

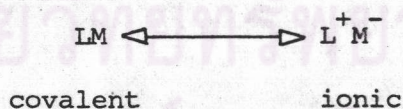


CHAPTER II

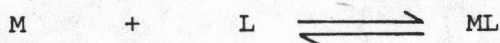
THEORETICAL AND PRACTICAL ASPECTS

2.1 Organic Compounds as Metallochromic Reagents

Organic molecules that function as metal complexing agent which formed coloured products with metal ions were called "Metallochromic Indicator". They contained auxochromic group(s) in their structures. The organic molecule can bind a metal ion only if it contains in addition to the atoms in the auxochromic group(s) other electron donating atoms in suitable positions that together with the metal ion they can form chelate structure usually five or six membered rings which are highly stable. The auxochromic groups containing heteroatoms e.g. nitrogen, oxygen, sulfur, and halogens involve unshared p-electrons for metal ion and exhibit absorption spectra. This absorption band arises from the formation of a charge-transfer complex formed between a donor molecule and an acceptor molecule. The complex can be described by the resonance structures :



The tendency of charge-transfer complex formation and the energy change in the transition of the electrons must depend on the ionization potential of L and the electron affinity of M, and such correlation have been made.



$$K = \frac{[ML]}{[M][L]}$$

The equilibrium constant (K) for the reaction

The absorbance (A) of the complex as a function of the concentration is determined by the absorption law.

$$A = \epsilon_{ML} b [ML]$$

When L_0 and M_0 are the initial concentration of the organic ligand and metal ion respectively and since $[L]_0 \gg [M]_0$

$$\therefore K = \frac{[ML]}{[L]_0 \{ [M]_0 - [ML] \}}$$

Equating ML for the last two equations and rearranging,

$$\frac{1}{A} = \frac{1}{\epsilon_{ML} [M]_0 b} + \frac{1}{K \epsilon_{ML} [M]_0 b} \cdot \frac{1}{[L]_0}$$

Thus a plot of $1/A$ versus $1/L_0$ gives a straight line and from the slope and intercept both ϵ_{ML} and K can be obtained.

The heteroatomic ligands are usually contained groups of atom such as C=O, C=N-, -N=N-, -OH, -SH, -NH₂ and -NO₂ containing n, π or conjugated π electrons. These electron donor parts of the ligand structures act as the active site to bind with metal ions. The frequencies and the intensities of the absorption bands are nevertheless sensitive to the nature of solvent and the inductive or resonance effect of the substituents. For oxime compounds (C=N-OH), N and O atoms are donor atoms. The mode of co-ordination of this group may be influenced by other group(s) present in the oxime. On this basis the oximes may be grouped into the following main classes.

1. Simple oximes
2. vic-Dioximes
3. Carbonyl oximes
4. Nitrosophenols
5. Imine-oximes
6. Pyridine oximes
7. Azo-oximes
8. Hydroxyoximes
9. Amine oximes
10. Amido oximes

The effect of chromophores on the energies of transition and sensitivity of the absorption has been examined. It is suggested by Huckel molecular orbital theory that the transition frequency decreases with increase in conjugation.

2.2 Solvent-Extraction Spectrometry

2.2.1 Solvent-Extraction Method

By using an immiscible liquid (usually organic) for extraction, the separation of a desired constituent from a solid or colloidal sample dispersing in a solution (usually aqueous) may sometimes be conveniently achieved. The compound should be effectively dissolved in the liquid while the solubility of any other substances present is so small as to be negligible. In many cases the dissolved compounds are coloured so they can be quantitatively determined by visible spectrometric method. The technique is applicable to trace level and large amounts of material. The performance of extracting process is quite simple, clean, rapid and convenient. The effect of shaking may be considered but can be lessened by applying most ultimate contact between the solute and the solvent.

The various terms used for expressing the effectiveness of a separation must be considered. For a solute A distributed between two

immiscible phases a and b, the Nernst distribution law provided the distribution coefficient or distribution ratio as :

$$D = \frac{\text{Concentration of solute in solvent a}}{\text{Concentration of solute in solvent b}} = \frac{[A]_a}{[A]_b}$$

Considering the extraction of a solute A from aqueous solution to an organic layer, when $[A]_o$ and $[A]_w$ are concentration of solute in organic layer (volume = V_o) and water layer (volume = V_w) respectively, the percentage extraction (E %) of the distribution of the solute A between water and organic solvent may be obtained from:

$$E\% = \frac{100 [A]_o V_o}{[A]_o V_o + [A]_w V_w} = \frac{100 D}{D + (V_w / V_o)}$$

In solvent extraction analysis for metal, it is concerned with methods by which the water solubility of inorganic cation may be caught by interaction with appropriate (large organic) reagents. These complexes derived from metal ions are usually soluble in organic solvents. In chelation complexes the central metal ion co-ordinates with a polyfunctional organic base to form uncharged stable ring compound. Such complexes may form clusters larger than just simple pairs with increasing concentration and can be easily extracted into organic solvent.

