Single Electron Transfer Reaction Studies By ESR

(A CASE STUDY OF N - CHLORO, BROMO & IODO SUCCINIMIDES)

ABSTRACT

By

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SUBMITTED

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SINGLE ELECTRON TRANSFER (SET) REACTION STUDIES BY ESR SPECTROSCOPY

(A CASE STUDY OF N - CHLORO, BROMO & IODO SUCCINIMIDES).

This thesis describes the results of SET reaction studies involving N - Chloro, Bromo and Iodo succinimides. The major thrust is on the phenomenon of SET chemistry. An extensive application of ESR spectroscopy has been made to study electron transfer processes. The contents of the thesis is distributed over six chapters.

Chapter I presents a brief general introduction pertaining to the work embodied in the thesis. It describes the fundamental aspects of SET chemistry and the various models proposed to describe the SET phenomenon. The methodology used to provide evidences for SET reactions such as :
(i) Detection of radicals by ESR spectroscopy.
(ii) Formation of radical derived secondary products etc. are listed.

The formation of charge transfer complexes ; precursor in electron transfer reactions through UV study is highlighted. The scope and the basic principles of ESR spectroscopy is described in brief. The direct detection and identification of radicals by ESR is possible only if

the radicals are produced in high concentration in situ within the ESR cavity, an indirect method called " Spin Trapping " employed in this work, is described.

Chapter II reviews the work carried out by various researchers in the field of N- Halosuccinimides under different conditions. The N- Halosuccinimides gained recognition when N- Bromosuccinimide was recognised by Karl Ziegler and co - workers as a brominating agent of olefins at allylic positions. Although the reaction became a standard synthetic procedure but the actual chain carriers involved have been the subject of recurrent controversy. Various controversies surrounding succinimidyl chemistry are underscored in this chapter. The work of Eberson is reviewed at the end of this chapter.

Objective This part describes the major objective of the present study. The recent development of the so called Single Electron Transfer (SET) chemistry is gaining ground very fast. The SET reaction is one that is initiated by the transfer of a single - electron from nucleophile to the substrate, producing a radical intermediate. The resulting radical intermediate can than be involved in any number of events. Many organic reactions which were previously classified as polar reactions actually involves radical intermediates formed by

a process initiated by SET from the nucleophile to the substrate. Yet despite the growing evidence that SET processes are far more widespread than originally thought, the relationship between SET and polar pathway remain obscure. Chemical community seems to be coming around to accept SET pathway as a major one but still some reluctance is there. One of the reason could be that their are still some fundamental questions that need to be addressed before SET gains a wider acceptance e.g.,

(i) What are the factors that determine whether a particular reaction proceeds via SET or a polar pathway ?.

(ii) What is the precise relationship between the two ?.

Therefore, one of the objective of the present study would be to answer some of the questions at least to some extent if not in totality.

We feel that in this endeavor ESR spectroscopy (its full potential is yet to be realised) can play an important role. We have made an extensive application of ESR using spin trapping to study the SET aspects of N-Halosuccinimides. The mechanism of N- Halosuccinimide reactions have been the subject of number of investigations however, a definite reaction mechanism could not be established. The controversy over the nature of the chain propagating species have been widely recognised and still

continues to attract attention. The areas of disagreement involve both experimental results and their interpreta - tions.

It is an attempt to elucidate the mechanism, the effect of environmental factors and of added substances of potential catalytic / inhibitory action on the reaction mechanism. The suggestion that the succinimidyl radical undergoes ring opening is also investigated. This study is the first of its kind where, nitrones are used in a dual role. The purpose of the nitrone to use for example, as a reductant was to ensure that if at all an electron is donated by it then it will become a cation and the electron captured specie will undergo dissociation and one of the product will be an anion. The probability of anion being trapped by a nitrone cation would be certainly higher then the probability of free radical being trapped by neutral nitrone and thus we may succeed in identifying some of the primary products of ET process. The identification of primary products always imparts some authenticity to the mechanism rather than mechanism derived from end products.

Chapter III deals with the reagents and chemicals used. Their purification and drying etc., is also described. The actual details of the experimental procedures are described. The specifications and limitations of all the

instruments used in the present study are mentioned. The calibration and standardisation of the instruments used are also explained. The determination and calculation of various ESR parameters are explained. The computer simulation program developed is given in the appendix of the thesis.

Chapter IV is devoted to the results obtained in electron transfer reaction between N-Chlorosuccinimide (NCS) and nitrones. The formation of charge transfer complex between NCS and nitrone (PBN : N- tert. butyl α - phenylnitrone) is studied. The appearance of an isosbestic point reveals the feasibility of electron transfer. The ESR results obtained under different conditions of concentration, solvent polarities etc., are described. In benzene at 1:1 concentration of NCS and PBN, chloro adduct of PBN with ^{35}Cl and ^{37}Cl isotope signals Fig. 1 along with spectra assigned to benzoyl tert.- butyl nitroxide (PBNOX) were observed. PBNOX was the only signal left after all other signals decayed out. At a concentration of PBN to NCS 4:1, the succinimidyl adduct of PBN was observed. The reaction mechanism formulated in Scheme 1, is proposed. The reaction studied at various concentrations of NCS and PBN reveals that, succinimidyl radical ($S^{\cdot}$) and chloride ion (Cl^{-}) are the two species formed from the electron

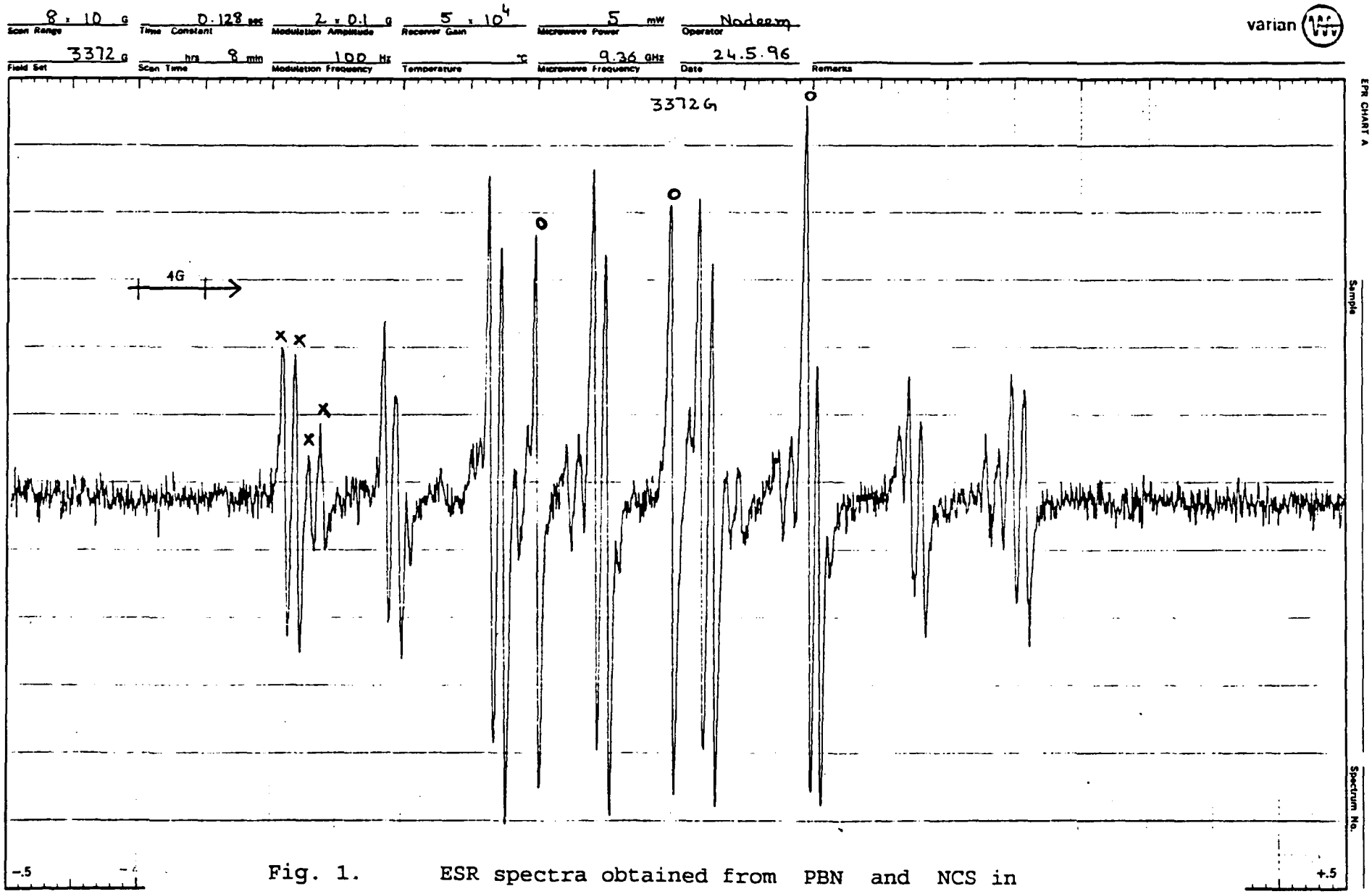
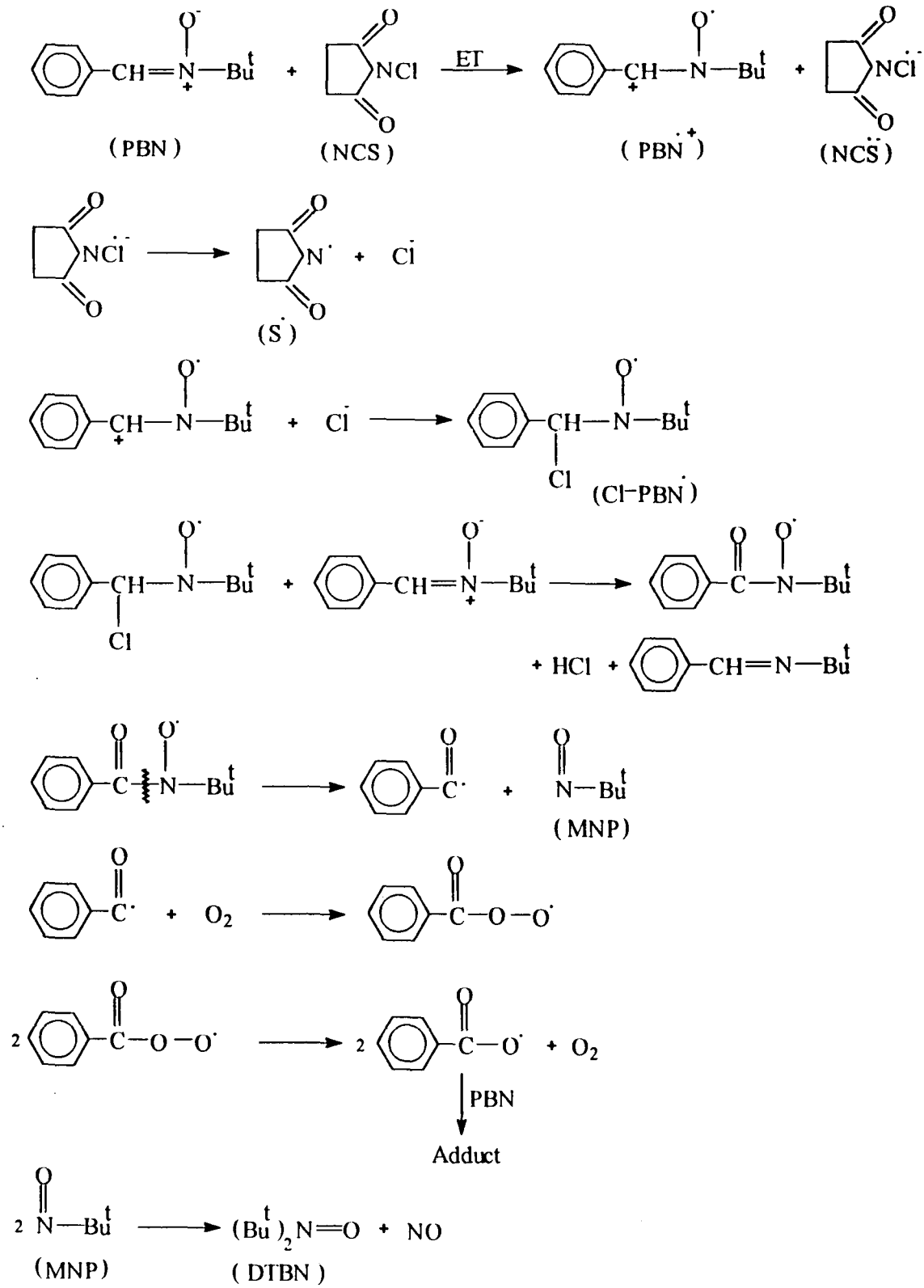


