CHAPTER  I
CHAPTER I

INTRODUCTION

The intense colouration obtained from the interaction of electron-deficient nitro aromatics with nucleophiles has fascinated chemists since 1900. Several kinds of interactions, which depend upon the reactant structure and solvent environment have been reported.\textsuperscript{1-4} Strong interaction between the base and the nitro aromatic compound results in the formation of sigma adduct 1.\textsuperscript{1} A partial transfer of electronic charge from the base to the aromatic nucleus depleted of $\pi$ electron density gives rise to $\pi$- complex 2 known as donor–acceptor or charge–transfer complex.\textsuperscript{2} Complete transfer of electron from the base to nitro aromatic compound results in the formation of radical anion 3.\textsuperscript{3} If the nitro compound bears a substituent alkyl group, carbanion 4 is formed due to proton abstraction.\textsuperscript{4}
Jackson and Gazzalo\textsuperscript{1} proposed structure 5b for the red colored species resulting from the reaction of picryl ethers with potassium alkoxides and the first chemical evidence for this structure was obtained in 1902 by Meisenheimer,\textsuperscript{5} compounds of this type are commonly known as “Jackson–Meisenheimer” or “Meisenheimer” complexes.

The presence of nitro groups activates the aromatic ring to nucleophilic substitution and good leaving groups such as halogens, are readily replaced. Many studies of these reactions have been made and several reviews written.\textsuperscript{6-11} Strong evidence has been produced that many of these reactions proceed through cyclohexadienate ion 6 of finite stability, analogous to 5a.\textsuperscript{12-14}

As aromaticity is disrupted during the formation of the sigma complex of type 6, considerable changes occur in electronic conjugation and hence visible spectroscopy
has been a primary tool in deducing complex-forming reactions. The visible spectra of a variety of sigma complexes symmetrically or unsymmetrically substituted are all very similar with two maxima at approximately 415 nm ($\varepsilon = \sim 28,000$ mol$^{-1}$ l cm$^{-1}$) and 500 nm ($\varepsilon = \sim 19000$ mol$^{-1}$ l cm$^{-1}$). In general the extinction coefficient of the shorter wavelength absorption is usually about twice that of the absorption at longer wavelength and both are much higher than the extinction coefficient associated with charge-transfer bands of aromatic $\pi$-complexes. The exact $\lambda_{\text{max}}$ and $\varepsilon_{\text{max}}$ depend on the nature of $R_3$, $R_4$ and $R_5$ and to a lesser extent on $R_1$ and $R_2$ (7).

