

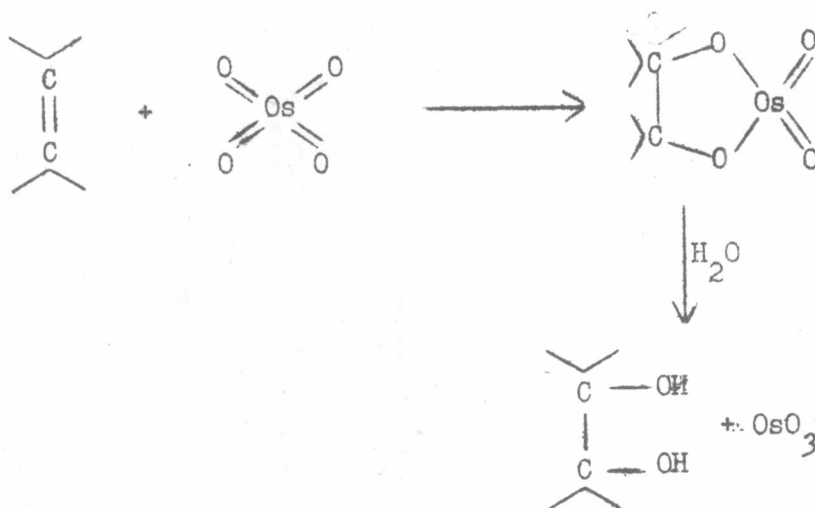
## CHAPTER 1

### INTRODUCTION

Oxidation and reduction are familiar words used to describe a very large number of reactions, although the term may be somewhat difficult to define precisely and comprehensively for organic chemistry. One traditional inorganic definition, involving a change in the valence of an element, is inapplicable, since the valence of carbon is nearly always 4. A second inorganic definition, involving the gain or loss of electrons, is difficultly applicable, since organic oxidations or reductions are not often carried out at electrodes and are usually irreversible.

One useful definition of oxidation for an organic compound is the gain of oxygen or loss of hydrogen; conversely, reduction of an organic compound is the loss of oxygen or gain of hydrogen. Thus, hydrogenation, the addition of hydrogen to a molecule, is an example of a reduction, whereas dehydrogenation is an example of an oxidation. This definition covers most but not all oxidations and reductions of organic compounds. It can be ambiguous, since both hydrogen and oxygen are sometimes gained or lost from an organic compound in a single reaction. For example, water can be added to alkenes or eliminated from alcohols, and alkenes can be converted to glycols.

Although a completely comprehensive definition may be difficult, one can nearly always decide whether a compound is oxidised or reduced (or neither) in a particular reaction. One of the most useful criteria is the fate of the inorganic reactant. For example, in the conversion of an alkene to a 1, 2-glycol, osmium (VIII) is converted to osmium (VI); since the inorganic reagent is reduced, the organic compound must have been oxidised.



On the other hand, the addition of water to an alkene does not involve a change in the oxidation state of the oxygen atom, and this reaction is neither an oxidation nor a reduction.



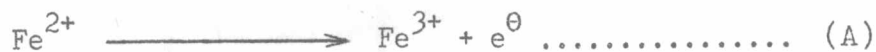
Thus, another useful definition might be that an organic compound is oxidised if the second reactant is reduced, and an organic compound is reduced if the second reactant is oxidised.

To summarize, the term oxidation is now used to cover any one of the following processes:

- (a) increase of valence.
- (b) loss of one or more electrons.
- (c) gain of oxygen.
- (d) loss of hydrogen or a metal.
- (e) gain of any non-metal (other than hydrogen) or non-metallic radical.

Reduction is the reverse of any of the above processes.

The term oxidation-reduction potential or "redox potential" is the potential for process in which the electrolyte contains two oxidation states of a substance in equilibrium with each other. Suppose a platinum wire is inserted in a solution containing both iron (II) and iron (III), the processes that are liable to occur are



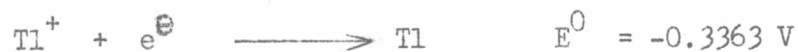
The half-reaction (A) involves oxidation and its potential is an "oxidation potential" whose sign is that of the so-called "American sign convention". The half-reaction (B) involves reduction

and its potential is a "reduction potential" associated with the "European sign convention". There is no doubt about which potential is relevant provided the half-reaction to which it refers is written out in full.