Fig. 1. ESR spectra obtained from PBN and NCS in benzene. x , Cl-PBN· adduct ; o , PBNOX.

Scheme 1



captured dissociation of $NCS^{\cdot -}$. By using substrates like N- Methylsuccinimide and / or succinimide, the stability of the chloro adduct was considerably enhanced. The mechanism for such a stability is discussed. We are successful in observing satellite signals from ^{13}C in all the different positions of PBNOX. Such examples are rare for conforma - tional studies by ESR. The well resolved succinimidyl adduct of DMPO under the present conditions is being reported for the first time.

Next we studied the reaction in CH_3CN and CH_2Cl_2 in varying concentrations of NCS and PBN. PBNOX and the corresponding solvent derived radicals were observed. H - abstraction by succinimidyl radical is postulated as a possible mode. The observance of chloro and succinimidyl adducts under photolytic conditions through a different reaction mechanism is postulated. Keeping in view the solvolytic properties of alcohols, reactions were carried out in different analogues of alcohols. The chloride ions are removed via solvation while succinimidyl adduct is clearly observed. The active participation of all the alcohols is observed. Methanol is found to be a poor solvating agent. The formation of succinimidyl adduct of MNP (2- Methyl - 2 - nitroso propane) in later stages of the reaction is postulated through β - cleavage of

succinimidyl adduct of PBN. The stability of the chloro adduct in CCl_4 is attributed to solvent participation in the reaction mechanism. With 1,4 - Dioxan, we are successful in detecting both the species, chloro and succinimidyl adducts of PBN under different relative concentrations of NCS and PBN, again establishing the formation of only these two species from $NCS^{\cdot -}$. Reaction in DMF as solvent, yielded chloro adduct of PBN and PBNOX in the beginning. At a later stage, spectra due to $(CH_3)_2NCO$-MNP$^{\cdot}$ was identified. This points out H-abstraction from the formyl group of DMF. With DMSO as solvent, succinimidylmethyl adduct of MNP is observed. The spectral assignment is confirmed by simulation. A new pathway for the generation of methyl radicals is postulated. The proposed mechanism is supported by other experimental evidences.

Chapter V describes the results of N- Bromosuccinimide (NBS) and N- Iodosuccinimide (NIS) with nitrones. The possibility of charge transfer complex formation through the appearance of an isosbestic point was observed. At 1:1 concentration of NBS and PBN in benzene, intense signals due to PBNOX (with well resolved satellite signals from ^{13}C in different positions along with ^{15}N) and benzoyloxyl adduct of PBN were observed. We could not see any signal

due to bromo or succinimidyl adduct of PBN. This suggests that, (i) spin adducts of the primary products are perhaps highly unstable (ii) $NBS^{\cdot -}$ follows a different mode of dissociation. At all other concentrations of NBS and PBN similar results are obtained. The formation of PBNOX is attributed to oxidation of PBN by Br_2 formed by rapid dimerisation of bromine atoms. This was confirmed by the appearance of PBNOX signal when dilute solution of bromine was added to PBN solution. The light yellow colour also suggests the formation of Br_2. The absence of succinimidyl adduct is proposed to be due to oxidation by Br_2. At this stage an opposite cleavage mode of $NBS^{\cdot -}$ appears as compared to $NCS^{\cdot -}$. This conclusion is supported by the observance of well resolved succinimidyl adduct of PBN and very weak PBNOX signals when traces of bicyclopentadiene, a known free radical scavenger was added to the system. This indicate that succinimidyl adduct can only be observed when Br_2 is effectively removed from the system. It would not be out of place to mention that addition of bicyclopentadiene in similar conditions in NCS did not make any qualitative difference in the spectra. This confirms that dissociation of $NBS^{\cdot -}$ gives bromine atoms and succinimidyl anion, while $NCS^{\cdot -}$ gives chloride ions and succinimidyl radicals.

In n- Hexane, major adducts observed at various relative concentrations of NBS and PBN, were PBNOX and benzoyloxyl adducts. The absence of succinimidyl adduct in presence of bicyclopentadiene could be due a higher rate of dimerisation of bromine atoms. Results in solvents such as CH_3CN, CH_2Cl_2 are in line with our postulations of cleavage mode of $NBS^{\cdot -}$. The observance of chloro adduct in CCl_4 is attributed to a different mechanism. The results clearly indicates solvent participation in the reaction. In DMF, $(CH_3)_2NCO^{\cdot}$, $(CH_3)_2N^{\cdot}$ and $BrCH_2\dot{C}H_3NCO$ radical adducts were observed. In alcohols PBNOX, benzoyloxyl and corresponding solvent derived radical adducts were observed. In DMSO, succinimidylmethyl radical adduct of MNP (also observed with NCS) was observed though through a different reaction pathway.

With N- Iodosuccinimide, only PBNOX and benzoyloxyl radical adducts were observed under all the conditions. The electron transfer mechanism and subsequent reactions are identical to that of NBS. The non observance of succinimidyl adduct in the presence of bicyclopentadiene suggests that the rate of dimerisation of iodine atoms is much faster than addition to bicyclopentadiene. This results in the oxidation of PBN to PBNOX as the major pathway.

Last part of the thesis is the concluding chapter. Only some of the salient features are mentioned below :

1. The technique of spin trapping has been very success - fuly applied in this system. A new role of nitrone is presented.
2. This work provides another clear example of single electron transfer phenomenon.
3. We are successful in studying electron transfer reaction between N- halosuccinimides and nitrones under
   (i) mildest conditions and
   (ii) At ambient temperatures.
4. We are successful in observing satellite signals from ^{13}C isotope in all the different positions of PBNOX.
5. The observance of succinimidyl adduct of DMPO under the conditions employed is reported first time.
6. The electron capture dissociation of $NCS^{\cdot -}$ leads to succinimidyl radical ($S^{\cdot}$) and chloride ion (Cl^-), while $NBS^{\cdot -}$ and $NIS^{\cdot -}$ leads to S^- and corresponding halogen atoms.
7. The studied system involves only two major chain carriers succinimidyl and the corresponding halogen moieties with no sign of ring opening of succinimidyl moiety.

8. The role of polar and hydroxylic solvents in solvating the charged species and thus diverting the reaction pathways have been clearly observed.
9. A new route for the generation of methyl radicals from DMSO is postulated.
10. It has been observed that the rate of dimerisation of bromine atoms are relatively slower than iodine atoms.
11. The strong evidence of the charge transfer complexation suggests that the electron transfer proceeds through an " outer - sphere " mechanism.

SCOPE OF THE PRESENT WORK

Since this is a first attempt of this kind at room temperature under mildest conditions, the positive results appears to be quite promising. Therefore, it is certainly worth pursuing with other substituted and structurally similar molecules for example N- Halophthalimides.

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Dedicated to my parents

declaration

The North - Eastern Hill University
Month : October, Year : 1997

I MD. NADEEM KHAN, hereby declare that the subject matter of this thesis is the record of work done by me, that the contents of this thesis did not form the basis of the award of any previous degree to me or to the best of my knowledge to anybody else and that the thesis has not been submitted by me for any other research degree in any other University / Institute.

This is being submitted to the North Eastern Hill University for the degree of DOCTOR OF PHILOSOPHY in CHEMISTRY.

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A large debt of gratitude to all my friends whose names have not been listed here. I humbly say "Thank You".

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Lastly but most importantly I wish to say that I am profoundly indebted to my parents, brother, sister and grandfather for the love and affection showered on me to reach this stage of my life.

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CHAPTER I

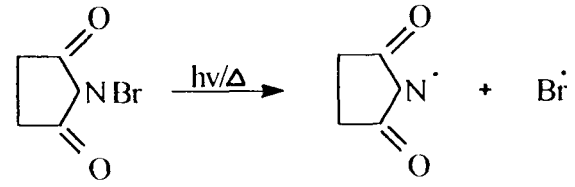
INTRODUCTION

Interest in the succinimidyl chemistry can be traced to the recognition by Karl Ziegler and co - workers [1] that N- Bromosuccinimide (NBS) is a versatile but highly specific brominating reagent of olefins at allylic positions. He demonstrated that the decomposition of NBS in the presence of olefins selectively brominates allylic positions under the appropriate conditions, i.e. thermolysis and / or photolysis of NBS in boiling Carbon tetrachloride. This allylic bromination has been shown to occur by a radical chain mechanism [2 - 4] and has been used in synthesis primarily because of its simplicity and good yield. Although, the reaction was quickly recognised as a free radical chain process and has become a standard synthetic procedure, the actual chain carrier involved have been the subject of recurrent controversy.

