GENERAL INTRODUCTION
Some of the most important and common reactions in organic chemistry involve oxidation and reduction. Reactions involving oxidation and reduction are among the most common of chemical processes. However, in contrast to many other types of reactions which have received continued attention for many years, it is only recently that oxidations have been subjected to detailed study.

To the inorganic chemist, the statement that oxidation is equivalent to electron loss and reduction to electron gain e.g.

\[
\begin{align*}
\text{Fe}^{2+} & \xrightarrow{\text{oxidation}} \text{Fe}^{3+} + e^- \\
\text{Fe}^{3+} & \xrightarrow{\text{reduction}} \text{Fe}^{2+}
\end{align*}
\]

is adequate for describing reactions of ionizable substances. By developing this concept, physical chemists compare the oxidizing powers of different ions by reference to redox potentials, which are measures of free energy changes in thermodynamically reversible equilibria, but often have unwarrantably been calculated from enthalpy data for irreversible reactions.

These concepts, however, are not so clearly applicable in organic chemistry, because, when carbon compounds are oxidized, their component atoms are very seldom deprived of their surrounding complete electron shells. Again few oxidations of organic compounds are reversible reactions and the formation of a reaction scheme that would lead to an overall free energy decrease, gives no warranty that such a reaction can be effected.

It is instructive, however, to examine the movements of valency electrons that occur in any simple oxidation. The study of oxidation is essentially an examination of ways by which
electrons can be removed from organic compounds. Organic compounds are essentially covalent and have their valency electrons associated together in pairs. Moreover, they are mainly composed of a electron skeleton surrounded by a skin of hydrogens and consequently have few superficial electrons accessible for direct attack by colliding reagents. Covalent bond fission is an essential feature of organic reactions and it can be effected by two different pathways, viz., homolytic reactions in which electron pairs are symmetrically disrupted and heterolytic reactions in which electron pairs are transferred from one particle to another as an undivided entity. Electron removals by these two pathways have clearly distinguishable characteristics.

All homolytic electron transfer reactions require very much less activation energy than that for the direct breakage of a covalence. Hence homolytic oxidations, when once started proceed very rapidly indeed. The traces of free radicals, required for the initiation of homolytic oxidation, may be formed by the thermal dissociation of molecules which have weak covalences by disruption of molecules by exposure to radiant energy, high energy particles or electrons or by single electron transfer from ions of some transition elements.

Heterolytic oxidations involve the attack on organic compounds of electrophilic reagents which can, by a single process, gain control of a further electron pair. Heterolytic oxidants, therefore, attack the exposed electron pairs of atoms such as oxygen, nitrogen or sulphur or the loosely held electrons of olefins, rather than the buried electron pairs of C-H, OH or N-H bonds. Again, heterolytic reactions yield
stable molecular or ionic products in one or at the most two consecutive stages and, very seldom, lead on to chain reactions. On the other hand they usually require more activation energy than homolytic reactions and so tend to be slower processes.

Numerous reagents have been developed which bring about certain oxidations or reductions selectively. There is a host of oxidants that operate by a one electron transfer process, such as ceric sulphate\(^1\), ferricyanides\(^2\), perchlorates\(^3(a)(b)\) and acetate\(^4\) of Co (III), Ce (IV), Cu (II) and Mn (III) etc. Many of the most commonly used oxidizing agents such as dichromate and permanganate, however, may be classified as electrophilic, since they attack olefinic bonds and other functions known to be sensitive to the action of electrophiles. In recent years several oxidizing agents, specific and sensitive to varying degrees, have been added to the literature of organic chemistry. Selenium dioxide, aluminium alkoxide, tert-butyl chromate, chromium trioxide, organic per acids, periodic acids, potassium ferricyanides, etc. have greatly enhanced skill of the organic chemist in introducing and effecting particular groups in simple or large molecules. It is not to be expected that a single mechanism will satisfy every reaction; the nature of the substrate and of the medium profoundly affects the course of reaction.

In oxidation reactions, when the oxidizing species are not only capable of undergoing a series of simple valence changes but also contain oxygen, the substrate may be oxidized by one or more of the following processes:

(a) Hydrogen abstraction - in hydrocarbons to give free radicals.
(b) Electron abstraction - simple ionic oxidizing agents.
(c) Oxygen atom transfer.

Out of many available oxidizing agents, we are only concerned with those which purely bring about the oxidation or reduction by electron transfer mechanism.

The concepts of oxidation and reduction are much more precise in inorganic chemistry. It is, for example, quite plain that the oxidation $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ involves the loss of one electron and that the reduction $\text{In}^{2+} \rightarrow 2\text{In}^0$, the gain of two electrons. The reduction is seldom so clear in the case of organic compounds in which exchange of electrons often involves making and breaking of covalent bonds.

A sizable number of organic compounds exists which undergo reactions that involve electron transfer. A classic example is found in the reduction by an alkali metal in anhydrous ether of an aromatic hydrocarbon to its anion radical. In the same way variously substituted phenothiazines (I) may be successively oxidized to radical cation (II) and the dication (III); if the medium is properly chosen, reactions involving bond scission $[\rightarrow (IV)]$ or bond formation $[\rightarrow (V)]$ can be avoided.

![Scheme 1](image-url)
Two stable compounds which are interconvertible by gain or loss of one electron, form a simple system. For such system, it is well known that a standard redox potential can be defined. This potential is referred to the potential of a particular system. For example, in inorganic chemistry, oxidation-reduction potentials in aqueous medium are referred to the $\text{H}_2/\text{H}^+$ couple which is not a simple system but which has a very well defined potential under convenient conditions. Similarly, in all organic or aqueous organic media the standard potential of a simple system may be referred to a judiciously chosen reference. This is not the only criterion for the oxidation or reduction to take place and one must add to these thermodynamic considerations also the kinetic aspect, taking into account both the rates of electron transfer and of mass transfer which likewise may be limiting.