Visible spectrum of the solution of 2,4,6–trinitroanisole and sodium methoxide in methanol indicates that at high base concentrations a higher complex is formed. The absorption of the 1:1 adduct 8 with maxima at 410 and 490 nm is replaced by a single visible band with maximum at 480 nm, attributed to a di-adduct.9 At very high base concentrations, 2,4,6–trinitroanisole is converted into a colourless species 10 (tri-adduct).9 Infrared, proton nuclear magnetic resonance spectroscopy and crystal structure determinations have also played a significant role in structural characterization of sigma complexes.16, 17, 20-29
Solvents have marked effect on the stabilities of sigma complexes. Although the formation of sigma complexes has been reported in a variety of solvents, the most widely used are methanol, water and dimethyl sulphoxide (DMSO). Generally it has been found that the production of 1:1 adduct is enhanced in the dipolar aprotic solvents such as DMSO relative to protic solvents such as MeOH. The sizes of the attacking nucleophiles have a large influence on the stabilities of sigma complexes. As 1,3,5-trinitrobenzene is a symmetrical molecule, no diversity of attack is possible. However for substituted derivatives such as 2,4,6-trinitroanisole or 2,4,6-trinitroaniline, the mode of interaction might vary on changing the nucleophile. Thus structural measurements showed that the thermodynamically stable adducts of 2,4,6-trinitroanisole with OMe− (or) NEt2− result from addition at C1, while the apparently stable adducts with SO3−2 or CH3COCH2− are formed at C3. The failure to detect addition of these latter nucleophiles at C1 has been ascribed to steric strain. The sulphur bases such as thioethoxide and thiophenoxide ions would preferentially add at the 3-position. The structure of the substrate also has remarkable influence on the stabilities of adducts formed with a given nucleophile. For similarly activated substrates, the adduct formed by addition at a ring carbon carrying a methoxyl group has considerably greater stability than those formed by addition at a ring carbon carrying hydrogen. Thus the equilibrium constant for addition at the C1 position of 2,4,6-trinitroanisole was about 500 times greater than that for addition to 1,3,5-trinitrobenzene. This result was interpreted by Gold and Rochester in terms of inductive and steric effects. Spirocyclic Meisenheimer complexes, have also attracted many scientists and a number of articles have appeared in recent years on such complexes.
Though covalent addition of oxygen, sulphur, nitrogen and phosphorus bases to the activated aromatics and heteroaromatics has been investigated by a number of workers and their work has been thoroughly reviewed,\textsuperscript{17} carbon-bonded sigma complexes have gained considerable interest. The interest stems mainly from the remarkable stabilities of such complexes. Thus, it has been found that amongst the oxygen and carbon-bonded $\sigma$ complexes of phenoxide ion (ambident nucleophile), the former complex 12, is less stable than the latter 13.\textsuperscript{15}
However, Strauss et al.\textsuperscript{46} have proved that the carbanionic sigma complex, 14, which has a potential nucleophilic site $\gamma$ to the tetrahedral ring carbon, is unstable and it readily undergoes an internal cyclization reaction as indicated in Scheme 1 to yield the stable nitropropene nitronate salt 15. The distance between C$_{\gamma}$ and C$_{\delta}$ of 14 is quite appropriate for bonding. Conversion of sigma complex to bicyclic adduct occurs only when the ketone used is acidic enough and when no bulky substituents are present at the C$_{\gamma}$ position.\textsuperscript{47-49} Addition of excess triethylamine to a saturated solution of TNB in acetone results in the rapid formation of the triethylammonium salt of the complex 14a which precipitates from solution as purple crystals after a short time.\textsuperscript{46} No further reactions of the triethylammonium salts of 14a have been observed to occur in such solutions. Since NEt$_3$ is a weak base, the less acidic H$_{\gamma}$ of acetone is not readily removed and hence 14a is obtained as a stable species. When NEt$_3$ is replaced by HNEt$_2$, bicyclic adduct 17 is observed to be formed as shown in Scheme 2 through enamine intermediate 16.\textsuperscript{50-52} Kohashi et al.\textsuperscript{53} have reported that when a strong base such as NaOH is mixed with a simple ketone like acetone, tetracyclic salt like 18 results (Scheme 3).
Scheme 1

14  14a  R = R' = H

15
Scheme 2

Acetone + Diethylamine → 1,3,5 TNB

HNO₂
N(C₂H₅)₂
NO₂
H₂O

16

H₂O formed with 16

17
Scheme 3
The nucleophilicity of enolate carbanion towards electron-deficient aromatic carbon has been expected to be considerably greater than that of enolate oxygen. In accordance with this expectation, the 1:1 TNB – phloroglucinol adduct 19, in the presence of tertiary amine, cyclizes to 20, not 21.\textsuperscript{54}

Although extensive studies have been made on the carbanionic sigma adducts of trinitro aromatics, there are relatively a few comprehensive studies on such type of adducts of dinitro aromatics.\textsuperscript{55-66} The reaction of 1,3-dinitrobenzene with alkaline acetone gives a purple–coloured solution. Pollitt and Saunders\textsuperscript{55} have suggested that the purple colouration is due to the formation of 22.
Chemical and spectroscopic evidence is in support of formula 22 and dark purple crystals have been prepared from the solution.\textsuperscript{56} Foster and Fyfe\textsuperscript{57} have proved through NMR spectrum produced by the addition of base to meta dinitrobenzene in acetone – dimethylsulphoxide that the product formed is 22 and there is no indication of formation of the isomer product by addition at C\textsubscript{2}. In the substitution reaction of 2,4-dinitrofluorobenzene with diethylsodiummalonate in benzene–dimethylsulphoxide mixture, the transient species 23 has been reported as the intermediate.\textsuperscript{58}