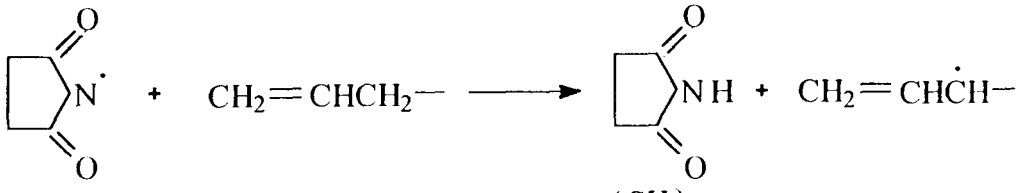
By the mid 1970's, it was generally accepted that the original Bloomfield mechanism (scheme 1) involving the succinimidyl radical as chain carrier was easily observable [5] only with unreactive substrates, such as saturated hydrocarbons, preferably in the presence of halogen atom traps.

Scheme 1

Bloomfield Mechanism



(NBS) (Ṡ)



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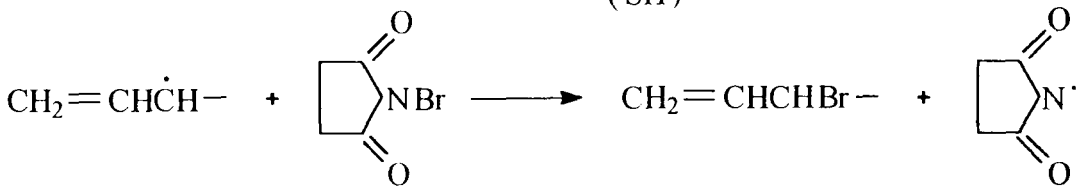
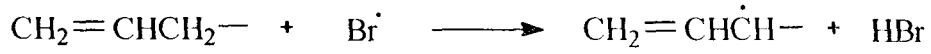
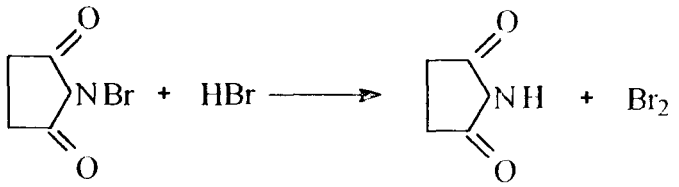


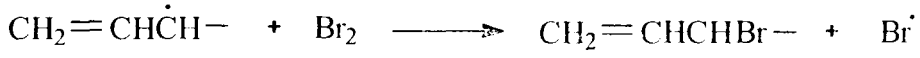
On the other hand, in allylic and benzylic bromination, the condition under which NBS is most commonly used, the reaction was believed to occur through a bromine atom chain as was originally suggested by Goldfinger [6] (scheme 1.1), the NBS simply acting as bromine source.

Scheme 1.1

Goldfinger Mechanism







Actually, the two processes have not proved easy to distinguish, since they predict similar kinetics and the chain carriers were not observed by any spectroscopic technique. The question as to whether the mechanism involves the succinimidyl radical (Bloomfield mechanism) or the bromine atom (Goldfinger mechanism) as the chain carrying species is still a matter of controversy. Besides this aspect, the other interesting part of this chemical reaction " the study of succinimidyl radical " was inadvertently overlooked. The properties of the succinimidyl radicals are novel in many aspects and their role had been a subject of many investigations [1] e.g., it was held for a long time that these radicals are relatively inert towards hydrogen abstraction, addition to double bonds and arenes. Recently, it has been proved otherwise.

Eberson [7, 8] has studied the electrochemical reduction of NBS and N- Chlorosuccinimide (NCS) and has postulated that the major products are succinimide and low molecular weight succinimide polymers in which the succinimide units are joined by both C - N and C - C linkages. Still, some of the novel features of this radical e.g., ring opening and follow up reaction have been a subject of controversy and different explanations have been propounded so far. This subject was reopened by Skell

and co - workers [9]. They examined the ring opening reactions and other aspects of this mechanism in detail. The area of disagreement involves both experimental results and their interpretations. The most unusual feature had been the postulation of two kinds of succinimidyl radical : ground state (π) and excited state (σ_N and / or σ_O).

However, in a recent communication [10] Skell has withdrawn the σ - π postulation, but reiterates the presence of two chain carriers in addition to Br·. Tanner and co - workers [11] has interpreted their results as a mixed chain reaction of a single succinimidyl radical and Br·. Walling et al. [12] initially recognised the involvement of two radical chain carriers along with Br· but recently [13.a] arrived at the same conclusion as that of Tanner.

With this controversial background and recently developed interest in the chemistry of the succinimidyl radical [13.b], we embarked upon this subject through a simple and different path, where ESR (Electron Spin Resonance) spectroscopic technique plays a major role.

SINGLE ELECTRON TRANSFER (SET) CHEMISTRY

Fundamental Aspect

Mechanisms of organic reactions are largely described as two - electron centered [14]. Electron movements are pictured as taking place two by two in the familiar curved arrow mechanism and with rare exception [15] notions of one - electron organic chemistry did not enjoy much acceptance in the past. Although in inorganic chemistry " Single Electron Transfer " (SET) concept is very well accepted, it was only in organic chemistry that some reluctance was there, may be due to lack of convincing evidences. Most classical Polar mechanisms have proved resistant towards re - evaluation in terms of electron transfer but in 1960's novel Single Electron Transfer processes made their way into the knowledge base of organic chemistry. In 1966, Kornblum [16] and Russell [17] independently provided details of the $S_{RN}1$ mechanistic pathway (" electron - initiated " radical chain mechanism of nucleophilic substitution) for the specific reactions that they were studying and in 1970 Bunnett [18a] discovered that such a pathway was also in effect in some cases of nucleophilic aromatic substitution (Scheme 1.2).

Scheme 1.2

S_{RN}^{1} Mechanistic Pathway

$$RX + Y^{-} \longrightarrow RX^{\cdot -} + Y^{\cdot} \quad (i)$$

$$RX^{\cdot -} \longrightarrow R^{\cdot} + X^{-} \quad (ii)$$

$$R^{\cdot} + Y^{-} \longrightarrow RY^{\cdot -} \quad (iii)$$

$$RY^{\cdot -} + RX \longrightarrow RY + RX^{\cdot -} \quad (iv)$$

Step (i) involves Single electron transfer from the nucleophile (Y^{-}) to the substrate RX. In step (ii) the radical anion ($RX^{\cdot -}$) dissociates rapidly to radical ($R^{\cdot}$) which then reacts with (Y^{-}) in step (iii) to form the product radical anion ($RY^{\cdot -}$) which in step (iv) serves as the one - electron donor in the radical chain process. Their preparative usefulness no doubt contributed strongly to the ready acceptance of the mechanism, which paved the way for related types of electron transfer (ET) catalyzed mechanism such as cycloadditions and oxidatively catalyzed aromatic substitution [18b].

What is Single Electron Transfer Phenomenon ?

Single Electron Transfer reaction is defined as one that is initiated by the transfer of a single electron from the nucleophile to the substrate, producing radical intermediates. The fate of the resulting radical

intermediate can then be involved in any number of events, one of which is described in the S_{RN}^1 mechanistic pathway in scheme (1.2). The possible role of SET in organic reactions, as opposed to classical notion of electron - pair transfer, has attracted continuous and active attention in the past. Another important development in SET chemistry has been the discovery of nucleophilic substitution reactions proceeding via anion radical intermediates and taking place at benzylic carbon centers [16] or at aromatic carbon centers [18a].

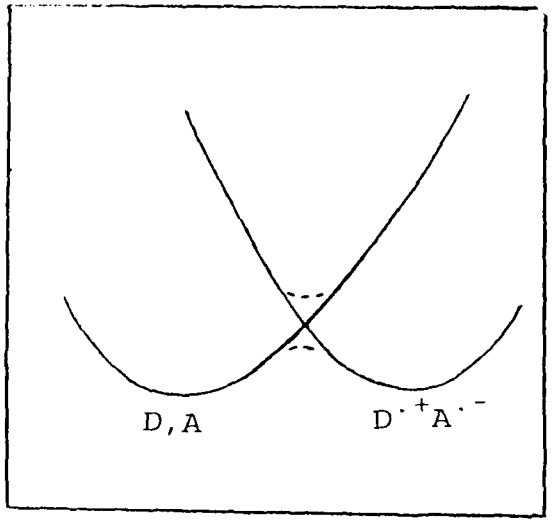
On the other hand, the continuous development of organic electrochemistry, particularly in its mechanistic and kinetic aspects [19, 20] has been another source of interest and information for reactions triggered by SET. Since then many reactions between nucleophiles and electrophiles which were previously believed to follow polar mechanism, have now been recognised to proceed via initial one electron transfer and subsequent radicoloid steps.

Different Models for explaining SET.

Pross [21a] and Shaik [21b] have developed a Configuration Mixing model (CM) to compare these processes, [21c]. In the (D,A) nomenclature of the CM

treatment picture (D = donor and A = acceptor), the electron transfer (ET) step as coming about by the avoided crossing of the two crossing curves as shown in Fig.1

Fig. 1



The curves are the plot of the potential energies of the electron configuration for the precursor (DA) and the successor complex ($D^{\cdot+}A^{\cdot-}$). The movement along the reaction coordinate consist of solvation changes and geometric distortions (changes in bond lengths, bond angles etc.) which increases the energy of (DA) until it reaches the same energy level as a similarly activated ($D^{\cdot+}A^{\cdot-}$) configuration. At this point ET occurs.

Pross has concluded that following factors should work in favour of ET processes :

(i) Strong donor - acceptor pairing will move the avoided

crossing towards the initial state.

(ii) Steric interaction between D and A, which will decrease the probability of group coupling between $D^{\cdot +}$ and $A^{\cdot -}$.

(iii) Low $D^{\cdot +}$- $A^{\cdot -}$, bond strength will decrease the likeli - hood of group coupling between $D^{\cdot +}$ and $A^{\cdot -}$ and

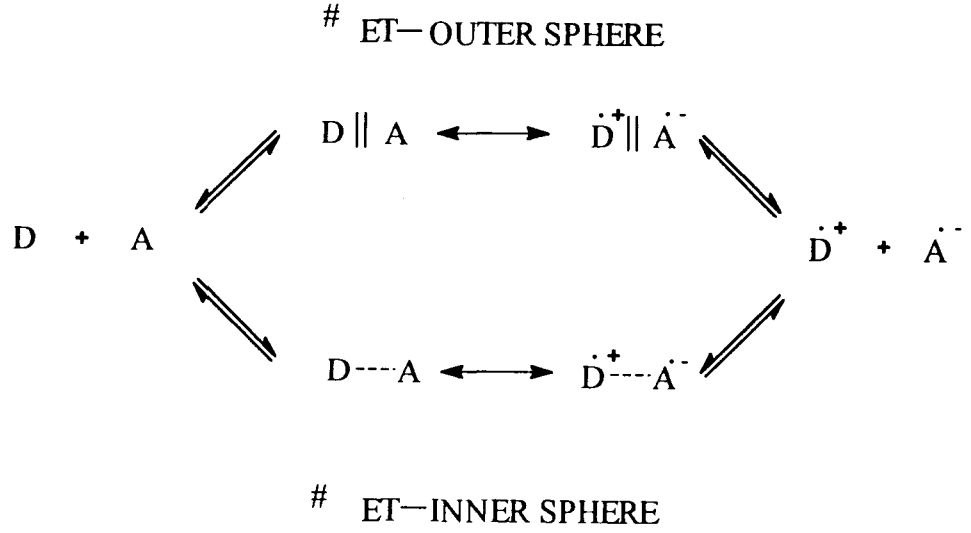
(iv) Strong delocalisation of the radical centres of $D^{\cdot +}$ and $A^{\cdot -}$.