The oxidation of organic compounds by electron transfer reactions has been relatively neglected field, surprisingly, so when the reactions of this type may prove to be of great synthetic value. Most of the published work in this area has, however, been concerned with the radical cation intermediates, their e.s.r. spectra and the mechanistic pathways through which these primary one electron transfer species decompose or remain stable.

Electrochemistry has been the most general technique for generation of both stable and transient cation radicals. In principle, any successful electrochemical reaction should have its chemical counterpart provided the specific chemical oxidant is known. In practice, the two techniques for most of the reactions, however, are not exactly analogous at present, but it can be conceived that the situation will assuredly change as a knowledge of the factors deciding chemical and electrochemical oxidation increases. Moreover, the homogeneous solution
chemistry of radical ions in most cases the first intermediate in a one electron transfer reaction, is not as well developed as the chemistry of other intermediates viz. carbonium ions, neutral radicals, carbanions and carbenes. However, a number of papers exist\textsuperscript{70,73,104} which report the oxidation in homogeneous solution by (1) Metal ions and (2) Stable radical cations in properly chosen solvents. Oxidation with some stable radical cation salts has not until recently received much attention. A few papers\textsuperscript{72,74} which have recently appeared speak of radical cation salts as most promising candidates in simulating anodic oxidations of organic compounds. As such the topic deserves a special treatment which is given in the following paragraphs.

Reactions of Radical Cations:

Electro-oxidation has been the most general technique for the generation of both unstable and stable cation radicals. Stable cation radical can be produced if (a) a non-nucleophilic but polar solvent is used; (b) the orbital from which an electron is lost is of high energy; (c) the reactive positions are substituted. An example is 9,10-diphenyl anthracene.\textsuperscript{7} In acetonitrile, dichloromethane and nitrobenzene a stable cation radical is formed by electrooxidation at platinum electrode. This can be demonstrated by cyclic voltammetric experiments; the e.s.r. measurements offer unequivocal evidence towards the formation of radical cation species.

Cation radicals are discreet intermediates in a number of organic electrode processes. The primary species, the cation radical is too reactive to survive and participates in follow up chemical or electrochemical reactions that
determine its fate. The study of these interesting species is fast becoming a new frontier in organic chemistry. Understanding of the chemistry of radical cations has been greatly enriched through studies on aromatic compounds. Various aspects of anodic oxidation reactions of aromatics have been reviewed by Fleischmann and Fletcher, Peover, Sasaki and Newby, Weinberg and Weinberg, and Sterson and Schafer.

The critical elementary steps in anodic hydrocarbon oxidation are conceptually simple. An initial electron transfer gives a cation radical which can transfer a second electron to form a dication. Alternatively, the cation radical can transfer a proton to a suitable base in the system to give a radical, and the radical so formed can loose an electron to the anode to give the mono cation.

\[ R H \rightarrow R H^+ \rightarrow R H^{++} \quad - \quad - \quad - \quad (i) \]

\[ R H^+ \rightarrow R^+ \rightarrow R^+ \quad - \quad - \quad - \quad (ii) \]

The cation radical, the dication and the monocation are all subject to attack by nucleophiles, of which the nature, the concentration and the reactivity are all subject to investigators control. The cation radical, \( RH^+ \) and the radical \( R^+ \), can undergo product forming reactions by the multitudinous pathways available to radical species. These four reactive inter-mediates, the cation radical, the dication, the radical, and the monocation can, therefore, lead to a very large variety of products. The overall reaction mode can be one of addition, dimerization or substitution.

electrochemical oxidation of aromatic hydrocarbon provides an entry into rich areas of radical cation chemistry. A number of
oxidations of benzencoid aromatics have been performed. These reactions may all involve discreet cation radicals but all that has been proven is that electron transfer from the aromatic is the initial reaction. Some examples are:

\[
\text{dimerization} \quad \xrightarrow{\text{ArCH}_2\text{Cl}_2\text{Ar}} \quad \xrightarrow{-\text{e,} \text{H}_2\text{O}} \quad \xrightarrow{\text{ArCH}_2\text{Cl}} \quad \xrightarrow{\text{ArCHO}} \quad \xrightarrow{-\text{e,} \text{Cl}_2\text{C}^+} \quad \xrightarrow{\text{ArCH}_2\text{CHCl}_2\text{C}\text{C}_2\text{Cl}}
\]

\[
\text{CH}_2\text{CN} \xrightarrow{\text{H}_2\text{O}} \quad \xrightarrow{\text{ArCH}_2\text{NHCOCH}_3} \quad \xrightarrow{\text{H}_2\text{O}} \quad \xrightarrow{\text{ArCH}_2\text{OH}} \quad \xrightarrow{\text{HOAc}} \quad \xrightarrow{\text{ArCH}_2\text{COAc}}
\]

An example which demonstrates the effect of base on the anodic oxidation of aromatic compound is offered by 9,10 dimethylanthracene (DMA) in presence of some lutidines. The base reacts with DMA\(^{2+}\) at the methyl group to provide the dimer in high yield.\(^{20,21}\)

\[
\begin{align*}
\text{anodic oxidation} & \quad \xrightarrow{\text{e}} \quad \text{lutidone} & \quad \xrightarrow{\text{dimerization}} & \quad \text{dimethylidyne anthracene}
\end{align*}
\]

**Scheme II**

The situation is, however, not always as simple as indicated in Scheme II. 9,10-dimethylanthracene undergoes a one electron transfer oxidation of 1.1 v vs. s.c.e. in CH\(_2\)CN-HOAc containing sodium acetate and lithium perchlorate giving the cation radical which, in turn, reacts with acetate and
dimerizes according to scheme III$^{22}$ (ECE mechanism).

\[ \text{Scheme III.} \]

Electrolysis at 1.8 V gives the dication which must be the product forming species$^{22}$ (ECE mechanism).

\[ \text{DNA} \xrightleftharpoons{1.58V} \text{DNA}^+ \xrightarrow{0} \text{UAG} \]

These reaction schemes are well substantiated with cyclic voltamograms, e.s.r. studies and product isolation.

