R.filler, *J.Org.Chem.*, **39** (1974)3304.

53. F.Shirini, M.Khalenghi, Bull, *Korean.chem.Soc.*, **24** (2003)1021.

54. A.Bystrom, K.A.Wilhelmi, *Acta.Chem.Scan.,* **4** (1950)1131: F.Honic, D.Stempelova ,*Chem.Zvesit.,* **14** (1960)165: *Chem.Abst.*,20402.

55. J.Rocek, F.Sorm, *Collction.Czech.Comm.,* **20**(1955)1009:J.Rocek, *Collection Czech.Chem.Comm.*,**20**(1955)1249.

56. A.Pictet, P.Genequand, *Chem.Ber.*, **36** (1903)2215.

57. H.Wienhaus, Ber, **47**(1914)322:W.Huckel, M.Blohm, *Ann.*, **502** (1933) 114.

58. H.H.Sister, J.D.Bush, O.E.Accountius, *J.Am.Chem. Soc.,* **70** (1948) 3827.

59. Organikum,p.439,21st issue,Autorenkolletiv,Wiley-Vch, Weinheim, 2001

60. A.Bower, T.G.Halsall, E.R.H.Jones, A.J.Lemin, *J.Chem.Soc.*, (1953) 2548.

61. C.Djerassi,R.R.Engle,A.Bower,*J.Org.chem.*, **21**(1956)1547.

62. J.C.Collins, W.W.hess, *Organic Synthesis, Coll.*,6p.644.

63. Special precaution and procedure must be followed when mixing chromium trioxide and pyridine since the mixture is flammable.
64. N.Arumugam, P.C.Srinivasan, *Synth.Comm.*, **33** (2003)2313.
65. R.H.Cornorth, J.W.Conforth, G.Popjak, *Tetrahedron*, **18** (1962) 1351.
66. J.Thiele, E.winter, Liebigs.Ann.Chem. 311(1900)353; T.Nishimura, *Org.Synth.Coll.*, **4** (1963)713.
67. S.J.Flatt,G.W.F.Fleet,B.J.Taylor, *Synthesis(*1979)815.
68. J.Muzart,*Tetrahedron Lett.*,**28**(1987)2133.
69. J.D.Neuss, W.Reiman, *J.Am.Chem.Soc.*, **56**(1934)2238; J.Y.P.Tong, E.L.King, *J.Am.Chem.Soc.*,**75** (1953)6180.
70. M.L.Freedman, *J.Am.Chem.Soc.*, **80** (1958)2072.
71. K.B.Wilberg, T.Mill, *J.Am.Chem.Soc.,* **80** (1958)3022.
72. R.Wendland,J.Lalonde.*Org.Syn.Coll.,***4** (1963)757.
73. R.D.Abell,*J.Chem.Soc.*,(1951)1379.
74. R.Fittig, W.Ahrens, L.Mattheides, *Ann.*, **147** (1868)15.
75. E.Boedtker,*Bull.Soc.Chem.France,*[3],25(1901)843.
76. F.C.Whitmore, G.W.Pedlow, *J.Am.Chem.Soc.*, **63** (1991)758.
77. K.B.Wiberg, B.R.Lowry, T.H.Colby, *J.Am.Chem.Soc.*, **8** (1961)3998.
78. S.G.Brandenberger, L.W.Mass ,I.Dvoretzky, *J.Am.Chem. Soc.,* **83** (1961)2146.
79. M.I.Bowman,C.E.Moore,H.R.Deutsh,J.L.Hartman,*Trans.Kentucky Acad. Sci.*,**14**(1953)33.
80. F.H.Westheimer, A.Novick, *J.Chem.Phys.,* **11** (1943)506.
81. M.Cohen, F.H.Westheimer, *J.Am.Chem.Soc.,* **74** (1952)4387.
82. Karunakaran, Chockalingam, S.Sadasivan (Dept. of Chemistry, Annamalai University ,Annamalainagar) *J.Chem.Res.Synip.,* (3) (2000) 114, Science Reviews Ltd.
83. G.D.Yadav,B.V.Haldavanekar, *React.Funt.Polym.*,**32**(2)(1997)194, Elsvier .
84. R.Slack,W.A.Waters,*J.Chem.Soc.*,(1949)594.
85. Y.W.Chang, F.H.Westhimer, *J.Am.Chem.Soc.*, **82** (1960)141.