In short, the CM treatment represents the most successful attempt so far to provide deeper insight into the difference between ET and polar processes in terms that are akin to the organic chemist's thinking. Recognition of SET pathway in organic reactions are growing enormously in many areas of chemistry, both fundamental and applied ones [22-24].

Marcus Theory of SET.

Marcus [25] has done pioneering work on the theory of electron transfer mechanism and has proposed a very simple model in terms of outer - sphere and inner - sphere electron transfer mechanism. Fig. 1.1, summarises the ET mechanism for a donor D and an acceptor A.

Fig. 1.1

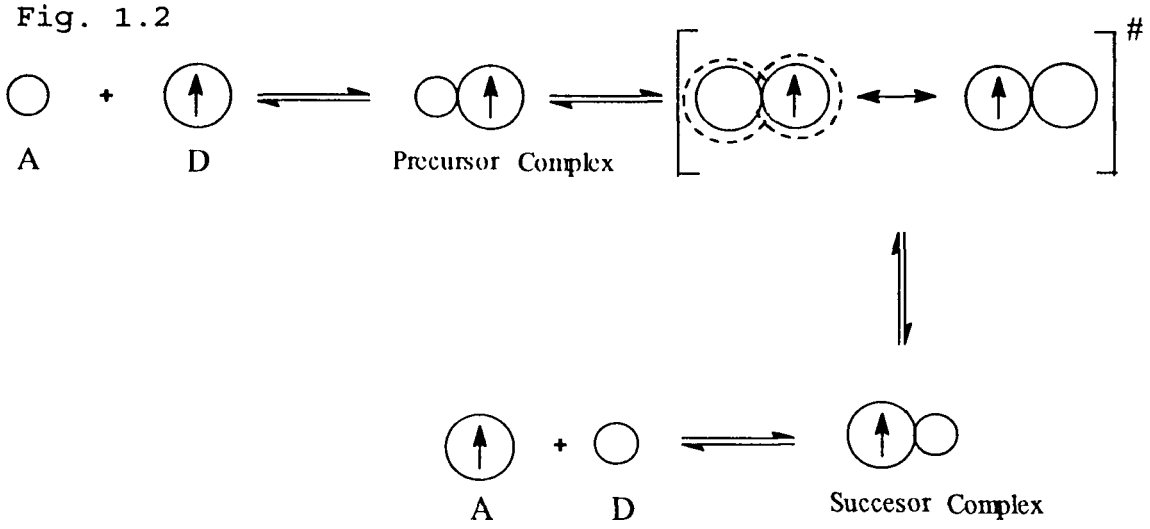


The fundamental difference between the inner and outer sphere mechanism as far as transition state is concerned is that, in inner - sphere mechanism, donor and acceptor moieties maintain a substantial interaction in the transition state. The physical model underlying Marcus treatment of outer - sphere ET is indeed simple, in that Donor (D) and acceptor (A) are approximated as two spheres of radii r_1 and r_2,

$$D + A \rightleftharpoons D^{\cdot +} + A^{\cdot -}$$

and charges z_1 and z_2, embedded in continuous medium of dielectric constant d. However, for organic molecules, the shapes of which are seldom spherical, ellipsoidal models have been used with some success [26]. The Marcus Model is shown in Fig. 1.2.

Fig. 1.2



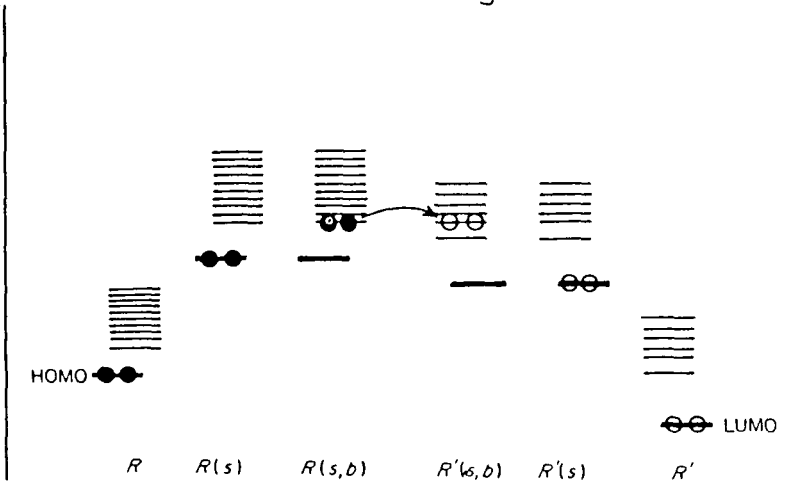
D represents the large sphere with the arrow denoting the electron to be transferred. The two spheres diffuse together and form the precursor complex with the distance between the centres of the spheres usually taken to be $r_{12} = r_1 + r_2$. This complex is also denoted as collision or encounter complex. In order to reach the transition state, Franck-Condon principle requires the energy levels between which the electron is to be transferred to be made equal to within $\pm$ RT, where R and T have their usual meanings.

This requirement is satisfied by increasing the energy of the system, until the energy levels match each other by bond and solvent reorganisation, associated with the bond (involves bond stretching and / or compression, angle deformation and torsional movements) and solvent (involves solvent induced changes in the electrostatic environment around the reactants) reorganisation energies. Bond

reorganisation is symbolised by expansion of the smaller sphere and shrinking of the larger one in transition state, which is a resonance hybrid of the (DA) and ($D^{\cdot+}A^{\cdot-}$) forms. After electron transfer, the transition state relaxes and transforms into the successor complex which eventually dissociates into the two new species.

The Marcus - Hush theory of outer sphere electron transfer [27] is based on the Born - Oppenheimer approximation and thus relates the activation barriers to the nuclear reorganisation that accompanies electron transfer. Classification of organic ET processes as well as qualitative and quantitative aspects of Marcus theory is well described by Eberson [28a]. Molecular Orbital picture of electron transfer between two species with even number of electrons is shown in Fig. 1.3.

Fig. 1.3



MO picture of an electron transfer process between the HOMO and LUMO of two reactants· R and R'. ● = electrons; 0 = vacancies.

The electron is transferred from the highest occupied molecular orbital (HOMO) of the reductant (R) to the lowest unoccupied molecular orbital (LUMO) of the oxidant ($R^{'}$). Solvent and bond reorganisation energies are symbolised by (S) and (b) respectively in order to match the energy of the two levels. In keeping with the assumed very small bond distortion necessary for many organic molecules, solvent reorganisation (S) has been assumed to be more important for R.

In any of these kind of redox reactions, orbital symmetry plays a major role, as it must in all chemical reactions. The requirement for a net positive overlap between the electron donating molecular orbital and the electron accepting orbital is a key part of the general theory of electron transfer.

The ideas expressed by Pross and Shaik are very important because they have presented an alternative to Marcus theory that is more comprehensible to organic chemists. Similar ideas were expressed by Kochi in Charge-transfer theory of electrophilic substitution and addition [28b] reactions.

Taube's [29] definition actually covers most cases, " The distinction is fundamentally between reactions in

which electron transfer takes place from one primary bond system to another (Outer - sphere) and those in which electron transfer takes place within a single primary bond system (inner - sphere mechanism) ".

Although the outer - sphere / inner - sphere terminology was coined originally for electron transfer reactions involving coordination complexes, it can be used profitably for organic processes after some extension of the definitions [30]. In outer - sphere electron transfer, either no bond is cleaved or formed within the time scale of the experiment or in the opposite case, bond breaking and bond formation take place in separate steps, distinct from ET step. Conversely, if all the three steps are concerted one will deal with an inner sphere electron transfer. An S_N^2 reaction may be considered as being formally equivalent to an inner - sphere electron transfer reaction or even close to being trully equivalent in many instances.

The outer - sphere / inner - sphere terminology may also be used to characterise the way in which the reactants react, rather than to characterise the overall reaction. The Marcus theory is thus very well applicable to inorganic as well as organic systems.

The methodology that are used to provide evidence for SET catalysed mechanism have been listed by Chanon [31].

These are :

(i) Detection of radicals by ESR Spectroscopy.

(ii) Stereochemistry.

(iii) Formation of radical derived secondary products, including induced polymerisation of added monomers.

(iv) Kinetics including the use of "radical clocks".

(v) Isotope effects.

(vi) Failure to confirm the simple LFER (Linear Free Energy Relationship).

(vii) Comparison with compulsory electron transfer processes i.e electrochemical processes that are as closely related as possible.

(viii) Photostimulation, particularly electron transfer catalysed reactions.

However, some additional criteria are the appearance of charge transfer complexes which are precursors to fully charged separated species, the observation of chemiluminescence is an indication that odd - electron species are involved in a possible ET mechanism.

Medium effects are important for ET reactions, as for other organic reactions, but are not very useful

diagonistically due to their unpredictable nature. A generally observed medium effects is that caused by extremes of acidity or basicity ; in strongly acidic media electron transfer oxidation of organic molecules is favoured, both due to an increase in oxidation potential of the oxidant (caused by for e.g., protonation of oxidising species or stripping of ligands from a metal complex) and kinetic and / or thermodynamic stabilisation of radical cations formed. The inverse situation seems to hold for the electron transfer reduction in strongly basic media.

Current experimental inquiries into solvent effects in electron transfer are broadly of two types. The first involves measurements of Time - Dependent Fluorescence Stokes Shifts (TDFS) for chromophores forming suitable charge transfer excited states [32]. Such measurements probe the real time dynamics of polar solvent relaxation around a newly formed dipole. In addition, measurements of ET rates, themselves either from photoexcited or ground states, can yield solvent dynamical information. The evidence for a SET pathway in the reaction of a nucleophile with a carbonyl compound involves the observation of a paramagnetic intermediate and kinetic data, establishing that the rate constant for the disappearance of paramagnetic intermediate is within the experimental error

of rate constant for the appearance of the product.

UV SPECTROSCOPY

Charge Transfer (CT) Complexes.