Oxidation of amines by anodic reactions or chemical oxidants, gives a better insight into the nature and reactivity of radical cation species. In the cation radical of aromatic amines, the unpaired electron tends to delocalize away from amine nitrogen into the one or more aromatic rings present. When this delocalization is extensive and ring sites are blocked with inert substituents, stable cation radical results. Perhaps in the various classes of aromatic amines, the possibility for studying cation radical properties is greater than in any other group of compounds. Much remains to be done on the effect of
various substituents on cation radical stabilities and the decomposition pathways. However, there exists a tremendous literature about the cation radical accompanied oxidation of amines.$^{23-25}$ The simplest example is provided by the oxidation of triarylanilines$^{26}$ described in Scheme IV.

$$
2\text{Ar}_2\text{N}^{++} \rightarrow \text{Ar}_2\text{N}^{++} \\
2\text{Ar}_2\text{N}^{++} \rightarrow \text{Ar}_2\text{N} \rightarrow \text{Ar}_2\text{N}^{++} \rightarrow \text{Ar}_2\text{N}^{++} \\
\text{Ar}_2\text{N} \rightarrow \text{Ar}_2\text{N}^{++} \rightarrow \text{Ar}_2\text{N}^{++} \rightarrow \text{Ar}_2\text{N}^{++}
$$

Scheme IV

The electrochemical oxidation of $N$, $N$-dimethylaniline has been studied in aqueous solution by Adams School$^{27-29}$; in acetonitrile by Dvorak et al$^{30}$ and Hand and Nelson$^{31}$ and in acetic acid by Dubois, LocaZe and Aranda$^{32}$. All these investigators, with the exception of Hand and Nelson found $N$,$N$,$N'$,$N'$-tetra methylbenzidine to be the predominant product.

Oxidation of phenylene diamines is of some historic interest. Pioneering studies of Michaelis$^{33}$ represent an early recognition of the generation and importance of cation radical intermediates. Discussion of this work is extensively available in the literature.$^{34}$ Cauquis et al$^{35}$ have recently studied the oxidation of nine $N$-substituted para phenylene diamines. All the substrates gave the initially formed cation radical which on further oxidation gave the dication.

A series of para dimethylamino substituted tetraphenylenethylenes have been investigated by Phelps and Bard$^{36}$ as possible examples of bonafide two electron redox systems.
Another area that has received considerable attention is the anodic oxidation pathways of aminoanthracenes. The simplest molecule in this series, 9-amino-10-phenylanthracene, affords a variety of decomposition pathways in NCS.\textsuperscript{37} The initial oxidation was found to be a one-electron process to generate a stable cation radical in the presence of an organic base such as diphenylguanidine; the radical is deprotonated and dimer formation follows. Chemical oxidation studies using permanganate and ferricyanide in alkaline solution also produces a dimer.\textsuperscript{38,39}

In the recent years, a host of publications have appeared in the oxidation of both aliphatic and aromatic amines undergoing decomposition pathways via the radical cation intermediates. An expanded treatment of this work is published in various reviews.\textsuperscript{40-43}

Studies on the oxidations of hydrazines, especially, tetra substituted hydrazines\textsuperscript{44} by chemical and electrochemical methods, also involve radical cations. The oxidation of tetraphenylhydrazine and the para substituted tetraphenyl hydrazines is of special interest because the degradation of the electrochemically generated cation radical results in the products similar to those obtained by treating the hydrazines by strong acid in the same solvent.\textsuperscript{45}

Progress has been made in understanding the oxidation of aromatic sulphides in the past few years. Sulphonium ions are usually formed via condensation of sulphide radical cations with unoxidized sulphide molecules.\textsuperscript{46}

\[
\begin{align*}
\text{Ph}_2\text{S} & \rightarrow \text{Ph}_2\text{S}^+ \\
\text{Ph}_2\text{S}^+ & \rightarrow \text{Ph}_2\text{S}^+ \quad \text{Ph}_2\text{S}^- \quad \text{Ph}_2\text{S}^+ \quad \text{Ph}_2\text{S}^+ \quad \text{Ph}_2\text{S}^+ \quad \text{Ph}_2\text{S}^+ \\
\end{align*}
\]

Extensive work has been done on the oxidation of thianthrene. The purple radical cation of the molecule is relatively stable.
in the variety of solvents and has been characterised by spectroscopic techniques.\textsuperscript{47,48}

The radical cations generated in the anodic oxidation of the substrate in the solvents MeCN, PhNO\textsubscript{2} or CH\textsubscript{2}Cl\textsubscript{2} could be stable if:

1. The nucleophilic attack of these species is reduced by the delocalization of the positive charge over the whole of the molecule.