Factors favouring solvent extraction of the chelation complexes include :

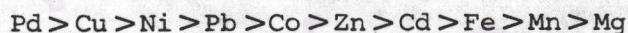
1. The basic strenght of the chelating group. The stability of the metal co-ordination complex will depend upon acidity of metal ion, basicity of the co-ordinating ligand and configuration of the resultant

complex. The reagent that co-ordinates with the metal ion must have basic character ; it rises with increasing pK_a value.

2. The electronegativity of the donor atoms of the basic group in the chelating agent. Atoms of lower electronegativity tend to form stronger bond, e.g., nitrogen and sulfur are better than oxygen.

3. Ring size. Five-or six-membered rings are most stable, since these have minimum strain. The functional groups of the base must be so situated in the molecule that they permit the formation of a stable ring.

4. The metal ion characteristics such as charge/ionic radius ratio. As the ratio increases, the stability of the metal complex usually rises, provided the metal ion has available binding orbitals for the electron pairs it accepts. The transition metals, possessing unoccupied low-lying d orbitals, form bonds much more readily than the non-transition metals. The orbitals involved in bond formation affect not only the bond strength but the stereochemical arrangement of the complex. The approximate order of stability of complexes of a limited number of bivalent ions toward a number of chelating agents has been given as:



5. Resonance and steric effect. The stability of chelate structures is enhanced by contributions of resonance structures of the chelate ring.

Solvent-extraction is generally employed in analysis to separate a solute (or solutes) of interest from substances which interfere in the ultimate quantitative analysis of the material. The choice of

solvent for extraction is governed by the following considerations:

- (i) A high distribution ratio for the solute and a low distribution ratio for undesirable impurities.
- (ii) Low solubility in the aqueous phase.
- (iii) Sufficiently low viscosity and sufficient density difference from the aqueous phase to avoid the formation of emulsions.
- (iv) Low toxicity and inflammability.

The extracted solute in the organic phase is removed for further preparation for the detailed analysis. In many colorimetric procedures involving an extraction the concentration of the desired solute is determined directly in the organic phase after extraction by measuring the absorbance of a known volume of the solution of the coloured complex.

2.2.2 Visible Spectrometry

One of the techniques most frequently used in trace analysis is the enrichment and isolation of the trace elements concerned, and their subsequent spectrometric determination. The inherent ease and simplicity of spectrometric methods coupled with the availability of inexpensive, reliable and now automated instrument are undoubtedly important reasons for this popularity. There are organic reagents available which form often intensely coloured complexes with the elements (usually inorganic) to be determined.

The basic principle of quantitative absorption spectroscopy lies in comparing the extent of absorption of a sample solution with that of a set of standards at a selected wavelength. When measurements of absorbances are carried out with spectrophotometers, the chosen wavelength should be appropriate to the spectral range concerned.

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In general, the maximum absorption-wavelength is chosen for maximum sensitivity. This chosen wavelength should not be in the region where the absorbance changes so rapidly with change in wavelength. The calibration curve obtained by the standard procedure usually becomes linear in a range of concentration of coloured complex. The molar absorptivity can be calculated from the slope of the curve. Many effects of experimental variables involving in the formation of absorbing compound are :

(1) pH. Since pH plays a very important role in complex formation, proper adjustment of pH or the use of a buffer often eliminates certain interfering reactions due to the acid-base properties of substances. The colour change associated with metal complex formation may be very pronounced when a proton (or protons) is displaced in the co-ordination process.

(2) Reagent concentration. The amount of reagent required for completing the complex formation is dictated by the composition of the absorbing species. An optimum concentration of reagents should be determined, since either not enough or too much reagent can cause deviation from Beer's law.

(3) Waiting time. Formation of some complexes is not immediately completed. It takes a period of time, several minutes or a few hours for full colour development or complete precipitate after addition of reagent.

