CHAPTER I

INTRODUCTION

Organic oxidation is defined as a loss of hydrogen or a gain of oxygen by the substrate, while inorganic oxidation is defined as a loss of electrons and increase in oxidation number. The reverse is true for reduction and they are complementary. Oxidation is applicable to virtually every type of carbon compounds, and takes the form of an addition, elimination, substitution, fission, coupling or rearrangement reactions. There is a great diversity in the nature and behaviour of the oxidants employed in organic chemistry. Not only some organic species but also a very wide range of inorganic species are found useful as the oxidants. In most cases, oxidation-reduction occurs between an organic and an inorganic compound in a solvent, and often in the presence of additional reagents or catalysts, both in homogeneous and heterogeneous phases. Studies of oxidation process have given substantial information necessary for the proposal of the mechanisms involved in reactions. The range of organic oxidation is continually being enlarged, often for specific types of reaction, and for compounds not previously investigated for this purpose. Whereas the use of permanganate and chromic acid were established during the 19th century, the more powerful oxidants, selenium dioxide and periodate became known and were widely used only a few decades ago. The recent review (1) includes ruthemium tetroxide, thallium (III) salts, lead (IV) salts, palladium (II) salt, carbonium ions. Other oxidants of similar nature have received much attention in recent years (2).

In the present survey of oxidation methods, classifications are made according to the different types of oxidant employed as follows:-

(1) Oxygen and related reagents containing oxygen-oxygen bonds, i.e. ozone, inorganic and organic peroxide compounds.

(2) Oxides and oxyanions of some non-metallic elements, those neighbouring to oxygen (Group V, VI and VII) in the Periodic Table.

(3) Salts, complexes oxides and oxyanions of the transition and post transition metals in their higher oxidation states, some catalytic and electrolytic processes of oxidation occurring on metal surfaces.

(4) Organic compounds capable of acting oxidatively, either by hydrogen removal or oxygen-donation.

A common mode of oxidation which employs an inorganic oxidant can be represented by the following equation

$M^{n}L_{x} + A \longrightarrow M^{n}L_{x}\text{----}A \longrightarrow M^{n-1}L_{x}$ + oxidized product where:-

M represents metal

L represents ligand

A represents organic substrate

$M^{n}L_{x}$ represents complexed metal ion

$M^{n-1}L_{x}$ represents complexed reduced metal ion

Production of an intermediate metal complex, with displacement of an existing ligand, may therefore be an essential step in an oxidation process (4). The oxidation of several organic compounds by certain oxidants such as 1, 2 diol by lead (IV) acetate, $Pb(OCOCH_3)_4$ is well known, the mechanism was proposed by Criegee (3).

Thallium (III) is isoelectronic with lead (IV) having $5\,d^{10}, 6\,s^2, 6\,p^1$ configuration, hence a similar reaction of thallium(III) to lead (IV) is expected. On the other hand thallium (III) differs from the other members of the same period in that stable derivatives are known of both the uni and ter valence states. Inorganic thallium compounds are usually more stable in the univalence state, while covalent organothallium compounds are stable only in the ter-valence state (4). The thermodynamic ease with which the transitions among the various oxidation levels occur is evident from the standard reduction potential.

$$Tl^{3+} + 2e^- \longrightarrow Tl^+ \qquad E^0 = 1.25\ V$$

$$Tl^+ + e^- \longrightarrow Tl \qquad E^0 = -0.33\ V$$

Reduction of thallium (III) to thallium (I) is thus an especially favorable process and can be usefully applied to organic synthesis.

The electron exchange reaction in the thallium (III) - thallium (I) pair has been intensively studied (8) and appears to be two electron transfer process, i.e. $Tl^{3+} + 2e^- \longrightarrow Tl^+$.