2. The reactive sites are blocked or stabilized by substitution.

3. The temperature is low.

4. The solvent used has a low nucleophilic power.

In methylene chloride containing neutral alumina or acceptors of nucleophiles, such as trifluoroacetic anhydride, the stability of the cation radical has been shown to increase considerably.\textsuperscript{49}

In solution, stable cation radicals have been produced in the variety of media including concentrated sulphuric acid,\textsuperscript{50} antimony pentachloride - methylene chloride\textsuperscript{51} and aluminium chloride - nitromethane.\textsuperscript{52} Direct oxidations have utilized electrochemistry\textsuperscript{53} (usually in acetonitrile), metal ions\textsuperscript{54} and other chemical oxidants.\textsuperscript{55} Some relatively stable radical cations of aromatic hydrocarbons have been studied by Zweig and Coworkers\textsuperscript{56,57} using cyclic voltammetry which allows an estimate of the stability of the cation radicals by scanning the potential at various rates. In these fluorescent compound, where the cation radical and the corresponding anion radical are sufficiently stable, successive electrochemical oxidation and reduction in
aprotic solvents results in luminescent emission\textsuperscript{53,59} (electro-
chemiluminescence).

With 9,10-diphenylantracene as substrate, the product of first oxidation wave is the cation radical with negligible coupled chemical reactions. The cation radical in acetonitrile has a half life of approximately fifty minutes.\textsuperscript{60} In a chemical oxidation method, using cobaltic acetate-acetic acid solution, it was found that the addition of trifluoroacetic acid to the medium dramatically increased the radical cation concentration of 9,10-diphenylantracene.\textsuperscript{54}

In an interesting communication, Maruoka et al\textsuperscript{53} report that, in nitrobenzene, diphenylantracene, 9,10-dimethylanthracene, rubrene and tetraphenylpyrene are all oxidized in one reversible one electron step, the resulting cation radical being more stable than in acetonitrile. \textit{N},\textit{N},\textit{N}',\textit{N}'-tetra methyl \textit{p}-phenylene diamine can be easily oxidized to its cation radical, Wurster's blue, which has an appreciable stability.\textsuperscript{61-63}

Tetra kis (dimethylamino) ethylene has been found to undergo two step oxidation at the ME to produce first, the cation radical which is comparatively stabler and then the dication. The structure of this cation radical has been studied by e.s.r. and compared with that \textit{N}, \textit{N}, \textit{N}', \textit{N}'- tetra methyl phenylene diamine.\textsuperscript{64}

Thianthrene cation radical is quite stable and has been investigated by Shine and Coworkers.\textsuperscript{65}
Thianthrene cation radical salts can actually be isolated and mechanistic studies of their reactivity have proven very interesting. It has been shown that thianthrene cation radical reacts with water to disproportionate. The corresponding oxygen compound, contrastingly oxidizes water. Water causes rapid formation of thianthrene and thianthrene 5-oxide in equal amounts which can be determined spectrophotometrically.

The stability of the cation radicals formed upon anodic oxidation of triphenyl amines varies markedly with para substitution. The cation radical of tri-panisylamine is extremely stable, not only in non-aqueous solvents but also in aqueous solutions of pH 2-6. The cation radical stability of a number of triphenylamines and the effect of para substitution on the extent and rate of benzidine formation has been determined.

In the recent years, attempts have been made in generating stable cation radicals by chemical means in homogeneous solutions. The perchlorate salt of tri-p-bromophenyl amine has been obtained, which is appreciably stable.

Cation radicals generated in solution are in thermally equilibrated conditions, whereas those produced in mass spectroscopy by high energy electron impact are in electronically and vibrationally excited state. Cation radicals in solutions are generally obtained from oxidation ofamines, sulphides or oxygen compounds.

Oxidation by stable cation radicals has been relatively little studied up till now and it is surprising that this area has
remained neglected. These reagents hold a great promise for consideration as analogues of anodic process in that a good comparison can be made between anodic oxidations and chemical electron transfer oxidation in homogeneous solutions. The radical cation salts of appropriate redox potential could thus be used as one electron transfer oxidants so that the secondary cation radicals formed from the substrate could be conveniently generated free from complications i.e. ligand transfer, etc. normally encountered in comparable reactions with metal oxidants. In fact, work along these lines has commenced since seventees especially by Ledwith's group.\textsuperscript{72,73,55}

In a recent paper, Parker and Svanholm\textsuperscript{74} have reported the kinetics of thermodynamically unfavourable electron transfer reactions between cation radicals and aromatic compounds. The cation radicals of thianthrone, dibenzo p-dioxin and 9,10-diphenylanthracene were used in the reaction with anisole and anthracene in MeCN and CH\textsubscript{2}Cl\textsubscript{2} medium.

The reactions of radical cations of the triphenylamine series with neutral free radicals e.g. 2,2,6,6 tetra methyl-1-piperidinyl oxy and its 4-oxo derivative have been kinetically studied and the mechanisms for several of the reactions have been proposed.\textsuperscript{75}

Electron exchange studies of certain radical cations with their parent molecules have been carried out by Nelson et al.\textsuperscript{76}

Oxidation of quinones, commonly assumed to proceed via hydride transfer mechanism\textsuperscript{77} involve, in some cases, oxidation by electron transfer. Quinones, 2,3-dichloro-5, 6-dicyano p-benzoquinone (DDQ) in particular, are capable of effecting the
removal of either an electron, a hydrogen atom, or a hydride ion.\textsuperscript{77}

There is a wealth of literature regarding charge transfer complexes of electron donors with quinones.\textsuperscript{78-84} Many reactions which take place between donor and acceptor types of reagents involve the charge transfer complex as reactive intermediates.\textsuperscript{85} There are stray references which report the subsequent reactions of these charge transfer transfer complexes giving cation and anion radicals.\textsuperscript{86} The work on complete electron transfer with DDQ, leading to unambiguous formations of radical cations, of appreciable lifetime, from suitable substrates, appears to have remained unexplored. Having selected the reaction conditions in a judiciously manner, perhaps one could capitalize upon using DDQ as a potential electron-transfer oxidant. We have achieved considerable success in this direction.