Gitis and Kaminskii\textsuperscript{28} have undertaken the kinetics and equilibrium studies and revealed the extraordinary stability of the adducts derived from the carbanions of esters and dinitrobenzene series. Acetonate ions have been noticed to add to unsubstituted 3-(or 5-) carbons of 2,4-dinitrophenyl and 2,4-dinitronaphthylphenyl ethers to form carbanionic sigma complexes.\textsuperscript{59-61} The relative thermodynamic stabilities of some ketone complexes of 1,3-dinitronaphthalene have been estimated from calorimetric measurements.\textsuperscript{62,63} The heteroaromatic meta-bridging of
dinitropyridine and nitroquinoline with amidines and carbanions have been described.\textsuperscript{64} Keto-enol equilibria and diastereo isomerism in carbon-bonded anionic sigma complexes of 4,6-dinitrobenzofuroxan has been investigated.\textsuperscript{65} Carbanionic adducts of 1,3-dinitrobenzene have been generated in the gas phase and examined by Witold et al.\textsuperscript{66}

Search of the literature indicates that sigma complexes of carbanions derived from cyclic molecules are limited.\textsuperscript{62, 67-69} The relative thermodynamic stabilities of a series of carbanionic sigma complexes derived from the reaction of acetone and cyclopentanone with various polynitroaromatics such as 1,3,5-trinitrobenzene, 1,3-dinitronaphthalene and 1,3,6,8-tetranitronaphthalene has been determined by Murphy et al.\textsuperscript{62} Kinetic and $K_{eqn}$ measurements for the formation of a series of 1:1 carbanionic sigma complexes, 24, from different electron-deficient aromatic nitro compounds in methanol-cyclohexanone mixture have revealed that those complexes which have a nitro group para to the sp$^3$ carbon are thermodynamically favoured.\textsuperscript{67,68}

\begin{center}
\includegraphics[width=0.3\textwidth]{24.png}
\end{center}

\textbf{24a} : $X = \text{CON(CH}_2\text{)}_5$, $Y = \text{NO}_2$

\textbf{24b} : $X = \text{COOMe}$, $Y = \text{NO}_2$

\textbf{24c} : $X = \text{CN}$, $Y = \text{NO}_2$

\textbf{24d} : $X = \text{NO}_2$, $Y = \text{CON(CH}_2\text{)}_5$

\textbf{24e} : $X = \text{NO}_2$, $Y = \text{COOMe}$

\textbf{24f} : $X = \text{NO}_2$, $Y = \text{CN}$
The carbanionic sigma complex derived from 1,3,5-trinitrobenzene and cyclopentanone has been identified to have very high thermodynamic stability. The abnormally high stability has been accounted for by a conformation of the complex in which the carbonyl oxygen is favourably located for a stabilising interaction with the positively polarized nitrogen of an adjacent nitro group as shown in structure 25, which has been supported by $^{13}$C and $^1$H NMR data.63,69

![Structure 25](image)