86. a] E.Lucchi, *Boll.Sci.Fac.Chim.Ind.Bologna*, **208**(1940)333.

    b] E.Lucchi, *Gazz.Chim.Ital*, **71**(1941)729.

87. G.T.E.Graham, F.H.Westheimer, *J.Am.Chem.Soc.,* **80** (1958)3030.

88. K.B.Wiber, T.Mill, *J.Am.Chem.Soc.,* **80** (1958)3022: K.B.Wiberg *ibid*, **76** (1954)5371.

89. W.B.Sagar, A.bradley, *J.Am.Chem.Soc.*, **78** (1956)1187.

90. K.Jablozynski, *Z.Anorg.Allgem.Chem.*, **60** (1908)38.

91. H.C.S. Snethlage. *Rec. Trav. Chim.,* **59** (1940)111.

92. D.J.W.Kreulen, D.T.J.Terhorst.*Rec.Trav.Chim.*, **59** (1940)1165.

Chapter-I

Section C
Ion exchange resins

History:

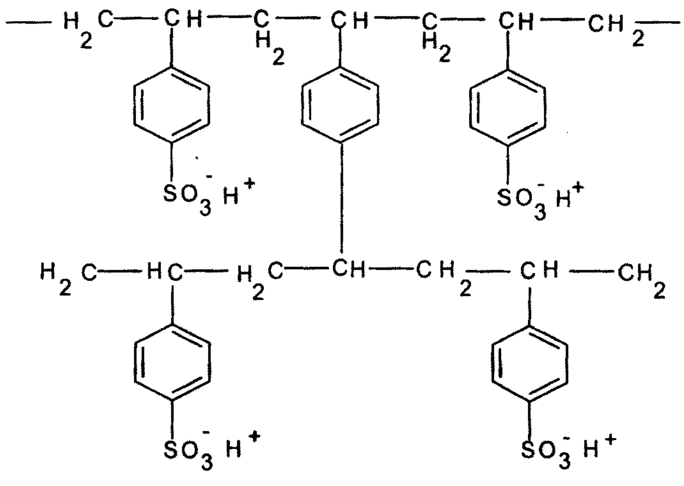
Until the mid-1960s synthetic polymers were of considerable technological interest largely as materials rather than as organic molecules in their own right. In mid-1960s synthetic macromolecules have been increasingly recognized as organic species, capable of behaving as organic reactant and susceptible under appropriate conditions, to all the chemical transformations of smaller organic species, ion exchange had previously been widely examined as acid and base catalyst[1] though no technological application appears to have developed at that time.

The rediscovery of polymer as organic molecule and their use in organic synthesis was made by Merrifield[2] in 1963 when he introduced his "solid-phase technique" for the synthesis of peptide, in which an insoluble crosslinked macromolecule was used as protecting groups, simultaneously providing a facile method for isolating and purifying the product of each condensation step. Since that announcement functionalized polymers have found widespread application in organic chemistry and related fields. They have been employed as stoichiometric reagents, as catalysts, as protecting groups, as substrate carriers, in analytical chemistry, in ion exchange, in the detection of reaction intermediates, in chromatography, in biologically and pharmalogically active systems, in the immobilization of enzymes and cells, in the application of dyes and colorant, and in the field of agricultural chemicals.