**Oxidation with metal ions:**

Oxidation and reduction are conjugate processes. The oxidation and reduction of free radicals with metal complexes follows two general mechanisms; electron transfer and ligand transfer. Direct analogy exists with wholly inorganic descriptions of outer sphere and inner sphere mechanism. The redox process is derived largely by transfer of an electron from reductant to oxidant with only indirect combinations from the solvent and ligand. In contrast, ligand transfer in inner sphere mechanism demands maximum involvement of the ligand in the transition state.

Electron transfer oxidation occurs mainly with the oxy salts of metal ions, for example, nitrate and perchlorate salt of Cu (II), whereas ligand transfer oxidation predominates with the halides particularly chloride and bromide and pseudohalides e.g. cyanide, azide and thiocyanate salts. As expected, the
singlet state of dimeric copper (II) is unreactive in electron transfer reactions. However, it has also been demonstrated that the triplet state of the dimer is largely inactive. Therefore, only paramagnetic copper species functions as electron transfer agents, for example, in the oxidation of alkyl radicals.

It has been seen that extensive co-ordination of the metal ion, significantly decreases its capacity to function as an electron transfer oxidant. For example, the 2-cyano, 2-propyl radical is inert to oxidation by electron transfer, but is readily oxidized by ligand transfer.\(^6\) There are several examples of ligand transfer oxidations, the sandmeyer and Meerwin reactions being classic.\(^89-92\)

The use of non-aqueous solvents as media for oxidation reduction reactions has been limited by a lack of oxidizing titrants of suitable stability. The availability of such titrant system should permit oxidation of a variety of components insoluble or unstable in water. While investigating several oxidation-reduction couples in acetonitrile, copper (II) was found to have, in addition to a high reduction potential,\(^33,34\) good stability in solution and the ability to oxidize rapidly several compounds.

Besides copper salts several other metal ions have been used in the oxidation of organic compounds. Some are known to react by an outer sphere process, some by an inner sphere process, but for the majority of oxidants, the precise means of electron transfer has yet to be discovered. Kinetic studies indicate that oxidation of alkyl-benzenes by cobalt (III) or manganese (III) salts proceeds by an electron transfer mechanism with the initial formation of a radical cation.\(^95,96\) The radical cation (I) generated in the oxidation of arenes by Co (III) trifluoroacetate undergoes nucleophilic attack by the solvent to give trifluoro-
acetoacates, the isomer distribution of which is typical of that encountered in electro-philic aromatic substitution. The radical cation may also react with another molecule of arene to give a dimeric radical cation (II). Methyl benzenes also react by loss of proton from the radical cation to give benzyl radicals which give rise to either benzyl trifluoroacetates or diarylmethanes.

\[ \text{PhC} \rightarrow \text{PhC}^+ \text{Ph} \]

One electron oxidation of toluene is distinguished from the electron oxidation by lead (IV) trifluoroacetate by the absence of tolyl esters. The dimeric radical cation (II) have been detected in several instances by e.s.r. spectroscopy. These radical cations are also detected in oxidations by thallium trifluoroacetate, implying that this may act as a one electron oxidant. Lead tetraacetate in trifluoroacetic acid acts as a one electron oxidant in its reactions with methylenes and anisole, giving biaryls and diarylmethanes. The products from these reactions bear close resemblance to those from anodic oxidation. From the relative case of oxidation of arenes it is concluded that in the arylation step the radical cation behaves more as a radical than as a cation, thus the intermediate in the oxidation of a mixture of anisole and durene is (III) and not (IV).
The formation of mixed biaryls, in the anodic oxidation of naphthalene and alkyl benzene mixtures, arises through attack by the naphthalene radical cation on the alkylbenzene, the rate being roughly proportional to the basicity of the alkyl benzenes. Anodic coupling of arenes in the presence of strong acid has also been investigated. The precise mechanism of formation of biaryls in anodic oxidations of arene has been postulated to involve either attack by the radical cation on the parent arene or dimerization of the cation radical.

Ce (IV) oxidations of bibenzyls proceed by a radical cation mechanism followed by cleavage of central C-C bond.

\[ \text{ArCH}_2\text{CH}_2\text{Ar'} \xrightarrow{\text{Ce(IV)}} [\text{ArCH}_2\text{CH}_2\text{Ar'}^+] \rightarrow \text{ArCH}_2^+ + \text{ArCH}_2^+ \rightarrow \text{Products.} \]

The oxidation of a series of aromatic hydrocarbons and of cyclohexene by cobaltic perchlorate in aqueous acetonitrile solution were studied by Cooper and Waters. Sheikh and Waters in the oxidation of amines by Co (III) perchlorate in aqueous perchloric acid, reported direct outer sphere attack of the cobaltic ion on the hydrocarbon skeleton of the amines. Thus the oxidation of amines by Co (III) perchlorate differs mechanistically from oxidation by neutral permanganate, lead tetracetate in benzene or the free radical chlorine dioxide in which the free amines are attacked at, or at least adjacent to the nitrogen atom.