Charge transfer complexes play a very important role in SET reactions as these are the precursors of the ET process. This is the phenomenon observed when a molecule whose ionisation potential is low comes in contact with a molecule whose electron affinity is quite high and as a result of this interaction, the molecular energy levels of both are perturbed. The magnitude of this interaction may be high or low depending upon the ionisation potential and electron affinity of the donor and acceptor respectively. A very low ionisation potential of the donor and a very high electron affinity of the acceptor will result in the complete transfer of an electron from the HOMO of donor to the LUMO of the acceptor, giving rise to new band in the electronic spectra. Such a band is called charge transfer (CT) band [33] which is the property of the new specie formed.

In cases where the ionisation potential of the donor and the electron affinity of the acceptor are not favourable for the complete transfer of electron, only a perturbation of the energy levels of both donor and

acceptor will occur. In charge transfer complexes, the charge distribution is considerably different in the ground and the excited state. According to Mulliken, the wave function of the ground state Ψ_N of the molecular complex DA, can to a first approximation, be written as sum of the two terms :

$$\Psi_N = a\Psi_0(DA) + b\Psi_1(D^+A^-)$$

Wave function Ψ_0 relates to the hypothetical " No Bond " state of the system and the function Ψ_1 relates to the state in which the electron is transferred from the donor to the acceptor (D^+A^-), a and b characterise the fraction of " no bond " structures and the structures with charge transfer in the ground state. The wave function of the complex in the excited state has the form

$$\Psi_E = a^*\Psi_1(D^+A^-) - b^*\Psi_0(DA)$$

Coefficients a, b, a^*, b^* are related to the orthogonality and normalising condition of the wave functions Ψ_N and Ψ_E .

$$\int \Psi_E \Psi_N \, d\tau = 0$$

$$\int \Psi_N^2 d\tau = \Psi_E^2 d\tau = 1$$

Since, charge transfer complexes are stabilised by electrostatic forces, they are bound to be affected by the

polarity of the solvents. It may solvate the initial molecules and the intermediate complexes non specifically or it can form specific chemical bonds (for example hydrogen bond) with the initial molecules and the intermediate complexes. If solvation or the ability to form these bonds is stronger in the intermediate complex than in the initial molecules, that particular solvent will accelerate the reaction. If on the other hand, the formation of these bonds is energetically more advantageous in the initial molecules than in the reaction complex, the solvent will delay the reaction. These effects may be so powerful that the direction of the reaction may also be changed. For this reason, results obtained in one solvent must not be directly transferred to other solvent.

Isosbestic Points

It has been found that in the electronic spectra of multicomponent systems, there are certain wavelengths where the absorbance remains constant for all compositions of the system, provided the overall concentration is fixed. Such points are called Isosbestic points or the isoabsorptive points [34]. The appearence of an isosbestic points are indicative of the presence of a charge transfer interaction between the donor and the acceptor present in the system. Observance of no charge transfer bands and only isosbestic

points indicates only weak CT interaction. The shift in the isosbestic point with the relative change of concentration can be related to the different stoichiometry of the complex formed.

ELECTRON SPIN RESONANCE SPECTROSCOPY

ESR spectroscopy is a technique for the study of species containing one or more unpaired electrons. The scope of the method includes the detection and characterisation of some transition - metal ions, cations, anions, organic free radicals, including biradicals and triplet states. ESR is a magnetic resonance technique which achieves a response only from molecules with at least one unpaired electron. The signal obtained from the unpaired electron is a single line which reflects the net absorption of energy by the electron when the following "resonance" condition is met.

$$h\nu = g\beta H$$

Where $h\nu$ is the energy of absorbed photon, β is a constant for the electron, the Bohr magneton, H is the magnitude of the external field applied and g is the constant characteristic of the spin system (approximately 2.0 for organic free radicals). The absorption of energy by the electron corresponds to a change in sign of the

electron spin or change in direction of the electron magnetic moment vector. If the unpaired electron experiences the field of another spin system, say a nucleus with a spin ($I \neq 0$), the magnetic field felt by the unpaired electron is slightly greater than, or smaller than, the field experienced in the absence of nuclear spin system, depending upon the direction of perturbing additional field.

Thus, for a spin $I = \pm 1/2$, resonance now occurs at $H_1 = H - \delta H_1$ and $H_2 = H + \delta H_1$, where δH is the perturbing field. Two signals or lines are observed. The coupling constant " a " is defined as the spacing between the observed lines, usually in gauss (G) or millitesla (mT). Since the original line due to unpaired electron is " split " into two lines, the spacing is also called a splitting constant or hyperfine splitting. If the unpaired electron experiences the field of more than one nuclear spin, two possibilities arise :

(i) Either the interaction between each nuclear spin and unpaired electron is equal for all nuclei (equivalent),

(ii) or not equal for all nuclei (non equivalent).

For equivalent nuclear spins, the system is considered

to have a total spin of nI, where the number of lines are predicted by the expression (2nI + 1).

For non - equivalent nuclei, the number of lines is predicted by the product of individual sets of equivalent nuclei : $(2n_1I_1 + 1).(2n_2I_2) \ldots$, where n_1 is the number of equivalent nuclei with spin I_1, n_2 is the number of equivalent nuclei with spin I_2 etc. The intensity of lines from interaction with n equivalent nuclei are best obtained from Pascal's triangle i.e the coefficients in the expansion of $(1 + x)^n$. The spacing between the lines are always symmetrically disposed about the centre of the spectrum (to first order approximation).

An ESR spectra is characterised by three parameters : the hyperfine splitting, the g factor and the line width. A fourth parameter, the electronic splitting, applies to triplets (species with two unpaired electrons which interact with each other) and will not be discussed here.

The three important factors which determine the magnitude of interaction of the unpaired electron with the nuclear spin are :

(i) The magnitude of the magnetic moment and spin of the nucleus.

(ii) (a) The S character of the orbital containing the

unpaired electron (for orbitals with S character), and

(b) The extent of " spin - polarisation " of the inner shell electrons (for essentially pure p or d orbitals).

(iii) The spin density of the nucleus in question.

If all other factors remains constant, the magnitude of the splitting constant is directly related to the nuclear magnetic moment (μ) and inversely related to the spin, for e.g., for hydrogen atom, I = 1/2, a = 508 G [35], and μ = 2.793, and for deuterium atom I = 1, a = 78 G, and μ = 0.857.

Thus, 508 / 78 = (2.793 / 0.857) x [1 / (1/2)]= 6.51.

The splitting constant is also related to spin density on the nucleus in question, since in delocalised systems the interaction between the electron and the nucleus must necessarily reflect the " time " spent in the vicinity of the nucleus. Thus, the spin density on each carbon atom in cyclopropenyl radical must be one - third of unity.

Hyperfine splitting is also observed from nuclei which are bonded through one or more bonds to atoms bearing the unpaired electron e.g., the hydrogen hyperfine coupling is 23 G for the methyl radical, 25 G for the ammonium

radical and 26 G for the methyl group in the ethyl radical [35]. A relationship between the hydrogen hyperfine splitting and spin density on a sp^2- hybridised carbon atom was first obtained from the ESR spectra of aromatic ions of known structure [36],

$$a_C^H = Q_C^H \rho_C$$

where a_C^H is the coupling constant of hydrogen attached to carbon, ρ_C is the spin density on carbon and Q_C^H is the proportionality constant relating the magnitude of hydrogen coupling constant to spin density on carbon. In organic radicals in solution, the orbital angular momentum of the electron is almost completely quenched, so that g factors are close to the value for the free electron (2.0023). However, differences from this value are observed, particularly when the unpaired electron is associated with atoms which have unshared pair of electrons e.g., g factor for $\cdot CH_3$, $\cdot CH_2OH$ and $\cdot CH_2CHO$ are 2.00255, 2.0031, and 2.0045 respectively and in general, hydroxyl and carbonyl - substituted radicals have g - factors about 0.001 and 0.002 respectively, greater than the free spin value [37]. These differences, though numerically small, provides valuable information about the structure of a radical [38]. In short, the information obtainable from

ESR spectra of free radicals is contained in :

(i) the number and position of the spectral lines,

(ii) the line width and

(iii) the total absorption intensity.

Analysis of the number and positions of lines leads to the determination of the chemical and steric structure of the radicals and provides insight into the odd electron distribution. Line width may offer additional information on structure as well as on kinetics of reversible radical reactions. The concentration of the radicals is determined from the absorption intensity [38].

SPIN TRAPPING

The direct detection and identification of short - lived free radicals by ESR is possible, only if the radicals are produced in relatively high concentration in the ESR cavity by intense in situ irradiation or by rapid - mixing flow system. One of the indirect technique which is often used for the detection and identification of low concentrations of free radicals or very reactive species in reacting system is " Spin - Trapping ". It was reported that nitroso compounds add organic free radicals to form persistent aminoxyls which are readily detectable by ESR spectroscopy [39,40]. This work was extended by showing

that aminoxyls are also formed by addition of short lived free radicals to nitrones [41 , 42]. The importance of this reaction was soon realised as an analytical tool for detection and identification of short lived radicals [43 - 46] and Janzen et al. [47] coined the expression " Spin Trapping " for a reaction where a short lived radical R· is scavenged by a diamagnetic compound (ST), to form persistent radical adduct R-ST·, detectable by ESR.

$$R^{\cdot} + ST \longrightarrow R\text{-}ST^{\cdot}$$

The diamagnetic scavenger is called " spin trap " (ST) and the resulting persistent radical R-ST· is named as " Spin - adduct ". The detection and characterisation of transient radical intermediates produced in reactions which are initiated by ET processes, are essential to the mechanistic definition of those processes.

Spin trapping with various nitroso and nitrone derived moieties has proved to be fruitful for the detection and characterisation of transient radical intermediates ensuing from various substrates in solution, gas phase reactions [48] and in many other areas. An extensive compilation of spin adduct ESR data have been published by Buettner [49].

An immediate requirement of the technique is that, the spin trap and spin adducts should be soluble in the medium of interest and free diffusion of the spin trap to the location of free radical event should be allowed. The environment should also permit high mobility of the spin adduct, so that ESR spectra consists of pattern of sharp lines. The bulk and group electronegativity of the radical trapped determines the magnitude of the nitrogen and β - hydrogen coupling constants. Since solvent effects the nitrogen coupling constant (increases to larger values in protic solvents) and in turn the β - hydrogen coupling, it is advantageous to have spectra of nitroxides of " Known " structures available for comparison in the same solvent.

