KINETICS AND MECHANISM OF OXIDATION OF SOME ORGANIC MOLECULES

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I certify that the thesis entitled "KINETICS AND MECHANISM OF OXIDATION OF SOME ORGANIC MOLECULES" submitted by Miss Mitra Bhattacharjee for the Degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by her under my supervision. She has been duly registered, and the thesis presented is worthy of being considered for the Award of the Ph.D. Degree. This work has not been submitted for any Degree of any other University.

Mahendra K. Mahanti

(Dr. MAHENDRA K. MAHANTI)
Signature of the Supervisor

Date : December 12, 1983.
Place : SHILLONG.

DEDICATED

TO

MY PARENTS

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CONTENTS

INTRODUCTION

Metal ion oxidants can function either as one-equivalent or two-equivalent reagents. One-equivalent oxidants are those which accept a single electron by direct transfer or by interaction with a hydrogen atom. Two-equivalent oxidants can accept two electrons from the substrate.

In one-equivalent redox processes, the change of valency can be brought about by either an inner-sphere or an outer-sphere mechanism (1).

1. Inner-sphere mechanism:

The inner-sphere or bonded mechanism envisages a direct contact between the oxidant and the reductant, and the transition state is characterised by a ligand which is bonded to both metal ions. It can therefore act as a bridge between them for the transfer of an electron. The typical reaction is (2):

$$Cr^{2+}(aq) + (NH_3)_5\ Co^{III}\ Cl^{2+} \longrightarrow$$

$$CrCl^{2+}(aq) + Co^{2+}(aq) + 5\ NH_3$$

The formation of an inner-sphere transition state would lead to considerable distortion of the ions, which may thus assist electron transfer by reducing the energy terms involved. In order that an inner-sphere mechanism can operate, the ligand present should behave in a bidentate manner.

The ligand must possess available pi-orbitals, and one of the reagents involved must have a ligand which can be easily displaced.

2. <u>Outer-sphere mechanism</u>:

Outer-sphere electron exchange reactions constitute the simplest class of electron transfer reactions. In an outer-sphere mechanism, the inner co-ordination shell of both reagents is preserved intact in the transition state. Since the metal-ligand distances will be affected by valency change, some distortion of the inner shells would occur, but no metal-ligand bond would be broken or formed.

The essential steps in these reactions would be:

(a) the approach of two reagent ions, which may be aided or hindered by electrostatic forces;

(b) before electron transfer can occur, two conditions must be obeyed (3), in accordance with the Franck-Condon principle:

(i) the electron transfer must not alter the energy of the system. This electron transfer occurs in a very short time, and the only possible loss or gain of energy would be by radiation. Electron transfer can occur only if the oxidant and reductant have been vibrationally excited to the same total energy. Thus, when the valency states of a reagent are closely similar in bond energy and geometry, the outer-sphere process would be expected to be most facile.

(ii) the overall spin angular momentum should not be altered.

(c) the process of electron transfer itself. If the reagent complexes are sufficiently close and of suitable symmetry, such that there is some interaction between the orbitals involved in electron transfer, then the probability of electron transfer would be essentially unity. The requirement of orbital overlap can be related to the orbitals of the reagents. This would suggest that in octahedral complexes, t_{2g} electrons might be more easily transferred than e_g electrons which are in orbitals directed along the metal-ligand axis.

In order to establish that an outer-sphere or non-bonded electron transfer can occur from an organic compound to a metal oxidant, it is necessary to choose a suitable model system in which the probability of non-bonded mechanism would be a maximum, and that of the competing bonded process a minimum. The oxidant should be so chosen such that it possesses ligands which are slow or difficult to replace. The organic substrate should be so chosen such that it is not likely to displace ligands from a metal ion complex. Examples of such exchange-inert oxidants are the iron (III) tris-o-phenanthroline complex (4), Ir Cl_6^{2-} ion (5), Mn (III) tris-acetylacetone complex (6), ceric ions (7), and hexacyanoferrate (III) ion (8,9).