Heiba et al has proposed the mechanism for the oxidation of aromatic hydrocarbons (alkylbenzenes) by cobaltic
acetate. They suggested the reversible interaction of Co (III) with the aromatic hydrocarbon leading to the formation of the corresponding radical cation. The radical cation in a subsequent step, loses an α-proton yielding a benzyl radical. The benzyl radical is then rapidly oxidized by Co (III) to the corresponding benzyl acetate. This mechanism is similar to that suggested for the oxidation of p-methoxy toluene by manganic acetate.\(^{112,113}\) Cyclohexene has been oxidized by cobalt (III) salts, showing that such oxidations are not confined to aromatic systems.\(^{114}\) The mechanism differs from that for the oxidation of aromes in that the rate of the reaction is governed by the rate of formation of the radical cation (K\(_1\)) rather than by the rate of loss of the proton from the radical cation (K\(_2\)).

\[
\begin{align*}
R^+ + Co^{\text{III}} & \xrightarrow{K_1} R^{\text{II}^+} + Co^{\text{II}} \\
R^{\text{II}^+} & \xrightarrow{K_2} R^* + H^+
\end{align*}
\]

Oxidations of aromatic amines by ferricyanide give products derived from iminium ions formed as a result of two consecutive one electron transfers, rather than from the initially formed radical cation. Dimeric products are formed in the lead (IV) acetate oxidations of 2,4,5-triarylimidazole and related compounds as a result of coupling of imidazyl radicals.\(^{115}\) Dimers are also produced in the oxidation of phenothiazine\(^{116}\) and carbazoles\(^{117}\) through coupling of their radical cation.

Amine radical cations are generated in oxidations with chlorine dioxide.\(^{118}\) 2,3,5,6-tetra chlorobenzoxquinone diimine is obtained on oxidation of 2,3,5,6-tetra chloro p-phenylene diamine.\(^{119}\) Aromatic amines are oxidized by Pb(IV) in methylene-
chloride-trifluoroacetic acid to give radical cations which can be detected by flow e.s.r. techniques.\textsuperscript{120}

In the discussion so far, the metallic species and cation radical salts have both been implicated as good one-electron oxidants which give rise to radical cation intermediates with certain organic substrates. It is to be noted that there is a mechanism common to many of the redox reactions whether brought about by electrode reactions or by chemical means. It involves electron-transfer-chemical reaction-electron transfer, (ETCE mechanism).\textsuperscript{121} One reason that it must often occur is that an oxidant or reductant powerful enough to transfer the first electron will transfer the second even more rapidly. This is predicted from molecular orbital theory. A simple example which can be cited for the ETCE type mechanism is found in the chlorine-dioxide oxidation of aliphatic amines.\textsuperscript{122}

\[
\text{RCH}_2\text{NR}_2 + \text{ClO}_2 \xrightarrow{\text{slow}} \text{RCH}_2\text{N}^+\text{R}_2 + \text{ClO}_2^- \quad -- \quad -- \quad (1)
\]

\[
\text{RCH}_2\text{N}^+\text{R}_2 \xrightarrow{\text{fast}} \text{RCH} \quad \text{NR}_2^+ + \text{H}^+ \quad -- \quad -- \quad (2)
\]

\[
\text{RCH} \quad \text{NR}_2^+ + \text{ClO}_2 \xrightarrow{\text{K}_2} \text{RCH} = \text{NR}_2^+ + \text{ClO}_2^- \quad -- \quad (3)
\]

The first step of oxidation involves removal of an electron from a bonding orbital i.e. reaction (1), the second from a formally non bonding orbital i.e. reaction (3).

Chlorine dioxide and chlorite ion have, approximately at least, the same configuration and differ principally only in their charge. It is reported\textsuperscript{123} that electron transfer will occur on the close approach of \text{ClO}_2 and \text{ClO}_2^- in solution.

Detailed investigation by \textit{null et al}\textsuperscript{124} show that
electrochemical oxidation mix of amines and chemical oxidation by ClO₂ are similar. The anodic oxidation of primary amines⁷¹ and of triarylamines¹²⁶ have been reported. Although the reactions of the two classes are rather complex and in many aspects different, it is thought that the initial steps are similar.

This introduction only mentions a few of the reactions that involve radical cation intermediates. Nearly all of electrochemistry can easily be treated as if it were controlled by ion radical reactions. The role of radical cations as organic reactive intermediates is becoming increasingly important. Besides their role in organic synthesis, they provide a conceptual foundation that is extremely important. The scope of ion radical chemistry, indeed, is rapidly expanding.

**Electron transfer reactions involving radical anions:**

Electron transfer to an unsaturated organic substrate sometimes gives a long lived radical anion, preferably in polar aprotic solvents like tetrahydrofuran (THF). Electron sources can be alkali metals, electrodes, population of solvated electrons and even stable radical anions or dianions.

\[
\text{Naph} + e^- \rightarrow \text{Naph}^- \\
\text{Phe} + \text{c} \rightarrow \text{Phe}^- \\
\text{Naph}^- + \text{Anth} \rightarrow \text{Naph} + \text{Anth}^- 
\]
The reduction of organic molecules using alkali metals have generated some radical anions which were difficult to prepare by any other means. The reduction of benzene and alkylated benzenes\(^{127}\) to their radical anions exemplifies the application of this method to the hydrocarbons. The ketals derived from hindered aliphatic ketones such as hexamethylacetone\(^{128}\) and small ring ketones\(^{129}\) silyl ketene\(^{130}\) and even from simple aliphatic ketones such as methyl ethyl ketone,\(^{131}\) have been reported.

Electrolytic reductions have been the most general method of producing radical anions. Ma-ki and Geske\(^{132-135}\) have added a new dimension to this field by developing a method whereby radical ion may be generated and observed in the e.s.r. cavity.