In the spectra of nitroxides, splitting by hydrogen is often clearly resolved when the hydrogen is attached directly to nitrogen or is in the β - position, a_H is frequently comparable in magnitude with a_N. Since β - hydrogen splitting arise predominantly by a hyperconjugative mechanism, there is a pronounced angular dependence. Large values of a_H^β are found with N- methyl nitroxides and specially in certain cyclic nitroxides, where the C - H bond is correctly aligned with the p orbital on nitrogen. In general a relationship of the form

$$a_H^\beta = \text{constant} \times \cos^2\theta$$

is obeyed. The angle θ is the dihedral angle between C - H and the nitrogen P orbital, the constant depends on the solvent.

Spin trapping is a kinetic method i.e the success of the spin trapping experimentaly depends critically on the rate conditions which exist in the system. For a favourable rate of spin adduct formation, the rate of spin trapping must be much faster than the rates of other reactions of the radical. Moreover, the ideal spin trap would give spin - adducts which are stable and unreactive to other reagents in the environment, even free radicals. More than hundred different compounds have been proved to be suitable spin - traps. However, nitrones (for example PBN, DMPO) and C- nitroso compounds (for example MNP) are preferred.

An important pathway for the formation of spin adduct has been recently revealed by Lennart Eberson [50, 51] involving redox processes and is termed as " Inverted Spin Trapping ", because of the inverted electron configuration of the reagent pair, Nu^- / $ST^{\cdot +}$ vs $Nu^{\cdot}$ / ST.

Proper Spin Trapping :

$$NU^- \xrightarrow{-e^-} NU^{\cdot} \xrightarrow{ST} NU{-}ST^{\cdot}$$

Inverted Spin trapping as proposed by Eberson :

$$ST \xrightarrow{-e^-} ST^{\cdot +} \xrightarrow{NU^-} NU{-}ST^{\cdot}$$

We have observed radical cation of spin traps [52], using low temperature ESR, giving more ground to inverted - spin trapping mechanism.

Note :

PBN : N - tert.Butyl α - Phenyl Nitrone.

IUPAC recommended name : N - Benzylidene -tert.-Butylamine N - Oxide.

DMPO : 5,5 - Dimethyl - 1 - Pyrroline 1 - Oxide.

IUPAC recommended name : 2,2 - Dimethyl - 3,4 - Dihydro - 2H Pyrrole 1 - Oxide.

MNP : Nitroso Butane.

IUPAC recommended name : 2 - Methyl - 2 - Nitrosopropane.

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CHAPTER II

REVIEW

During 1970's, the mechanism of radical bromination of alkenes and in particular the influence of a bromo substituent on the selectivity in the hydrogen abstraction step, have been studied and debated by several group of investigators [1-4]. Radical reactions of alkyl bromides with molecular bromine generally produce mixtures of dibromides in which the vicinal dibromide predominates. This selectivity was first attributed to kinetic assistance by the bromo substituent [1] but later it was claimed to result from the relative rates of reaction between the isomeric bromo alkyl radicals and hydrogen bromide [2]. The data on which this latter interpretation was based has been disputed by Skell [3] and finally retracted [2d]. Central to this controversy is the mechanism of bromination by N- Bromosuccinimide (NBS) which is extensively used both in the bromination as well as in oxidation of many classes of organic compounds [5].

Karl Ziegler's [6] finding that NBS is a highly specific and convenient reagent for bromination of olefins at allylic positions opened a new chapter of succinimidyl chemistry. This allylic bromination has been shown to occur by a radical chain mechanism [7 - 9] and has been

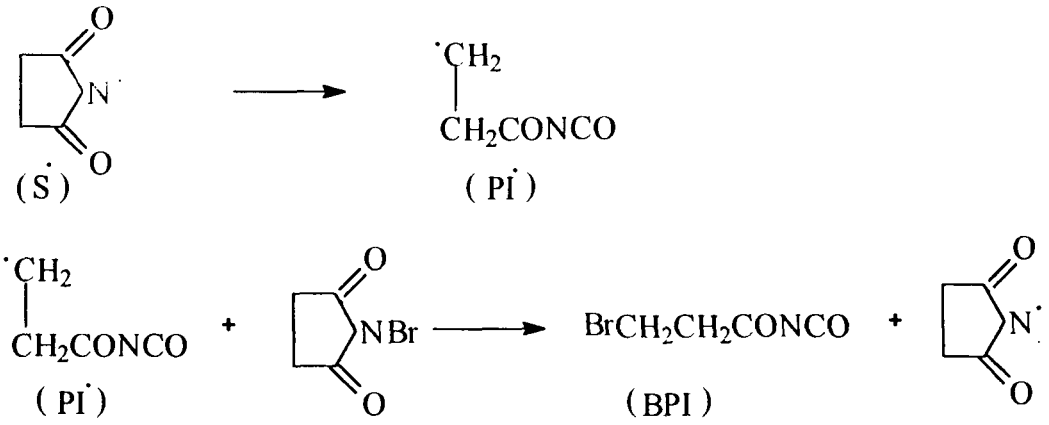
extensively utilised in synthesis primarily because of its simplicity and good yield [7]. Although the reaction was quickly recognised as a free radical chain process, the actual chain carriers involved have been the subject of recurrent controversy.

By the mid 1970's, it was generally accepted that the original Bloomfield mechanism [10] (scheme 1) involving the succinimidyl radical as a chain carrier, was easily observable [11, 12] only with unreactive substrates such as saturated hydrocarbons, preferably in the presence of halogen atom traps e.g., olefins lacking reactive allylic hydrogens [12], a technique which had previously shown to be effective in eliminating halogen atom reactions in alkyl hypohalite halogenations [13].

On the other hand, in allylic and benzylic brominations by NBS, the reaction was believed to occur through a bromine atom chain as originally suggested by Goldfinger [14] (scheme 1.1).

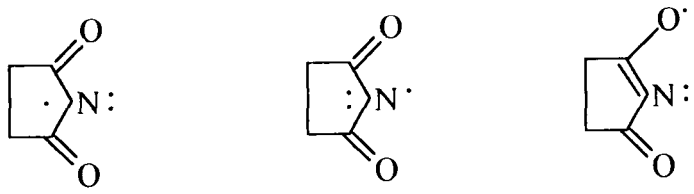
Actually the two processes have not proved easy to distinguish, since they predict similar kinetics and the chain carriers were not observed by any spectroscopic technique. The usual recourse was to relate reactivity data for pair of substrates, assuming a bromine atom chain

when these were the same as in photobromination with Br_2 alone (as in the case of allylic and benzylic substrates) [15, 16] and a succinimidyl radical chain when there were marked differences (saturated aliphatics and other unreactive substrate) [11, 12]. In unreactive media, particularly in the presence of olefin traps, the intermediacy of the succinimidyl radical was further supported by the competing formation of β - bromopropionyl isocyanate (BPI) [17, 18], presumably via a competing β - scission as shown below ;



This subject was reopened by Skell in a series of papers beginning in 1978 [19 - 22]. In these he examined the ring opening reactions in more detail for a number of succinimide and glutarimide derivatives, showing that its ease of occurence varies with ring strain and resonance stabilisation of the resulting radical. Skell, reported that the radical was reactive in hydrogen abstraction and

additions to double bonds and arenes [20]. The unexpected feature was the postulation of two kinds of succinimidyl radicals in thermal chain reactions, ground state (π) and a metastable excited state (σ_N and / or σ_O) as shown below ;



π σ_N σ_O

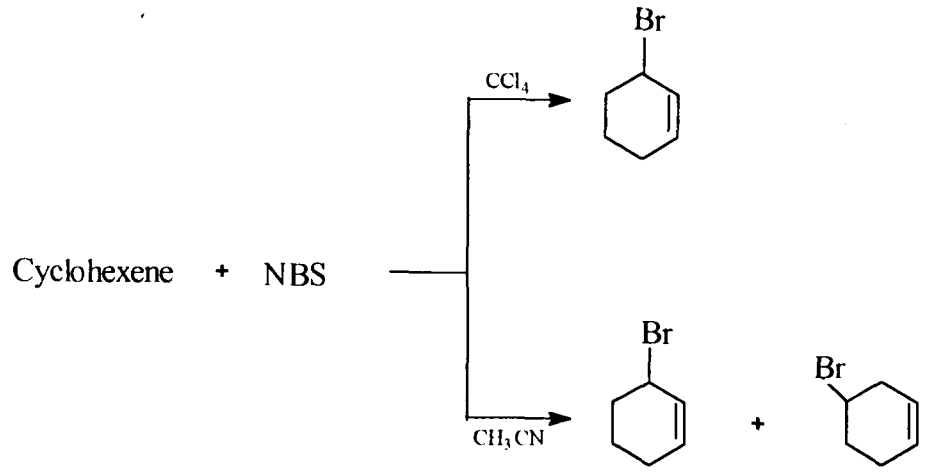
He suggested that substrate which can react readily with bromine atoms, the presence of small amounts of bromine preempts the succinimidyl radical as a chain carrier. Succinimidyl radical as a chain carrier can be observed with :

(a) substrate which do not react readily with bromine atoms and

(b) with more reactive substrates under conditions where exclusion of free bromine is attained.

As per his findings, the curious " Ziegler requirement " for the use of CCl_4 solvent in allylic bromination of olefins with NBS is for maintaining a very low concentration of NBS in the liquid phase (0.005 M solubility) and thus allowing Br_2 to be the major radical

trapping agent. In order to observe succinimidyl radical chain, a better solvent for NBS is required. For e.g., Cyclohexene - NBS, leads to 3- Bromocyclohexene exclusively in CCl_4 ($Br^{\cdot}$ atom chain reaction), but 3- and 4-bromocyclohexenes in the ratio 5:1 in CH_3CN, where NBS has 0.8M solubility.

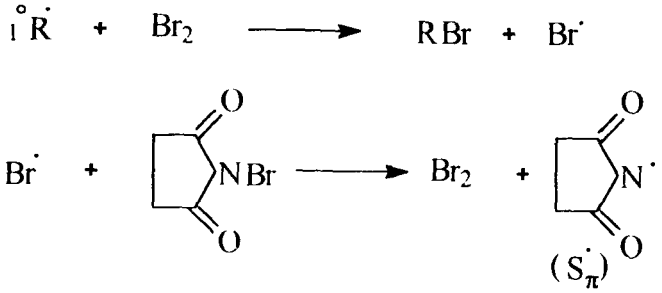


Skell also proposed that, increasing the concentration of NBS changed the dominant chain carrier from $Br^{\cdot}$ (in CCl_4) to succinimidyl (in CH_3CN). Chloroform and methylene chloride are also good solvents for succinimidyl chain reactions. He also proposed that NBS and N-Iodosuccinimide (NIS) undergo ring opening but N-Chlorosuccinimide (NCS) shows no ring opening. The ring opening reactions can be avoided by altering the ring, compounds which do not undergo ring opening are N-halophthalimide, - glutarimide, 3,3-dimethyl glutarimide,

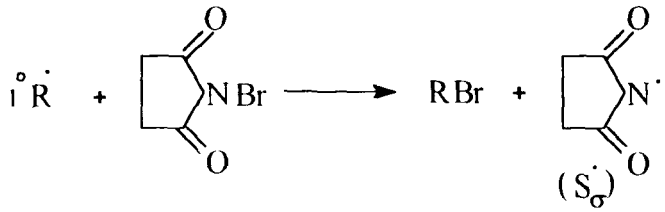
NCS and a variety of N-bromohydantoins.