Introduction:

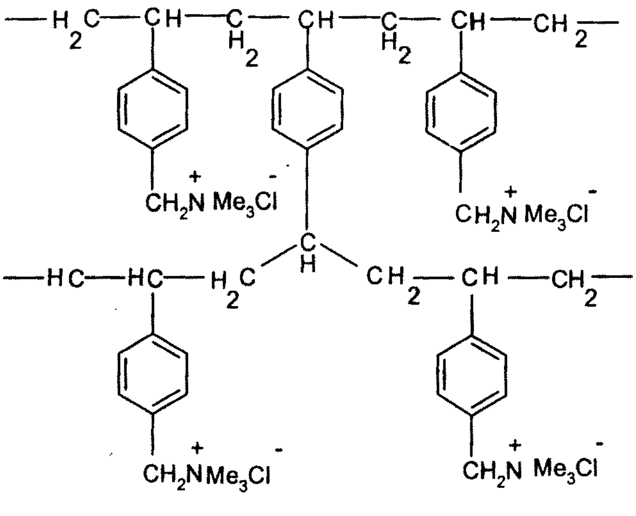
Polymer chemistry has become famous since synthetic organic chemical reactions give a byproduct, which can some times difficult to isolate from the desired product. On the other hand if a polymeric reagent is used in organic synthesis, then the byproduct will remain attached to the insoluble polymer and can be separated from the desired product by simple filtration.

The ion exchanger is of complex nature and is in fact, polymeric. The polymer carries an electric charge that is exactly neutralized by the charge on the counter ions. The active ions are cations in cation exchangers and anions in anion exchangers.e.g co-polymerization of styrene, and divinyl benzene and subsequent sulphonating it with concentrated sulfuric acid.



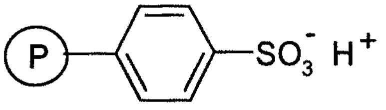
Thus cation exchange resin is a high molecular weight, cross-linked polymer containing sulphonic, carboxylic, phenolic etc.groups as an integral part of resin and equivalent amount of cations.

Anion exchangers[3] are likewise crosslinked, high molecular weight polymer. Their basic character is due to the presence of amino, substituted amino or quaternary ammonium groups, for example structure was shown below,

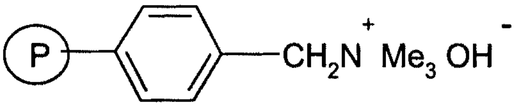


Thus anion exchange resin is a polymer containing amine (or quaternary ammonium) group as integral parts of the polymer lattice and equivalent amount of anions such as chloride, hydroxyl or sulphate ions.

Typical cation and anion exchange resins are represented by structure I and structure II.



(I)



(II)

Functionalized polymers:

Functionalized polymers are nothing but synthetic macromolecules.

Functionalized polymeric support must possess a structure which permits adequate diffusion of reagents into the reactive sites. Three main types of resins which can be identified are,

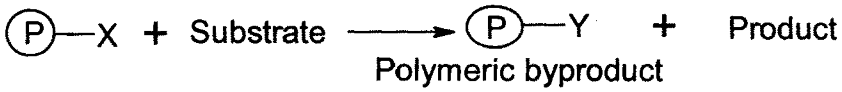
a] Microporous or gel type resin
b] Macroporous resin
c] Macroreticular resins[4]

Microporous species are prepared from a vinyl monomer and difuntional vinyl monomer in the absence of any additional solvating media. In dry state they are microporous, with polymer chains being separated by typical solid state intermolecular distances. On contact with good solvent, a soft gel network is formed with the generation of considerable porosity. Swollen resins generally have low mechanical stability and readily fragment even under careful handling. In contrast commercially available microporous resins with 78% cross-linking are mechanically very stable, but unfortunately give rise to accute diffusional limitations resulting in slow and incomplete reactions. In practice, resins of nearly 2% cross-link ratio provide a satisfactory compromise generally allowing adequate penetration by most reagents and yet retaining sufficient mechanical stability to provide ease of handling.

Very similar properties can arise with macroporous resins. These are prepared as before but with the inclusion of an inert solvent. Where the solvent solvates both monomer and polymer, a fully expanded network is formed with a considerable degree of porocity.[5] Removal of solvent causes a reversible collapse of the matrix, and in the dry state such materials are similar to microporous resins. In order to achieve mechanical stability in the solvent swollen state, it is usual to employ larger quantities of difuntional co-monomer in the preparation, upto nearly 20%. Materials of this type are not readily available from commercial sources.