Some of the more stable radical anions can be generated by using inorganic reductants. Sodium dithionite has been used in the generation of semiquinones from \(\alpha\)-diketones\(^{136,137}\) and nitrobenzene radical anions from nitrobenzenes.\(^{138}\) Swanwick and Waters\(^{139}\) have used sodium borohydride in basic solutions to produce nitro aromatic radical anions from nitro aromatics. High energy electron beams (2.3 Mev) have been used to reduce acetone, oxalic acid and nitroalkanes to their respective radical anions.\(^{140,141}\)

Because most of the radical anions react with oxygen, water and carbon dioxide, they are handled in scrupulously dry and degassed solvents. One of the most characteristic reactions of anion radical is the protonation reaction. An example is the quenching of preformed naphthalene anion radical with water\(^{142}\) leading to the products: dihydroxynaphthalenes in 41% yield and naphthalene recovered unreacted in 58% yield. There is a host of polycyclic aromatics which are reduced to the radical anion or dianion.\(^{143}\) Benzenes and many substituted benzenes do not,
however, produce a significant concentration of anion radicals; this has been overcome by Birch by using sodium-ammonia and alcohol as hydrogenating media.\textsuperscript{144} The sodium ammonia produces solvated electrons which, in turn, produce radical anions.

The more typical reaction of anion radical is not proton transfer but an electron transfer. This is true not only for sodium naphthalenide, which is nearly as powerful a reducing agent as metallic sodium, but is also applicable to other radical anions, for example, anthracenide, which is a much weaker reducing agent.

A reaction of considerable theoretical interest is the transfer of an electron from an anion radical to the corresponding parent molecule. Such electron exchange reactions have been revealed by e.s.r. studies since rapidly transferring the electron to various naphthalene molecules washes out the high-perfine splitting.\textsuperscript{145}

\[ \text{Naph}^{+} + \text{Naph} \longrightarrow \text{Naph} + \text{Naph}^{+} \quad - \quad (4) \]

The rates of these reactions have been found to be of the order $10^8 \text{ l. mole}^{-1} \text{ sec}^{-1}$, which is close to diffusion controlled.\textsuperscript{146}

\[ 2 \text{Naph}^{+} \rightleftharpoons \text{Naph} + \text{Naph}^{2+} \quad - \quad (5) \]

The equilibrium for such reactions lie to the left in most cases because of the extra electron repulsions in the diamagnetic dianion.\textsuperscript{147} It would be worth while to mention that a small equilibrium concentration of highly reactive diones could sometimes be responsible for many of the ion radical reactions.

The reaction of radical anion with atmospheric oxygen is depicted in eqn. (6)

\[ \text{Naph}^{+} + O_2 \longrightarrow \text{Naph} + O_2^{-} \quad - \quad (6) \]
Iodine may also serve as an electron acceptor as may another system of higher electron affinity. Russell and Denis\textsuperscript{143} observed almost quantitative formation of pot. super oxide on treatment of potassium nitrobenzenide with oxygen.

Radical anion reacts with alkyl halides to yield a variety of products. Though there has been considerable research in this area, only the radical anions of naphthalene, biphenyl and anthracene have received attention and most data are from naphthalene\textsuperscript{147} reactions. In solution the process usually leads to hydrocarbons.

\[
\begin{align*}
R-X & \rightarrow R^- + \text{ArH}^* \rightarrow \text{ArH}^*^- & R-X & \rightarrow R^- & \text{ArH}_2^- \\
& \text{e}^- & \text{SH} & \rightarrow \text{ArH}_2^R \\
& R^- & & (2R) & \rightarrow R-R \text{ or } (R-H + \text{Clefins})
\end{align*}
\]

Scheme VI

The first step is the fast electron transfer to the C-X bond, this is followed by rapid expulsion of halide ion. Halogen expulsion is not only fast but also complete as indicated by the use of sodium biphenylide for quantitative halogen analysis.\textsuperscript{150}

One product formed from the radical is alkane. This is conceivably derived by either of the two competing pathways.

\[
\begin{align*}
\text{SH} & \rightarrow R^- & \rightarrow R \rightarrow \text{H} \\
& & \rightarrow R - \text{H} & \text{(7)}
\end{align*}
\]

The carbonionic route predominates to the exclusion of the other. The carbenion may even be trapped by adding sodium bromide which forms Grignard reagent in good yield.\textsuperscript{151}
In the mechanism given in Scheme VI the individual steps seen reasonably certain except for the formation of the dimer i.e.

\[ R^\cdot + R - X \rightarrow (2R^\cdot) \rightarrow R - R \quad \text{(3)} \]

which is still subject to debate, for example the reaction of alkyl iodides with sodium naphthalenide gives alkyl dimers which exhibit no CIDNP signals; provided the reaction is carried out in magnetic fields of thousands of Gauss.\textsuperscript{152} CIDNP would be expected if scheme VI applies.

There are no elaborate studies which involve the kinetic studies of the reaction of radical anions and a comparative effect of various radical anions. In a recent paper, however, kinetic studies of reactions of radical anions of biphenyl, naphthalene, pyrene and anthracene with n-hexyl halides has been reported.\textsuperscript{153} An attempt was made in this investigation to correlate the rates with the reduction potential of the radical anions. The work of Sargent\textsuperscript{154} using sodium naphthalenide in the reduction of gem-dichloride has recently provided an evidence for the existence of carbene radical anions, a new class of organic reactive intermediates.

The main thrust of research on the reactions of naphthalenides radical anion has been on the reactions with alkyl halides. Much remains to done on the use of alkali metal aromatic radical anions; they offer a great promise in the reduction of organic compounds as compared to alkali metal reductions. The homogeneous conditions should permit the reaction to proceed faster and afford higher yields of the reduction products. This method also possesses inherent advantages in being successful for compounds which are inert to metal.