His assertion that BPI is observed only in presence of Br_2-scavenging alkenes, led to the postulation of two different kinds of succinimidyl radicals, ground state ($S^{\cdot}_{\pi}$) and excited state ($S^{\cdot}_{\sigma N}$ / $S^{\cdot}_{\sigma O}$). Skell proposed that $S^{\cdot}_{\sigma}$ is produced only when Br_2 is removed from the system and exclusively undergoes ring opening. This postulation was further supported by INDO calculations done by Koening et al. [23] who concluded that π is ground state whereas σ_N and σ_O are excited states.

With Br_2 present

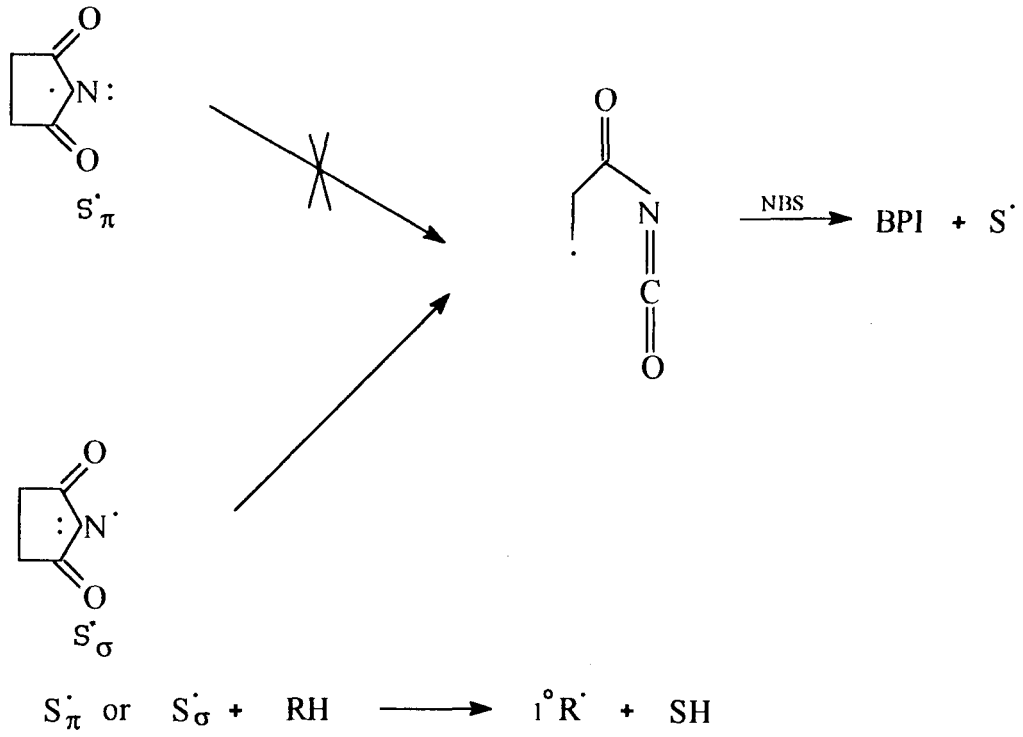


With Br_2 scavenged



Skell further proposed that the $S^{\cdot}_{\sigma}$ radical undergoes a reversible ring opening to propionyl isocyanate radical

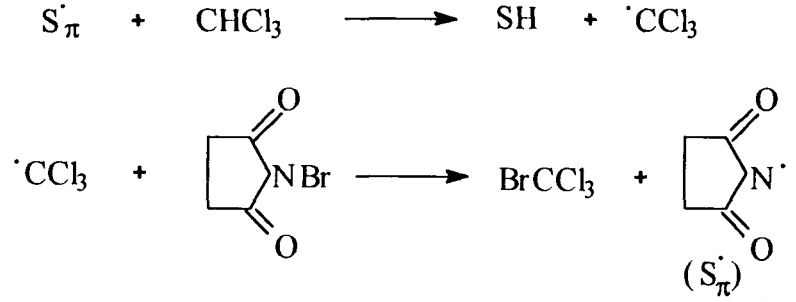
(PI·) which is effectively trapped by NBS to produce BPI. The $S^{\cdot}_{\pi}$ radical does not undergo ring opening reaction [21, 22] as shown below ;



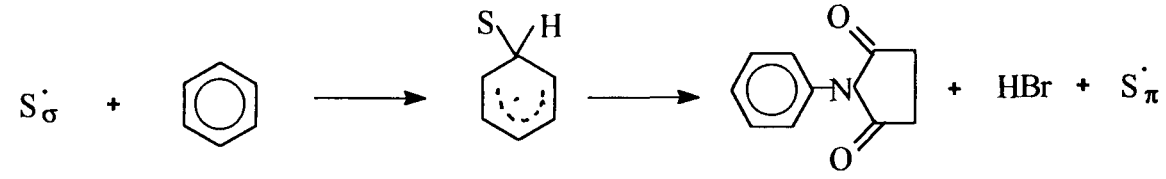
Skell studied the reactions of NBS with a series of radicals and proposed that more reactive radicals produces σ - succinimidyl radical and less reactive radical produces π - succinimidyl. The threshold for the change over from one reaction domain to other occurs with radicals less reactive than secondary alkyls. He interpreted these results with two transition states : an in - line transition state for more reactive radicals and out - of - plane transition state for less reactive radicals. He

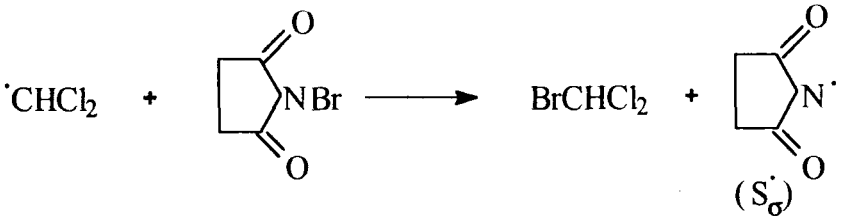
suggested two systems for generating $S^{\cdot}_{\pi}$ free of $S^{\cdot}_{\sigma}$.

(i) NBS-$CHCl_3$ in the presence of 1,1- dichloroethylene to scavenge any molecular bromine that develops.



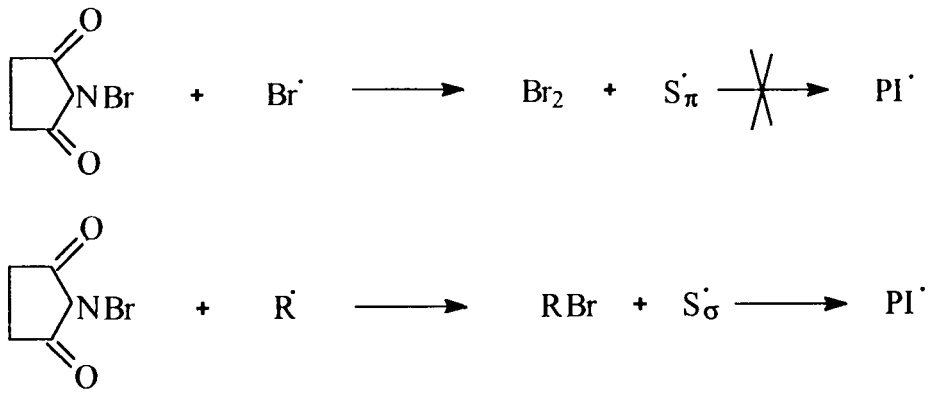
(ii) NBS-CH_2Cl_2, with sufficient benzene to trap all the $S^{\cdot}_{\sigma}$ and produce $S^{\cdot}_{\pi}$ specie.





Another experimental observation which led Skell [21] to $S^{\cdot}_{\sigma}$ / $S^{\cdot}_{\pi}$ hypothesis was the different behaviour of the succinimidyl radicals in the hydrogen abstraction in dichloromethane and neopentane. The succinimidyl radicals produced from reaction of NBS in presence of Br_2 showed

equal reactivity towards the C - H bonds of dichloromethane and neopentane and does not undergo ring opening. While the succinimidyl radicals produced in the halogen-scavenged systems strongly prefer H- abstraction from neopentane and undergo extensive ring opening. He concluded that ground - state $S^{\cdot}_{\pi}$ is produced with halogen present in the system, generated from the near thermoneutral reaction of NBS + Br· and excited state $S^{\cdot}_{\sigma}$ is generated from the exothermic reaction of NBS + $1^{O}R\cdot$, when free halogen is absent. Only $S^{\cdot}_{\sigma}$ undergoes ring opening, $S^{\cdot}_{\pi}$ does not. The presence of BPI in a product mixture may be taken as the identifying signature of a σ - succinimidyl radical.



In another communication Skell [24] has defined three methods free of ring opening reactions :

A. Employs NBS in CH_2Cl_2 or $CHCl_3$ solvent with Vinylidene chloride scavenger (for Br_2 and $Br^{\cdot}$) with approxi -

mately 0.3 mole fraction $BrCCl_3$.

B. Employs the same system as A, except that tert.-butyl ethylene is also equally effective and approximately 2.5 M benzene is used in place of $BrCCl_3$.

C. Employs Br_2 and NBS in CH_2Cl_2 or $CHCl_3$ solvents, with [Br_2] > 10^{-2}M and NBS at its saturation concentration (0.1 - 0.2M).

Method C was found to be most limited among the three methods, since it is applicable without ambiguity only if the substrate is relatively unreactive to Br· attack.

Skell [25] proposed that these halogen scavenging recipes are useful in generating succinimidyl radicals, which can participate in ;

(i) Ring - opening,

(ii) H - abstraction,

(iii) Alkene addition and

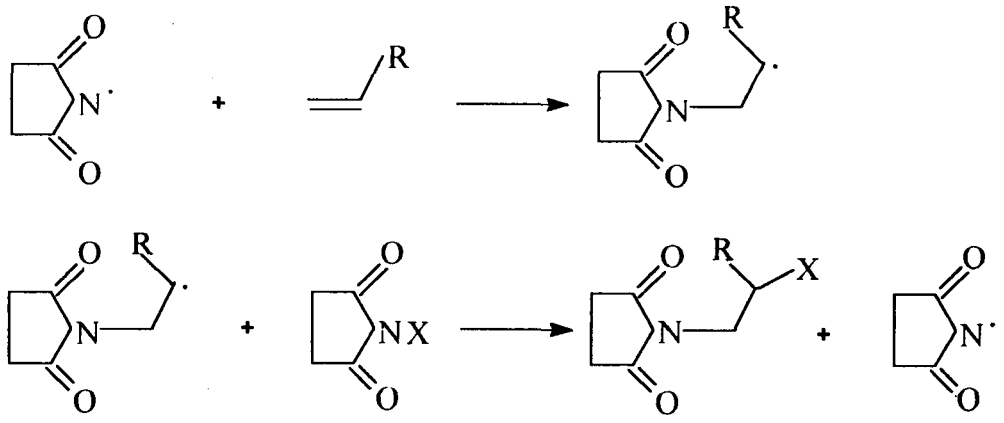
(iv) Reaction with arenes.