(4) Shaking time. The effect of shaking time on complex formation and on extraction of the complex should be examined. The effective shaking time which the absorbance remained constant is

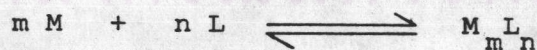
required for highest sensitivity of the method.

(5) Standing time. After shaking in the extraction process, both layers, organic and water, gradually separate. The measurement of absorbance should be performed after complete separation for clear solution and distributing equilibrium. If the absorbing complex formed is not very stable, the absorbance measurement should be made as soon as possible.

(6) Order of mixing reagents. Frequently it is important to add the reagents in a specific sequence, otherwise full colour development will not be possible.

(7) Coexisting ions and masking agents. Other ions existing in measured solution may interfere the quantitative results of interesting ion(s) or not if they are present in small amount. High concentrations of these electrolytes may form the ion-association complexes or ligand replacement of the metal that cause a distortion in quantitative results. Treating with some masking agents will help to eliminate the effect.

The spectrometric method is particularly valuable for studying complexes. The formation of many complexes can be represented by the equation :



The molar ratio of metal ion and ligand forming the complex is important. Various methods have been applied to the investigation of the empirical formulas of these complexes in solution. In this work, three common methods for establishing metal ion and ligand ratio of the complex were studied.

(1) Job method. A method for the identification of compounds formed in solutions by reaction of two components has been described by Job (24) and extended in applicability by Vosburgh and Cooper. (25) The substance M and L react according to the above equation and that solutions of M and L, both, are mixed in varying proportions while the total concentration and volume of both components are kept constant. The absorption of monochromatic light (a suitable wavelength) belong to each solution is measured and corrected for any absorption of the other unwanted species. The corrected absorbance is then plotted against the mole fraction. A maximum (or a minimum if the complex absorbs less than the reactants) occur at a molar ratio corresponding to the combining amount of M and L in complex. The use of the absorption for determination of the composition of the composition values corresponding to the concentration maxima is not as simple when two or more compounds are possible as when only a single compound is formed.

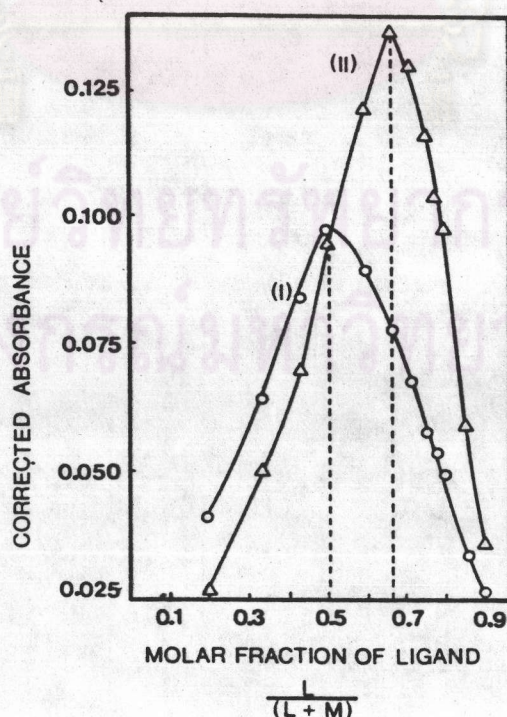


Fig. 2.1 The Job method plot of complex ML (I) and ML_2 (II)

(2) Molar-ratio method. This method applied by Yoe and Jones (26) is valid for stable complexes. The concentration of one component is fixed at a certain amount while the other varies to give a series of concentration ratios ($\frac{[M]}{[L]}$ of $\frac{[L]}{[M]}$). The absorbances of these solutions measured at a suitable wavelength are plotted against the ratios. The absorbance increase linearly up to the molar ratio of the complex. Further ratios of the component cannot increase the absorbance so the line becomes horizontal or shows a break as shown in Fig 2.2. The curve may not show sharp break at a molar ratio of the complex. This is caused by concerned other interaction(s) such as dissociation of the coloured complex. In some cases an increasing amount of a component may cause a decrease in absorbance owing to the formation of high-order complexes that have smaller molar absorptivity at the wavelength.