Some examples of synthetic uses of electron transfer
process are the sodium naphthalene cleavage of toluene-
sulphonates (equ. 9-11)\textsuperscript{155} and toluene sulphananides.\textsuperscript{156}

\[
\text{Nap}^- + p-\text{Pic}_{6}H_{4}SC_{2} \rightarrow \text{Nap} + [p-\text{Pic}_{6}H_{4}SC_{2}]^- \quad -- \quad (9)
\]

\[
[p-\text{Pic}_{6}H_{4}SC_{2}]^- \rightarrow \text{RO}^- + p-\text{Pic}_{6}H_{4}SO_2^- \quad -- \quad (10)
\]

\[
p-\text{Pic}_{6}H_{4}SO_2^- + \text{Nap}^- \rightarrow \text{Nap} + p-\text{Pic}_{6}H_{4}SO_2^- \quad -- \quad (11)
\]

The radical ions discussed so far are those which are
detectable by e.s.r. and in some cases, capable of long term
existence in suitable solvents or isolable in solid state. Radical
anions are also involved in several chemical and electro-chemical
reductions as short lived reactive intermediates. Numerous
examples of the transient radical anions, which are the product
of initial electron transfer reactions in organic electro-chemistry
are reported in several excellent reviews.\textsuperscript{157,158} Again there
is a host of literature pertaining to the reactions with radical
anions giving in turn, the secondary anion radicals from the
substrate. Singh & coworkers\textsuperscript{159} in a reaction of 2-chloro cis
stilbene with sodium naphthalenide, found that the cyclized
product phenanthrene was derived from the initially formed chloro
aromatic radical anion.

Radical anions have also been shown to be the intermediates
in several chemical reactions which do not formally involve
reductions. One of the most intriguing is the nucleophilic
substitution of \(p\)-nitrobenzyl halides. The anomalous nature of
these reactions, compared with other benzyl halide substitutions,
was discovered by Kornblum and co-workers,\textsuperscript{160} who found that
\(p\)-nitrobenzyl chloride reacted fast and gave carbon alkylation.
This anomalous reaction was thought to involve radical anion
intermediates and this was confirmed by Russell\textsuperscript{161} and by
Kornblum. The following chain reaction involving coupling of radicals and anions to form radical anions was suggested.

\[ \text{R}^* + p-\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Cl}_2\text{Cl} \rightarrow \text{R}^* + [p-\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Cl}_2\text{Cl}]^- \]

\[ [p-\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Cl}_2\text{Cl}]^- \rightarrow p-\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Cl}_2^* + \text{Cl}^- \] --- (12)

\[ p-\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Cl}_2^- + \text{R}^- \rightarrow [p-\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Cl}_2^- + \text{R}]^- \] --- (13)

\[ [p-\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Cl}_2^-]^- + p-\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Cl}_2\text{Cl} \rightarrow \]

\[ p-\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Cl}_2\text{R}^- + [p-\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Cl}_2\text{Cl}]^- \] --- (14)

Reactions (12), (13), (14) involve the propagation steps which could be diverted by oxygen or by some other electron acceptor like dinitrobenzene.

In an important publication Russell and co-workers have given the scope of the reaction leading to the products of electron transfer between carbanions, nitro anions and unsaturated organic molecules. They claim that many carbanions and nitreniums react with unsaturated molecules such as nitroaromatics, azobenzene and diaryl ketones to form the radical anions derived from the unsaturates. Many others are given by Bilevich and Okhlobystin. It was speculated that processes involving one electron transfer could be important in many reactions involving carbanions. The recognition of such processes can be traced to Schlenk's work, who reported that trityl sodium reacts with benzophenone to give trityl radical and benzophenone ketyl.

\[ \text{Ph}_3\text{Cl}^- \cdot \text{Na}^+ \cdot \text{Ph}_2\text{C} = \text{O} \rightarrow \text{Ph}_3\text{C}^* \cdot \text{Ph}_2\text{C}^* \cdot \text{O}^- \] --- (15)

Alkyl lithiurn also react with azobenzene, ketones and some polynuclear aromatic hydrocarbons to yield radical anions of these acceptors.

In recent years, attempts have been made to investigate
radical reactions of Grignard reagents which serve as electron source. In a recent review on the mechanism of the reactions of Grignard reagents with ketones, it has been reported that, in polar solvents, electron transfer from the organometallic to the ketone takes place. Many reactions of organic halides with Grignard reagent end up with products attributable to free radical intermediates. Singh and co-workers have given some interesting mechanism of the reaction of Grignard reagent with organic halides.

Investigations of organic electron transfer reactions and the radical anion intermediates are expanding at an exponential rate. Many reaction which appeared to be nucleophilic displacement processes are being now viewed to involve electron transfer free radical mechanisms. Reduction of alkyl and aryl halides with NaH or LiAlH₄ is well documented and has been reported to proceed via an SN¹ process and SN₂ process or nucleophilic attack on halogens depending on the structure of the halide, but evidences are appearing suggesting dehalogenation by free radical path.

Radical intermediates have also been proposed in the reactions of alkyl mercuric halides with NaBH₄ and LiAlH₄. Recently a free radical chain mechanism has been proposed in the reduction of gem-dibromides with NaBH₄.

\[ \text{NaBH}_4^- + \text{X}^+ \rightarrow \text{BH}_3^+ + \text{X}^- \]  
\[ \text{BH}_3^+ + \text{R} \rightarrow \text{R} + \text{H}_2\text{B} + \text{BH}_2^+ \]  
\[ \text{R} + \text{BH}_4^- \rightarrow \text{RBH}_3 \rightarrow \text{RH} + \text{BH}_3^+ \]

Scheme VII
A mechanism involving free radical chain process in bromo-cyclopropyl radicals (3) and bromo radical anion (4) was suggested as shown in Scheme VII.

In the recent years a large number of publications have appeared on the electron transfer reactions and it is so because of the extreme importance of this area of research. Besides providing a conceptual foundation that is extremely important, the electron transfer reactions may provide convenient synthetic routes and may give an insight into certain redox reactions of biological importance.
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