Polymeric reagents:

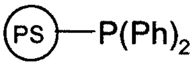
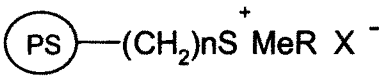
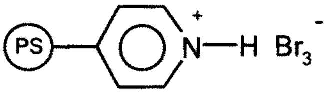
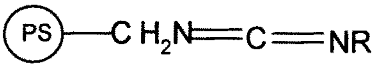
A polymeric reagent is a reactive organic group bound to a macromolecular support and used in stoichiometric quantities to achieve the chemical modification of an added substrate.

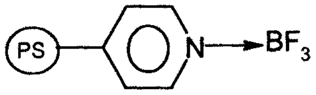
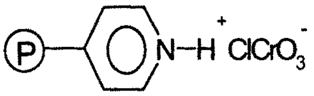


Such groups may be attached to polymeric carrier by physical adsorption or by chemical bonding. Physically adsorbed species are generally unsatisfactory since in use, the components tend to dissociate, and they are therefore unsuitable for column or cyclical application.

Those chemical reagents covalently attached to polymeric carriers and successfully used in organic synthesis are listed in Table 1. After reaction the byproduct remain attached to the insoluble polymer and can be removed by simple filtration. Some of these can regenerated for repeated use.

Table 1

Functional polymer	Appcation as reagent	References
1. Polymeric Phosphine reagents:		
	Wittig reaction	6,7
2. Polymeric sulphonium salt:		
		
a. n=0;R=Me;X=$MeS0_4$	Epoxidation of aldehyde	8
b.,n=0;R= Cl;X= Cl	Oxidation and selective mono oxidation of alcohols	9
3: Polymeric halogenating reagents:		
	Bromination of olefin	10
4: Polymeric condensing reagent:		
		
a,R=i-Pr	Conversion of acid to anhydride	11
b,R =Et	Peptide synthesis	12
5: Polymeric redox reagent:		

	Reduction of carbonyl compound	13
$(PS)-CMe_2OAlH_4$	Reduction of ketones	14
	Oxidation of alcohols.	15
	Oxidation of alkyl halides, to carbonyl compound.	16

6: Polymeric Protecting groups

$(PS)-CHO$	Glycoside synthesis	17,18

7: Polymeric Alkylation and Acylation reagent

$(PS)-COOCOR$	Conversion of amines to amide and Alcohols to ester	19,20

8: Polymer bound nucleophile

$(PS)-CH_2\overset{+}{N}Me_3\overset{-}{X}$

$X = Cl^-, Br^-, I^-$	Halogen exchange with alkyl halide	21
$X = OH-$	Condensation reaction	22
$X = HFe(CO_4)^-$	Conversion of alkyl halide to aldehyde	23
$X = HCrO_4^-$	Oxidation of alcohol	24
	and alkyl halide, to carbonyl compound	16
$X = IO_4^-$	Oxidation of phenol and sulphides	14
$X = MnO_4^-$	Oxidation of alcohols to aldehydes	25

Advantages and disadvantages using functionalized polymers:

Advantages:

1. Convenient use of excess reagent.
2. Retention of precious species.
3. Reuse or recycling possibilities.
4. Encapsulation of corrosive, noxious or toxic species.
5. Bach or column reactors.
6. Gas or liquid phase reaction.
7. Site isolation-indefinite dilution.
8. Reduced side reaction.
9. Stabilization of reactive species.

Disadvantages:

1. Initial extra cost.
2. Not available, "Off-the-Shelf".
3. Reduced reactivity-slower reaction.
4. Greater difficulty of analysis of the structure of supported species and of impurities.
5. Inability separate polymer bound impurity.
6. Lesser stability of organic support than of inorganic support.