Inspection shows that the reduction potential has the same sign as the potential of the actual electrode. For this reason the IUPAC recommendation that only reduction potentials should be called electrode potentials is adopted. Every half-reaction is therefore written in the form<sup>(1)</sup>



Thallium is one of the group III B elements, and its electronic configuration is (Xe)  $4f^{14}$ ,  $5d^{10}$ ,  $6s^2$ ,  $6p^1$ . While the trivalent state is important for all four elements, the univalent state becomes progressively more stable as the group is descended and, for thallium, the thallium (I)-thallium (III) relationship is a dominant feature of the chemistry. It forms two series of salts—thallous and thallic compounds in which the element is respectively uni- and trivalent. The general properties of the two series are very different. Inorganic thallium compounds are usually more stable in the univalent state, while covalent organothallium compounds are stable only in the trivalent state. The thermodynamic ease with which the transitions among the various oxidation levels can occur is evident from the standard reduction potential<sup>(1)</sup>.



Reduction of thallium (III) to thallium (I) is thus an especially favourable process, and one which is of critical importance in the applications of thallium compounds to organic synthesis.

The electron exchange reaction in the thallium (III)-thallium (I) pair has been intensively studied and appears to be two-electron transfer process, i.e.



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



Anion present	$E_f^{\circ}$ in volts
chloride	+ 0.789 <sup>(2)</sup>
acetate	+ 0.9518 to + 1.0488 <sup>(3)</sup>
sulfate	+ 1.2207 <sup>(4)</sup>
nitrate	+ 1.2303 <sup>(5)</sup>
perchlorate	+ 1.2650 <sup>(4)</sup>

Where  $E_f^{\circ}$  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 the anion present. As indicated above, thallium (I) chloride in hydrochloric acid solution is much more easily oxidised than thallium (I) sulfate, thallium (I) nitrate or thallium (I) perchlorate in the solution of appropriate acids. This difference is due mainly to the fact that 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<sup>(6)</sup>.

The reduction potentials of lead (IV), thallium (III) and mercury (II) to lead (II), thallium (I), and mercury (0) are 1.7, 1.25, and 0.85 V, respectively<sup>(7)</sup>. These values, of course, may be without meaning in derivatives of the ions which react in nonaqueous solutions. One of the largely untapped research areas is the study of the effect of attached ligands on the reactivity and selectivity of thallium (III).

Oxidation of a variety of substrates by lead tetraacetate<sup>(8)</sup> and mercuric acetate<sup>(9-11)</sup> have been studied extensively. Oxidation by thallium (III) has not been extensively examined and the majority of the research has been reported in the last decade. Unfortunately, a significant fraction of the reported work appears in notes and



communications which have not yet been reported in detail. The reduction potential of the thallium (III) is between those of mercury (II) and lead (IV), and thallium appears immediately between mercury and lead in the periodic table. It is surprising that oxidation by thallium (III) salts have not been investigated more extensively as they would be expected to be more selective than lead (IV) salt.

All the reactions of thallium (III) involve electrophilic attack of the organic molecule by a metal derivative. Using Pearson's<sup>(12)</sup> classification of hard and soft acids and bases, thallium (III) is classified as a soft acid as are mercury (II) and lead (IV). Reports of the relative electrophilicity of the three soft acids in comparable systems are limited only in the oxidative cleavage of cyclopropanes<sup>(13-15)</sup>. The rates of the reactions stand in the order Tl (III) > Hg (II) > Pb (IV). On the basis of the charge of the central metal atom, the anticipated order is Pb (IV) > Tl (III) > Hg (II). However, there are important structural considerations. Lead (IV) acetate is coordinatively saturated, whereas thallium (III) acetate and mercury (II) acetate are not. Thallium (III) derivatives should be examined more closely as oxidizing agents in organic chemistry because of their rapid rate of reaction.