As barbituric acid (a cyclic molecule) has an active methylene group, it is expected to form carbanion in the presence of base. The addition of the anion of 1,3,5-trimethyl-2-thiobarbituric acid to π–bonded unsaturated hydrocarbons (olefin, cyclohexadienyl, cycloheptadienyl, cycloheptatrienyl) in cationic complexes of rhenium, iron, ruthenium and chromium provides a method for the introduction of organometallic fragments into the barbituric acid moiety. Substitution of the C-5 hydrogen atom gives the complexes. The dianions of 1,3-dimethylbarbituric acid and 1,3-dimethyl-2-thiobarbituric acid yield the bimetallic complexes.70 Unsubstituted triazolo and tetrazolo 1,2,4-triazines have been reported to react with carbanions generated from dimedone and barbituric acid to give adducts with C:N double bond.71 Anion of 5,5-dimethylbarbituric acid has been used to prepare complexes with Fe(III), Co(II), Ni(II) and Cu(II).72 Dyes involving active methylene group of barbituric acid have gained considerable attention in recent years.73-88 Literature survey indicates that carbon-bonded sigma complexes of barbituric acid with electron-deficient nitroaromatics in the presence of base have not been reported so far.

Another important reaction of electron-deficient nitro aromatics with bases is the formation of donor-acceptor complexes. Donor-acceptor complexes have been
prepared from N-substituted anilines and aromatic nitro compounds and their infrared spectral data interpreted by Hindawey et al. The charge-transfer interaction between picramic acid and aromatic amines has been examined by Issa et al. Donor-acceptor complexes derived from anilines and 2,3-dichloro-5,6-dicyano-p-benzoquinone have been investigated by Dwivedi and Agarwal. The effects of steric characteristics of donor molecules (aniline and phenol derivatives) on complexation with symmetric trinitrobenzene have been analysed by Prayalkin. Lawrence and co-workers have observed that significant modulation of the electronic properties in anilines occurs upon complexation with tetracyanoethylene. The kinetics of the reaction of 2,4-dinitrochlorobenzene with aniline and substituted anilines have been studied. The results of the kinetic measurements are consistent with the fact that aggregates of anilines act as nucleophiles. Examination of the influence of the solvent component has also been undertaken by adding small amounts of methanol to toluene upto pure methanol. The results suggest that the aromatic solvent forms complexes with the substrate. Formation of yellow coloured charge-transfer complexes of aniline, N-methylaniline, N,N-dimethylaniline and N,N-diethylaniline with nitromethane in carbon tetrachloride has been studied by ultraviolet-visible spectrophotometry and proton nuclear magnetic resonance spectrometry. The molar absorptivities and association constants have also been determined. The stabilities of these complexes vary in the order aniline–nitromethane > N-methylaniline–nitromethane > N,N-dimethylaniline–nitromethane > N,N-diethylaniline–nitromethane. Hydrogen bonding contributes significantly to the stability of above mentioned complexes. Overtone spectra of aniline derivatives and the charge-transfer complexes of vitamin K\textsubscript{3} with a series of anilines have also been reported.