The reduction potentials of the thallium (III) - thallium (I) electrode in the presence of various anions are given below:-

$$Tl^{+3} + 2e^{-} \longrightarrow Tl^{+}$$

Anion present	E_f^o in volts
chloride	+0.789 (6)
acetate	+0.9518 to +1.0488 (7)
sulphate	+1.2207 (8)
nitrate	+1.2303 (9)
perchlorate	+1.2650 (8)

where E_f^o stands for the formal reduction potential

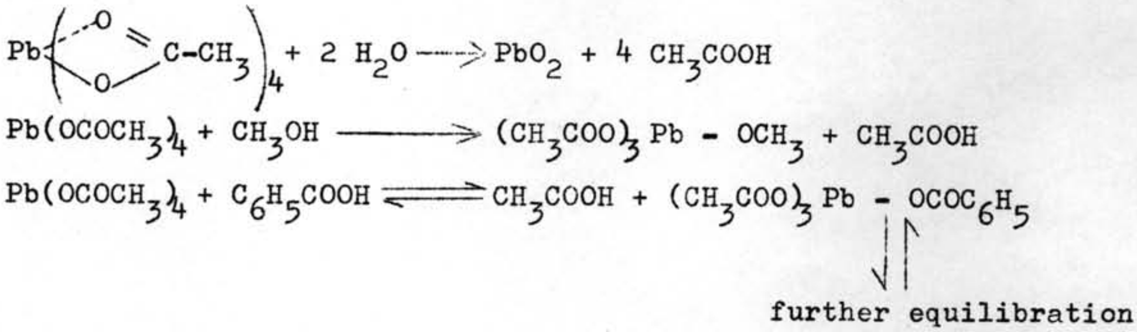
It is obviously seen that the ease of the oxidation of thallium (I) to thallium (III) salt varies greatly with the nature of anion present. As indicated above, thallium (I) chloride in hydrochloric acid solution is much more easily oxidized than thallium (I) sulphate, thallium (I) nitrate or thallium (I) perchlorate in the solution of appropriate acids. This difference is due mainly to the fact that the thallium (III) ion, which is the primary oxidation product of thallium (I) ion, is more or less converted into a complex anion with a consequent displacement of the equilibrium conditions of the thallium (I) - thallium (III) ion reaction of oxidation. The extent of those complex ion formations and the magnitude of the effect, vary with the nature of the anion of the salt and the acid present.

Among the isoelectronic elements with thallium (III), lead (IV) is widely employed as an oxidant in the oxidation of organic compounds. Its reduction potential is lower than that of thallium (III) and is an efficient two electron oxidant (10)

$$PbO_2 + H_2O + 2e^- \longrightarrow PbO + 2OH^- \quad E^\circ = +0.28\ V$$

$$PbO_3^{=} + H_2O + 2e^- \longrightarrow PbO_2^{=} + 2OH^- \quad E^\circ = +0.21\ V \text{ in } 8F\ KOH$$

Lead (IV) acetate is commonly used as a solution in glacial acetic acid or benzene. The covalent nature of lead (IV) acetate is characterised by its solubility and conductance property (11). The infrared absorption of acetate group suggests that both oxygen atoms of each acyloxy group coordinate with the lead atom. Lead (IV) acetate serves as a reagent used in non-aqueous media to accomplish the same type of reactions effected by periodates with water-soluble compounds. Its primary use has been for the oxidative cleavage of 1, 2-diols, α-hydroxy ketones 1, 2-diketones and α-hydroxy acids Being a more active oxidizing agent, lead (IV) acetate will cleave certain classes of compounds which are oxidized only very slowly by periodates. Although small amount of water appears not to be deleterious to oxidations with lead (IV) acetate, especially in acetic acid solution, the rapid reaction of this reagent with any molecules containing hydroxyl residue of lead (IV) acetate can also be equilibrated rapidly with the acyloxy groups of other carboxylic acids shown by the following equations:-



$$Pb\left(\begin{matrix}O\\ O\end{matrix}\!\!>C-CH_3\right)_4 + 2\ H_2O \dashrightarrow PbO_2 + 4\ CH_3COOH$$

$$Pb(OCOCH_3)_4 + CH_3OH \longrightarrow (CH_3COO)_3Pb - OCH_3 + CH_3COOH$$

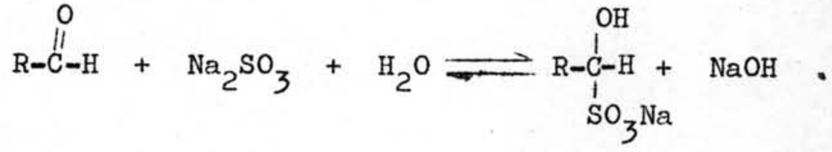
$$Pb(OCOCH_3)_4 + C_6H_5COOH \rightleftharpoons CH_3COOH + (CH_3COO)_3Pb - OCOC_6H_5$$

In the present work, the oxidative behaviours of thallium (III) compounds containing various anions in comparison to that of lead (IV) in the reaction with ethylene glycol and 2, 3-butanediol were investigated. The diols were chosen because they were readily available and are inexpensive. Since the cleavage of 1, 2-diol by lead (IV) acetate is well known qualitatively, only the techniques used in the determination of the product quantitatively was developed in this study, which was then applied to the thallium series. Briefly, the organic substrates were oxidized by the inorganic salts in question under the suitable conditions, the oxidized products were then separated, identified and analysed in the form of dinitrophenylhydrazones using infrared and ultraviolet absorption spectroscopic techniques. For the purpose of comparison, the chemical yield of products can be used as a measure of the oxidative power of various thallium salts relative to that of lead (IV) acetate.