Aim of the present work:

Hexavalent chromium compounds [chromic acid] are toxic and carcinogenic and the reduced chromate salts are the source of pollution. It would be advantageous to support the oxidizing chromate species itself on a polymer support, in this oxidation whereby the reduced chromate salts bound to the polymer could be easily separated and regenerated.

Oxidation is an important class of reactions from both industrial and academic point of view. In recent years, a large number of oxidizing agents have been used by different researchers for variety of industrial reactions. Supported oxidizing agents have attracted attention of many scientists due to their various unique features such as almost simplicity of workup where the catalyst or reagent can be separated from the reaction mixture by filtration, ease in the reaction set-up and operating conditions, improvement in the selectivity could be totally altered due to change in mechanism.

The present work of oxidation of substituted primary alcohols, using polymer supported chromic acid[26,27] is quit meager.[28]Although large number of reagents are known in the literature[29] for such transformation, there is still appears a need either to improvise the existing oxidation methods[30] or to introduce new reagents[31] to obtain,

A] Better selectivity under milder conditions.
B] Easy workup procedure.

Although the polymer supported reagent[32-34] has been frequently used in synthesis of organic compounds, there is dearth of information on kinetics of such reactions. Besides, there are some limited reports on selective formation of aldehydes from primary alcohols.

The use and reuse of polymer supported oxidizing agent without loss of capacity is another interesting factor, to undertake the present work.

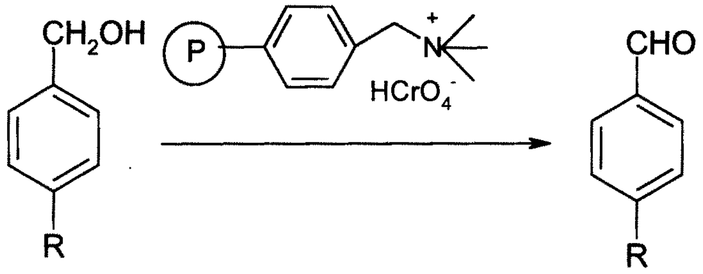
The present work is also important for the easy workup and safety or a unique reaction outcome. It also decreases side reactions. The oxidation process stops at product aldehyde only.

Cross-linked polystyrenes (with varying % of DVB) which are now a days widely used because of their chemical and mechanical stability and also because the polymer swells strongly in several solvents. The reactions carried out using such cross-linked polymers results into high yield transformations.

Considering all these advantages the present study is planned. The alcohols selected for study are,

1] Benzyl alcohol
2] 4-Methoxybenzyl alcohol
3] 4-Chlorbenzyl alcohol

General scheme:



R = -H, $-OCH_3$, -Cl

During survey it is found that, particularly when chromium (VI) derivatives were used, the efficiency of reaction was low[35,36] and the workup of reaction mixture is sometimes complicated.

The objective of the present study is not only to develop a method for the oxidation of these alcohols to their corresponding aldehydes, but also to determine the order of reaction, to study the effect of crosslinked polymer on the rate of reaction and to propose the plausible mechanism of the reaction and order of reaction.

The polymer used is **Ambersep 900(OH^-)** [strong anion exchange resin].