Restogi et al. have studied the kinetics of charge-transfer reaction between naphthalene and picric acid in the solid state by observing the phase boundary processes in a glass tube packed from one end with picric acid and from the other end with naphthalene. Association constants of alkynaphthalene-picric acid complexes have been studied by Hayman by spectrophotometric methods. Ashby et al. have prepared the picrates of some anilines, biphenyl, pyridine and quinoline and reported
the melting points and the characteristic, infrared frequencies. The charge-transfer complex formation between chloro, bromo, iodo, t-butyl and methoxy picric acids with aromatic hydrocarbons and salts with amines has been thoroughly investigated by means of phase-diagrams.\textsuperscript{101} Picrates of some aliphatic, alicyclic, aromatic polynuclear and heterocyclic compounds have been prepared by Benny et al.\textsuperscript{102} The association constants of 1:1 charge-transfer complexes of poly nuclear aromatic hydrocarbons with picric acid have been determined.\textsuperscript{103} Picrates of some aliphatic, alicyclic, aromatic polynuclear and heterocyclic compounds have been prepared by Akers et al.\textsuperscript{104} Dipole moment measurements have been utilised to study the nature of forces in charge-transfer complexes of picric acid with various types of amines.\textsuperscript{105} Infrared spectra of the picrates of twenty three amines have also been examined.\textsuperscript{106} Existence of tryptophan picrate as charge-transfer complex has been proved by Matsunaga\textsuperscript{107}. Structures of several amide-picric acid charge-transfer complexes have also been discussed.\textsuperscript{108} The hydrogen-transfer and charge-transfer complex formation of sym-trinitrobenzene, picric acid and trinitroanisole with substituted pyridines, 2,6-dimethylnaphthalene, acenaphthene, phenanthrene and naphthalamines have been examined through infrared spectroscopy.\textsuperscript{109} Enthalpies and entropies of fusion of a number of crystalline hydrocarbon picrates have been studied by differential scanning calorimetry.\textsuperscript{110} Charge-transfer and proton-transfer interactions in the formation of molecular complexes from o-aminobenzoic acid and picric acid have also been thoroughly investigated.\textsuperscript{111-113} N-substituted anilines such as N-methylaniline, N-ethylaniline, N,N-dimethylaniline and N,N-diethylaniline have also been reported to form donor-acceptor complexes with aromatic nitro compounds such as picric acid, 2,5-dinitrobenzoic acid and 2,4,6-trinitrobenzoic acid.\textsuperscript{114} Electrical properties of charge-transfer complexes of picric acid and some aniline derivatives have been scrutinized.\textsuperscript{115} New highly selective picrate sensors based on charge-transfer complexes have been reported.\textsuperscript{116} Charge–transfer complexes of Schiff bases derived from p-aminobenzoic acid with picric acid has also been reported.\textsuperscript{117} Charge–transfer complexes of some metal 2,4-pentanedionates with picric acid as \(\pi\)–acceptors have been synthesized and characterized.\textsuperscript{118} The interaction of the mixed
oxygen–nitrogen cyclic base 1,4,10,13-tetraoxa-7,6-diazacyclooctadecane with various \( \pi \)-acceptors such as picric acid, chloranilic acid and 2,3-dichloro–5,6–dicyano–1,4–benzoquinone has been studied spectrophotometrically in chloroform and methanol, spectral data indicate a strong interaction between the donors and acceptors associated with proton migration followed by intramolecular hydrogen bonding.\(^{119}\)

Although extensive studies have been made on the donor-acceptor complexes of picric acid, only a few reports have appeared on donor-acceptor complexes of styphnic acid.\(^{120-135}\) The molecular weights of a large variety of amines such as primary, secondary, tertiary, alkyl and heterocyclic have been established by the study of the absorption spectra of their picrate and styphnate derivatives.\(^{121}\) Chromatographic microquantitative analysis of adducts of morphine and some similar analgesics with styphnic acid has been reported.\(^{122}\) Thermodynamic parameters for the formation of charge–transfer complex between styphnic acid and 1-or 2-substituted naphthalenes have also been reported.\(^{123}\) Fusion enthalpy and entropy values of charge-transfer complexes of styphnic acid have been determined by differential scanning calorimetry.\(^{124}\) Some new crystalline organic semiconductors of styphnic acid have been reported by Abashev et al.\(^{125}\) Crystal and electronic structures of some salts of organic \( \pi \)-donors and styphnic acid have been examined.\(^{126}\) A new energetic compound has been prepared by reacting triaminoguanidine with styphnic acid in aqueous solution under nitrogen atmosphere and characterized by elemental analysis and FTIR. Its crystal structure was determined by single crystal X-ray diffraction analysis.\(^{127}\) Inspite of the fact that many crystalline complexes have been derived from styphnic acid and metals in recent years,\(^{128-134}\) only a few crystalline complexes are known from styphnic acid and organic molecules.\(^{125-127}\) It has also been pointed out that aromatic hydrocarbons (and also some amines) form 1:1 adducts with styphnic acid and these derivatives do not crystallize so well as the corresponding picrates.\(^{135}\) In the present investigation biologically active crystalline donor-acceptor adducts have been synthesized from styphnic acid and bases (tetrahydro-1,4-oxazine, 2-methylaniline and 2-methoxyaniline) and characterized.