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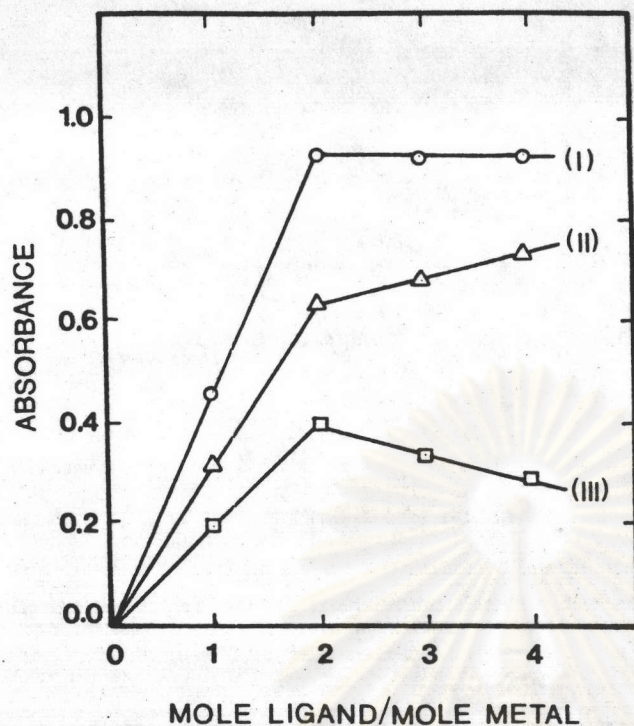
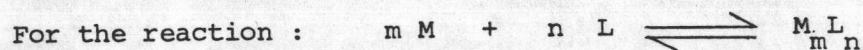


Fig.2.2 The molar ratio method plot of complex ML_2

- (I) Component L does not absorb at the wavelength (usually λ_{\max})
 (II) Component L absorbs slightly at the wavelength
 (III) An excess of component L causes a decrease in absorbance at the wavelength

(3) Slope-ratio method. The method was proposed by Harvey, Jr and Manning (27). The applicability of this method is suitable for systems in which a single complex is formed. When one component is kept constant in a sufficient excess amount for complete complex formation while the other one is varied in many amount so that the concentrations of the complex are proportional to those varying amounts.



$$\text{and } [M_m L_n] = \frac{[M]^m}{m} = \frac{[L]^n}{n}$$

Absorbances of each solutions were recorded under the Beer's law condition,

$$A = \epsilon b \left[M_m L_n \right]$$

When the absorbances of the combined complex is plotted against the varied amount of the component (M or L), the slope of the straight line is :

$$\text{The slope (when varying M)} = \frac{\epsilon b [M]}{m}$$

$$\text{and the slope (when varying L)} = \frac{\epsilon b [L]}{n}$$

The ratio of "n" to "m" in the complex $M_m L_n$ may be determined by taking the ratio of the two slopes.

$$\frac{\text{The slope (when varying M)}}{\text{The slope (when varying L)}} = \frac{n}{m}$$