The extensive survey of the analytical literature (12) revealed that in order to identify and determine specific compounds of carbonyl types, a wide variety of reagents and instrumental techniques were recommended. Nevertheless volumetric and gravimetric methods and to a lesser extent a colorimetric method are found to be generally applicable. These are summarized below:-

1. Volumetric methods

1.1. Bisulphite procedures Carbonyl compounds are allowed to react with sodium bisulphite with the formation of addition products, for example



$$R{-}\overset{\overset{O}{\|}}{C}{-}H + Na_2SO_3 + H_2O \rightleftharpoons R{-}\underset{SO_3Na}{\overset{OH}{C}}{-}H + NaOH .$$

The general procedure consists of the addition of an aliquot of standard acid to a large excess of sodium sulphite. The yield of the addition product formed in the reaction is found by back titration of the unneutralised acid potentiometrically. Results show that the formation of the addition product is a reversible reaction and the distribution at equilibrium depends upon the character of the carbonyl compound, the pH of the solution, and the excess of bisulphite. Ketones, in general, interfere with the determination of aldehydes only if they are present in excess of about 10 mole per cent. The reproducibility of the procedure is ± 0.2% .

1.2. The oximation method The method is based on the reaction of hydroxylamine with a carbonyl compound. The excess reagent is then titrated with a standard acid in order to determine the amount consumed. Although this reaction is rapid and complete, a serious limitation in its use is the instability of the reagent as a result of the air oxidation.

1.3. The oxidation method for aldehydes using silver ion

A sample of aldehyde is allowed to react with a freshly prepared standard solution of a modified Tollen's reagent. The excess silver ion is titrated potentiometrically with a standard solution of potassium iodide. The disadvantage of this method is that it is applicable mainly to water-soluble aldehyde, it also gives low recoveries and poor accuracy for formaldehyde, and acetaldehyde, especially when small amounts are used. Peroxides, acids and esters interfere with the results.

1.4. Determination of aldehydes using the reaction of primary amine Aldehydes are reacted with lauryl amine to form the Schiff base; and the excess lauryl amine is titrated against standard acid. The method is applicable to aromatic aldehydes and formaldehyde. The instability of the colour formed presents some difficulties in the quantitative use of this reagent.

2. Gravimetric method

Carbonyl compounds are characterised by the reaction with 2, 4-dinitrophenylhydrazine to form a highly coloured hydrazone precipitate. In this method, yields of pure 2, 4-dinitrophenylhydrazones of the aldehydes are determined gravimetrically. However, there may be some interferences of other material which can oxidize the hydrazone to form tars, and these are weighed with the hydrazones. The gravimetric method gives slightly low recoveries especially for the derivatives of the low molecular weight aldehydes due to the solubility of the hydrazones.

3. Colorimetric method

Trace quantities of carbonyl compounds, ranging from 3 to 300 ppm., can be determined effectively by a colorimetric method. The first part of the procedure is essentially the same as that given in the gravimetric method. After the separation of yellow pricipitate of 2,4-dinitrophenylhydrazone from the excess reagents by extracting with n-hexane, the amount of the derivative was determined from the absorbance at 330-340 nm. The procedure represents an improvement over other existing methods because reagent interference is eliminated the spectra of the pure, neutral 2,4-dinitrophenylhydrazones are very reproducible, and the colour is completely stable.

By comparing all methods described above, colorimetric method seems to be the most suitable one for the system under consideration. The obvious advantages over other methods are speed and simplicity of the technique. This is essential for such systems involving the low molecular weight aldehydes which are susceptible to volatilisation like the ones formed in the reactions in this work. Besides, the precision, accuracy and reproducibility of the result obtained by the colorimetric method are easily achieved. Details of the experiment are given in Chapter III.