In the reactions of one-equivalent oxidants with organic substrates, the most frequently encountered oxidation process would seem to correspond to an electron transfer between substrate and oxidant, accompanied by the breaking of a C-H bond and loss of a proton to give a substrate radical, as for example (10):

$$\mathrm{Co\ (III)} + C_6H_5CH_3 \longrightarrow \mathrm{Co\ (II)} + C_6H_5CH_2 + H^+$$

It would therefore be expected that the loss of a proton would be slower than electron transfer, and hence would correspond to the rate determining step.

The presence of radicals may be inferred by their oxidation or reduction of added inorganic ions, or by their ability to cause polymerisation to occur with added monomer, as for example, acrylamide or acrylonitrile. If the radical is present in sufficiently high concentrations, its presence can be detected by electron spin resonance spectroscopy.

Although the radical may undergo many other processes, it is most probable that in the presence of an excess of oxidant, the radical will be oxidised further. Examples are known where the main mechanisms of this step may be:
(a) a non-bonded electron transfer (conversion of a neutral radical to a cation), as for example the oxidation of 2,6-dimethylphenol by hexachloroiridate ion (5), and the oxidation of hydroquinones by ferric ions (11); (b) bonded electron transfer or the transfer of a ligand from the oxidant to the

radical, as for example, the reduction of $IrCl_6^{2-}$ by Cr^{2+} ions(12); (c) redox substitution, in which the radical remains attached to the complex, as for example, the phenylation of the ferricenium complex (13,14); (d) redox addition, where the radical remains attached to the complex, as for example, the reaction of hexacyanoferrate(III) with isobutyraldehyde(15).

Oxidation of organic substrates with potassium hexacyanoferrate (III):

Potassium hexacyanoferrate(III), $K_3Fe(CN)_6$, is essentially a substitution-inert transition metal complex(16). It does not exchange its ligands at a rate fast enough to compete with rapid electron transfer. Therefore, oxidations by hexacyanoferrate(III) ion occurs by means of a non-bonded electron transfer or outer sphere process, whereby an electron is transferred from the substrate to the metal ion through the cyano ligand.

In acidic medium, potassium hexacyanoferrate(III) has been used for the oxidation of sulphur containing compounds (17-25), and very recently, for the oxidation of toluene and substituted toluenes (26-29), diphenylmethane and triphenylmethane (30), unsaturated systems (31-32), and polynuclear systems (33-34).

In neutral medium, potassium hexacyanoferrate(III) has been used for the oxidation of aliphatic amines(35).

In alkaline medium, potassium hexacyanoferrate(III), has been extensively used for the oxidation of various kinds of organic substrates such as aldehydes(36-40), ketones (36-37, 41-46), amines (47-53), alcohols and diols(54-62), sulfur compounds (63-69), acids (70-78), sugars (79-82), hydrazines (83-85), amino acids (86-87), acyloins (88-89), As(III)(90-92), hypophosphite(93-94), hydrocarbons (95), and phenols (96-98).

Oxidation of phenols

The chemical oxidation of phenols is complex, in that:

(a) it usually gives a mixture of products; and

(b) with the same phenol, different oxidants can yield quite different product mixtures.

In the presence of oxidizing agents, phenolic molecules can undergo either carbon-carbon or carbon-oxygen coupling to give a variety of products. Simple phenols can be linked at positions ortho and/or para to the hydroxyl group to yield several possible dimers; these can be further oxidized to produce trimers, polymers and quinonoid-type structures. In more complex polyhydroxy aromatic compounds, coupling of both types may occur —— intramolecular as well as intermolecular coupling. Substitution products and compounds resulting from coupling at benzylic positions may also be observed.

In most synthetically employed phenol coupling reactions, polymers are obtained as the side products; polmerization of phenols via oxidative coupling is an industrial process of great commercial importance.

The choice of a phenol coupling reagent will not only increase the synthetic utility of phenol oxidative coupling reactions, but will also indicate the manner in which various enzymes might catalyze such reactions. This would open up vast possibilities for a further probe into the study of important biological reactions, wherein the key step involves the oxidative coupling of phenols.

The oxidation of phenols by hexacyanoferrate(III) in alkaline medium would give the aryloxy anion. This anion can transfer an electron to hexacyanoferrate(III), resulting in the formation of an aryloxy radical. The radical would then be free to react, and the formation of coupled products is a distinct possibility.

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