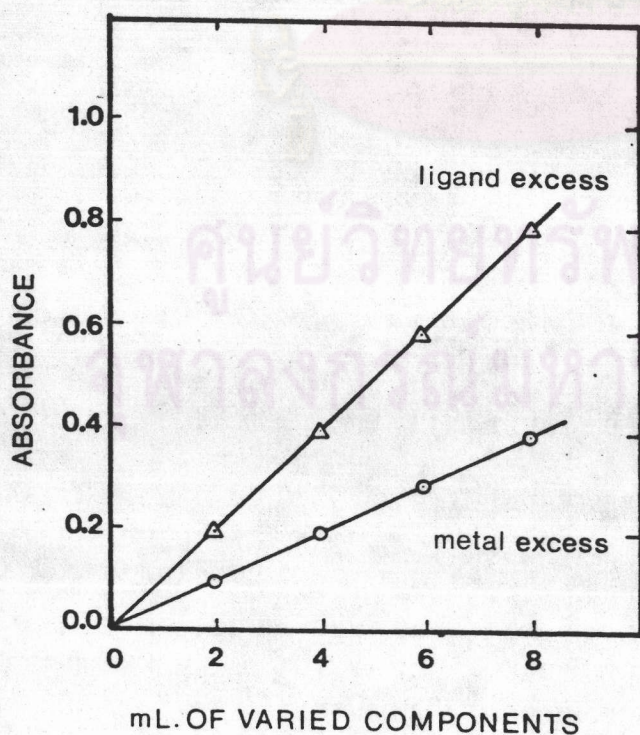


Fig. 2.3 The slope-ratio method plot of complex ML_2

2.3 Complexometric Direct Titrations with EDTA

Among the earliest methods of determining the presence of metal ions is the titration technique in which the metal complex is formed. The complexing reactions that proceed in simple exact stoichiometry with a large equilibrium constant to ensure completion at the equivalence point. Visual detection of the end point must be specific to each titration. The usefulness of EDTA, an organic reagent, as a titrant is due to the presence of four or six atoms which are available for co-ordination to a metal cation in such a way that five-membered ring are produced. The formation of metal-EDTA complex actually involves the replacement of indicator molecules in the coloured metal-indicator molecules. In the EDTA titration a metal ion-sensitive indicator is often employed to detect the changes of pM. Such indicators form complexes with specific metal ions ; these differ in colour from the free indicator and, in consequence, a sudden colour change occurs at the equivalence point.

There is always a competition in the solution between the metal ion and hydrogen ions seeking the negative sites on the EDTA molecule. The equilibrium situation is determined by relative bond strengths and the relative concentrations of the various species. The stability of metal-EDTA complexes are given in Table 2.1

Table 2.1 Stability constants of metal-EDTA complexes in the medium of ionic strength $\mu = 0.1$ at 20°C

metal ion	$\log K_f$	metal ion	$\log K_f$
Fe (III)	25.1	Al (III)	16.1
Cr (III)	23.0	Fe (II)	14.3
Hg (II)	21.8	Mn (II)	13.8
Cu (II)	18.8	Ca (II)	10.7
Ni (II)	18.6	H (I)	10.3
Pb (II)	18.0	Mg (II)	8.7
Cd (II)	16.5	Ba (II)	7.8
Zn (II)	16.5	Na (I)	1.7
Co (II)	16.3		

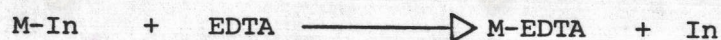
The efficiency of complex formation with EDTA is affected by variation of the pH of the solution. A decrease in pH will reduce the concentration of the complexing species, hence EDTA forms complexes with metal ions best in basic solutions in which the tendency to form slightly soluble metallic hydroxides is enhanced.

The procedure for the titration of metal ion with EDTA is direct titration. The solution containing the metal ion to be determined is buffered to the desired pH and titrated directly with the standard EDTA solution. At the equivalence point the magnitude of the concentration of the metal ion being determined decreases abruptly. This is generally determined by the change in colour of a metal indicator. The requisites of a metal ion indicator for use in the visual

detection of end point include :

- (1) The colour reaction gives strongly coloured solution before the end point (when nearly all the metal ion is complexed with EDTA).
- (2) The colour reaction should be specific or at least selective.
- (3) The metal-indicator complex must possess sufficient stability, however, be less stable than the metal-EDTA complex so that the change in equilibrium from the metal-indicator complex to the metal-EDTA complex should be sharp and rapid.
- (4) The colours of the free indicator and metal-indicator complex should be contrastable and the end point is readily observed.
- (5) The indicator must be very sensitive to small amount of metal ions.

The use of a metal ion indicator in an EDTA titration may be written in common 1:1 complex as :



(M-In is less stable than M-EDTA)

The stability of the metal-indicator complex may be expressed in terms of "indicator constant (K_{In})"

$$K_{\text{In}} = \frac{[\text{M-In}]}{[\text{M}][\text{In}]}$$

When $[\text{M-In}]$ = concentration of metal-indicator complex

$[\text{M}]$ = concentration of metal ion

$[\text{In}]$ = concentration of indicator not complexed

with metal ion

The equation may be expressed as :

$$\log K_{In} = pM + \log \frac{[M-In]}{[In]}$$

For a small titration error K_{In} should be large ($>10^4$), the ratio of K_{EDTA}/K_{In} should be large ($>10^4$) and the ratio of $\frac{[In]}{[M]}$ should be small ($<10^{-2}$).

2.4 General Methods for Preparation of Oximes.

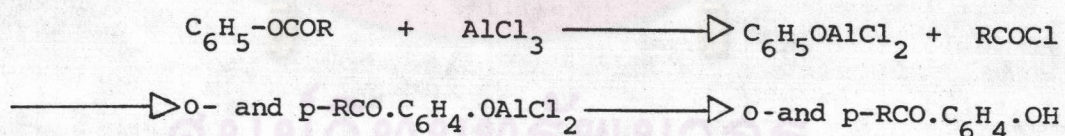
The two oximes, 2,5-dihydroxy acetophenoxime and 5-chloro-2-hydroxy-3-methyl acetophenoxime, have not been already commercially prepared. It is convenient to synthesis the aromatic oximes by using phenols as starting materials. The phenols can be acetylated with acetic anhydride to give acetic esters. The Fries rearrangement in the presence of aluminium chloride gives the o-hydroxy derivatives of acetophenone. The ketones are oximated to give the oximes. They are recrystallised several times from ethanol-water mixture.