Selectivity of thallium (III) is higher than that of mercury (II), which, in turn, is higher than that of lead (IV). Again, this relationship has been derived from the study of the cleavage of arylecyclopropanes<sup>(13-15)</sup>. Although the usual reactivity-selectivity

relationship appears to be reversed, it is important to note that subtle differences in the reaction mechanisms of apparently similar reactions may negate the relationship. It is necessary to consider the nature of the metal species in solution, the reactive species, and the structure of the transition state, all of which are functions of the ligands attached to the metal. Regardless of mechanistic interpretations, the conclusion that thallium (III) is the most selective reagent should prompt examination of its utility in cases where lead (IV) has been shown to give complex mixtures of products.<sup>(8)</sup>

One of the mechanistic advantages of the study of thallium (III) oxidations is that intermediate organothallium derivatives can be isolated if desirable<sup>(16-18)</sup>. Thus the direction of addition to electron-rich centers and the stereochemistry of addition may be ascertained. The solvolysis of the carbon-thallium bond is extremely facile and allows for easy conversion to nonthallium-containing products. Mercury (II) reactions lead to quite stable organomercury compounds<sup>(9)</sup>. The solvolytic lability of carbon metal bonds decreases in the order of  $Pb > Tl > Hg$ . It should be noted that since the solvolysis of these organometallic derivatives is in effect a redox reaction, the ordering is entirely consistent with reduction potentials.

It has been shown that organomercury derivatives can be easily solvolyzed by appropriate changes in the anion associated with the mercury<sup>(19)</sup>. It may be possible to find ligands which will stabilize the organothallium intermediates and allow them to be more readily isolated. Replacement of the ligand may labilize the derivatives



and allow the solvolytic reaction to occur.

It is clear that all thallium compounds should be regarded as extremely toxic<sup>(20)</sup>. In order to avoid contact with the salts of thallium, rubber gloves should be worn by the experimentalist. Great care should be taken to avoid spilling solutions of thallium derivatives on the skin. It is advisable to restrict the area of usage of thallium to one which may be readily cleaned. Both bench tops and hood surfaces should be scrubbed and an effort should be made to reduce the dust level of the laboratory in general.

A few words on the human toxicity<sup>(21, 22)</sup> of thallium compounds are in order. The human lethal dose of thallium sulfate is about 1.75 g.. Thallium is readily absorbed following ingestion; it is also absorbed by the skin. It is a cumulative poison (only 3.2% of the body burden is excreted per day). Acute evidence of poisoning appears in 1-5 days. It causes gastrointestinal and nervous system disorders. Symptoms of chronic poisoning are: weakness and pain in extremities (polyneuritis) and loss of hair. Acute poisoning causes: nausea, vomiting, diarrhoea, tingling, pain in extremities, weakness, coma, convulsions and death (by respiratory failure, pneumonia or circulatory disturbances). Radiographic studies of thallium poisoned human being revealed hepatic opacity due to the presence of thallium in the liver. The recommended maximum atmospheric concentration (8 hours per day) is 0.1 milligram thallium per cubic meter.

In the present study, the oxidative properties of thallium (III) compounds containing various anions were studied comparatively

in the oxidation of hydroquinone and 4-aminophenol. Since the oxidative behaviours of thallium (III) trifluoroacetate with hydroquinone and 4-aminophenol have been reported, other thallium (III) compounds were used to oxidise the same substrates under suitable conditions. The oxidised product was identified using infra-red and ultra-violet spectrophotometric techniques. For the purpose of comparison, the chemical yield of product can be used as measure of the oxidative power of various thallium (III) salts.

Thallium (III) salts that have been used in this study, are listed with some physical properties as follows:<sup>(23)</sup>

Compound	Formular weight	Color and Crystalline form	Melting Point °C	Boiling Point °C	Solubilities
$Tl(NO_3)_3 \cdot 3H_2O$	444.43	Col., rhomb., deliq.	-	s.100	d.in hot and cold water; s.in MeOH, dil. mineral acid, aqueous glyme
$Tl_2(SO_4)_3 \cdot 7H_2O$	823.03	Col., leaf.	$-6H_2O$ , 220	-	d.in hot and cold water; s. in dil. $H_2SO_4$
$TlCl_3 \cdot 4H_2O$	382.79	Col., need.	37	$-4H_2O$ , 100	v.s. in cold water, d.in hot water, s. in al., eth.
$Tl(OAc)_3$	-	-	-	-	-