References

1. M.J.Astle in, "Ion exchange in organic and Biochemistry", C.Calman, T.R.E.Kressman ,*Eds, Interscience, New York, Chapter* **36**(1957),658.
2. R.B.Merrifield, *J.Am.Chem.Soc.,* **85** (1963), 2149.Science (Washington,D.C.), **150**(1965)178; *Adv.Enzymol.,* **32** (1969),221.
3. U.S.Patent, **2591**, (1952), 573.
4. N.K.Mathur,C.K.Narang, R.E. Williams, Eds., *"polymers as Aids in Organic synthesis", Academic Press, New York,(*1980).
5. J.R.Miller,D.G.Smith,W.E.Marr,T.R.E.Kressman,*J.Chem.Soc.,* (1963) 218, .
6. W.Heitz,R.Michels,*Liebigs Ann.Chem.,*(1973),227.
7. F.Camps, J.Castells, M.Ferrando, J.Font, *Tetrahedron Lett.,* (1971)1713.
8. S.Tonimoto, J.Horikawa, R.Oda, *Kogyo Kagaku Zasshi,* **70**(1967) 1269.
9. G.A.Crosby, N.M.Weinshenker, H.A.Uk, *J.Am.Chem.Soc.,* **97** (1975) 2232.
10. J.M.J.Frechet, J.M.Farall, L.J.Nuyens, *J.Macromaole.Sci.Chem.,*A-**11**(1977)507.
11. N.M.Weinshenkar,C.M.Shen,*Tetrahedron Lett.,***3281**(1972)3285.
12. H.Ito, N.Takamastu, I.Ichikizaki, *Chem.Lett.,* **577**(1975).
13. M.L.Hallenenslen,*J.Poly.Symp.,***47**(1974),1.
14. P.Hodge,D.C.Shrrington,Eds, *"Polymer –Supported Reaction in Organic Synthesis, Wiley,London,*(1980)121.
15. J.M.J.Frechet, JWarock,M.J.Farrall, *J.Org.Chem.,***43** (1978)2618.
16. G.Cardillo, M.Orena,S.Sandri, *J.Am.Chem.Soc.,***98**(1976)6737.
17. J.T.Ayres, C.K.Mann, *Polym.Lett.,* **3**(1965)505.
18. J.M.J.Frechlet,C.Schuerch, *J.Am.Chem.Soc.,***93**(1971)492.
19. M.B.Shambu,G.A.Digenis,*Tetrahedron Lett.,(*1973)1627.
20. F.H.Tjoeng, E.K.Tong, R.S.Hodges, *J.Org.Chem.,***43**(1978)4190.
21. G.Canilli,F.Manescalchi,M.Panunzio,*Synthesis,* (1976) 472.
22. K.Shimo, S.Wakarmastu, *J.Org.Chem.,***28**(1963),504.

23. G.Canilli, F.Mnescalchi, A.U.Ronchi, *J.Org.Chem.*,**43**(1978),1598.

24. G.D.Yadav, B.V.Haldavankar,*Rea.Funt.Polym.*,**32**(1997)187.

25. F.Shirini,M.Dabiri, S.Dezyani, F.Jalili, *Russ.J.of Org.Chem.*, **41**(2005) 390.

26. I.Nongkyrinch, M.K.Mahanti, *Bull.Chem.Soc.Jpn.*, **69**(1966) 1403.

27. I.Nongkyrinch, M.K.Mahanti, *Bull.Chem.Soc.Jpn.*, **68**(1995) 3325.

28. S.V.Pitre,M.V.R.Reddy,Y.D.Vankar,*J.Chem.Research*,(S),462 (1997).

29. R.C.Lorock, I.Fleming, *Comprehensive Org. Synth.Pergamon Press, Oxford*, (1991)251.

30. A.Mancuso,S.L.Kurodo,T.Morimoto,*Bull.Chem.Soc.Jpn.*,**63**(1990) 2433;W.X.Lou,Synth.Comm.(1992)767;A.Mohand,F.Henin,J. Muzard, *Tetrahedron Lett.*,**36**(1995)2473.

31. D.B.Dess, J.C.Martin, *J.Org.Chem.*,**48** (1983)4155.

32. E.Santaniello, P.Ferraboschi, *Nouv.J.Chim.*, **4**(1980)279.

33. T.Tatsumi,H.Ohta,H.Tominaga,N.Kagaka,Kaishi,(1988)1759, (Chem. Abst.**110**(1989)191884 p)

34. M.S.Climent,J.M.Marinas,J.V.Sinisterra,*React.Kinet.Cata.Lett.* **38**(1989)13(Chem.Abst.**111**(1989)56795 r).

35. A.Marchaj,*Stasicka,Z.Pol.P.I.*,**124**(1984)451;*Chem.Abst.*,**101**(1984) 71817 m.

36. Lederer P. *Personal Communication.*