2.4.1 Esterification

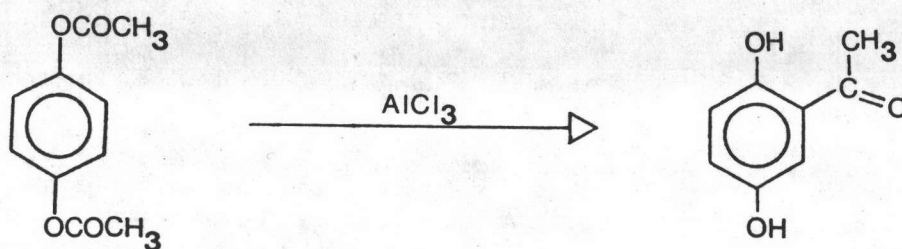
General esterification with an aromatic alcohol may readily achieved by using an excess of the acid to increase practical yield of ester. The use of a mineral acid as a catalyst and an excess of one of the components (generally acid) help the equilibrium reach sooner. The excess component may be largely removed by distillation (usually alcohol), pouring into a large excess of water or treatment with sodium bicarbonate solution (for acid).

2.4.2 Fries Rearrangement

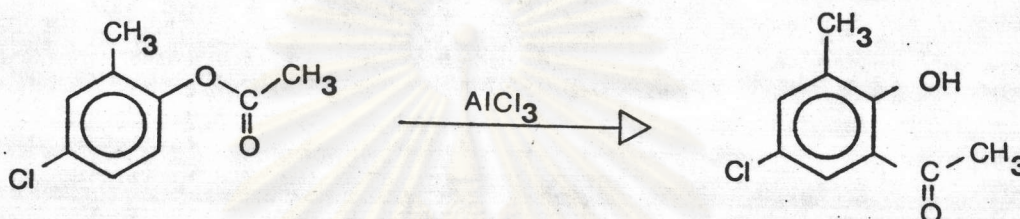
An ester derived from phenolic compound can rearrange to aromatic ketone in the presence of aluminium chloride. The ester and catalyst are usually employed in equimolecular amount. The nature of the product is influenced by the structure of the ester, by temperature, the solvent and the amount of aluminium chloride used. With phenylacetate ester, o- and p- hydroxy acetophenone are formed. Generally, low reaction temperature favour the formation of p-hydroxy ketones. The mechanism of the Fries reaction is not known with certainty. One mechanism regards it as a true intramolecular rearrangement in which the acyl group migrates directly from the oxygen atom to the carbon atoms of the ring. Another scheme postulates that the ester is claved by aluminium chloride to the corresponding phenol complex and acid chloride and the latter recombines in the normal Friedel-Crafts manner as shown in the equations:



2,5-Dihydroxy acetophenone can be prepared in good yield by heating hydroquinone diacetate in the presence of aluminium chloride.

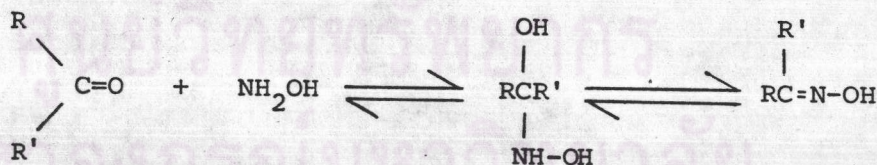


And 5-chloro-2-hydroxy-3-methyl acetophenone can be prepared in the same manner from 4-chloro-2-methyl phenylacetate ester.



2.4.3 The Oximation

Aldehydes or ketones containing C=O group can react with hydroxylamine to give oxime compounds. The procedure of oxime preparation by heating ketones or aldehydes with hydroxylamine hydrochloride and sodium hydroxide has wide application. The involving mechanism is condensation of the carbonyl groups with hydroxylamine as described:



Many of these oxime products are crystalline compounds of sharp melting point and therefore useful for identification and characterisation.