(i) Ring Opening reaction : The halogen transfer from the N- halosuccinimide to the ring - opened radical is slower for NCS than for NBS or NIS. The slower trapping of the ring - opened radical result in substitution exclusively, accompanied by isotopic scrambling in the succinimide.

Skell summarised his findings as " ring - opened product is diminished by choosing NCS instead of NBS, increased by substituting the α - position with methyl groups and decreased by using N-haloglutarimide and N- halophthalimides instead of N- halosuccinimides ".

(ii) Hydrogen Abstraction : Skell examined hydrogen abstraction selectivity of succinimidyl radicals for a number of substrates and proposed that halogen atom chains can be avoided by scavenging of halogen and halogen atoms with alkenes such as ethene, tert.-butyl ethylene or 1,1-dichloroethene for chlorine or bromine and allene for iodine. Skell has also proposed that hydrogen abstraction selectivity of $S^{\cdot}$ is similar to those of $Cl^{\cdot}$ or $OH^{\cdot}$ and differ sharply from those of $Br^{\cdot}$.

(iii) Alkene Addition : If radical chain reaction with succinimidyl radicals are carried out under conditions where more alkene is present than in experiments where it only serves as a halogen scavenger, 1:1 addition becomes a major reaction. The succinimidyl radical adds to an alkene forming an adduct radical which then reacts with N-halosuccinimide to form 1:1- addition product.

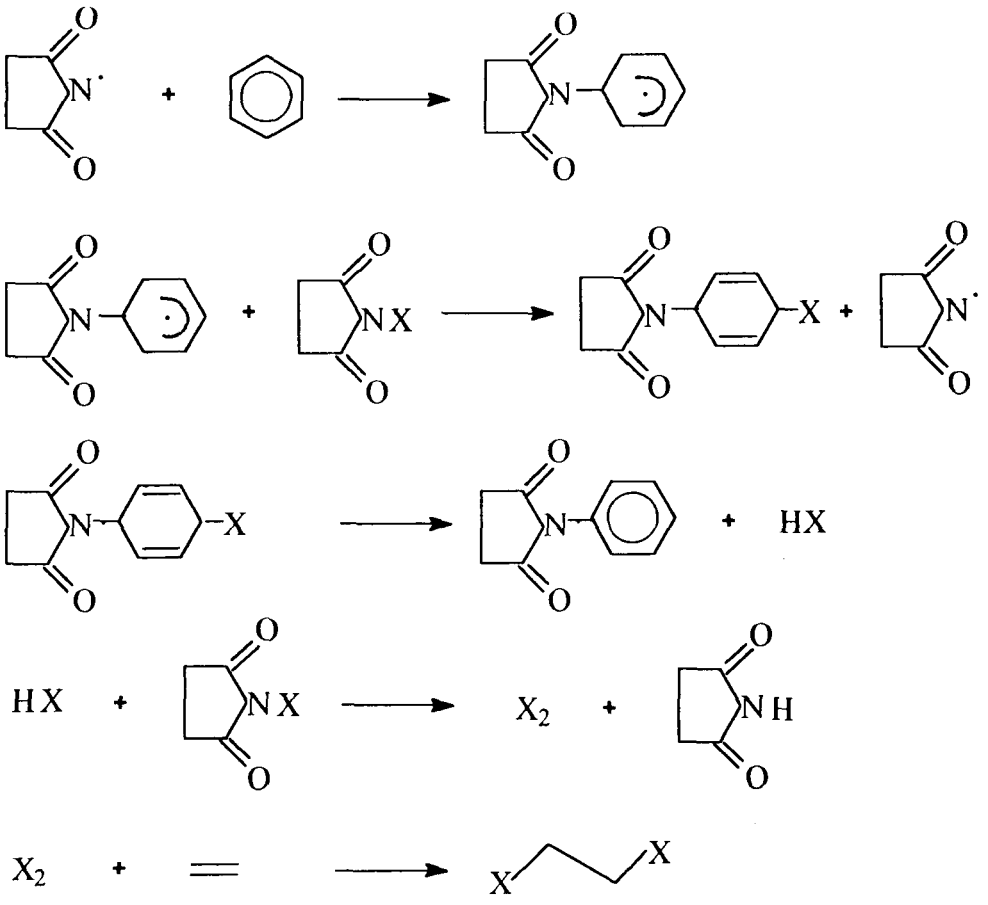


Skell suggested that succinimidyl radicals show electrophilic behaviour by adding easily to electron rich alkenes forming adduct radicals. These nucleophilic alkyl radicals [26] abstract bromine from NBS, thus regenerating the chain carrier. Electrophilic succinimidyl radicals prefers the addition to electron-rich alkenes while nucleophilic alkyl radicals prefer the reaction with the N- halosuccinimide.

(iv) Reaction with Arenes : Succinimidyl radicals also react with arenes. An addition / elimination sequence leads to substitution of the aromatic nucleus by the succinimidyl moiety. Succinimidyl radicals add to benzene with a rate similar to rate of addition to alkenes, forming a cyclohexadienyl radical. This cyclohexadienyl radical abstracts a halogen atom from the N- halosuccinimide to

give cyclohexadiene, which then loses HX to give the substituted arene. HX is scavenged by N- halosuccinimide giving succinimide and halogen (scheme 2). To ensure halogen - free reaction conditions, these reactions must be carried out with an alkene / N-halosuccinimide ratio of at least 0.5.

Scheme 2

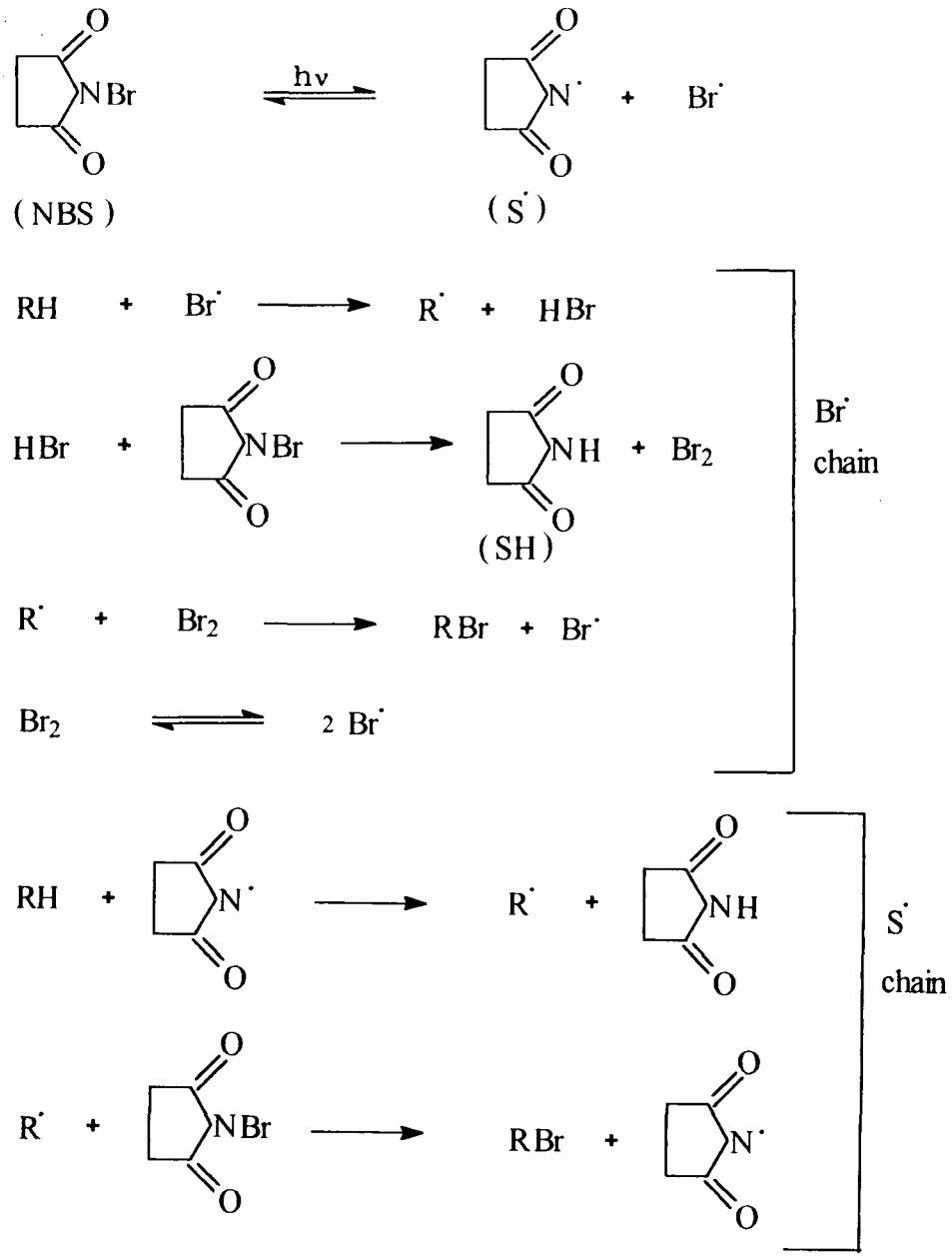


Skell proposed this mechanism by the observed 1:1:1 stoichiometry for N- phenylsuccinimide, succinimide and dihaloalkene. He observed that at 70°C this is a clean reaction, but at lower temperatures side reaction such as halogen scavenging by diene also occurs.

However, on re-examination Skell [27] found that the evidence for the specie " π " was not definitive and has withdrawn the conclusion based on his work with the statement " since there are doubts about the assignment of spectroscopic states, we propose to abondon such assignments and identify the chemistry formerly called "σ" as that of the succinimidyl radical ".

Traynham et al. [28], proposed that the mechanism of radical brominations of alkanic systems by Br_2 and NBS are different. He proposed that with alkanic systems, the succinimidyl chain have the lower activation energy and is the one which occurs. However, with benzylic systems, the alternate bromine atom chain becomes favoured because of stabilization in the transition state, while in mixtures containing both bromine and NBS, the bromine atom generation will far exceed succinimidyl radical generation (scheme 2.1).

Scheme 2.1



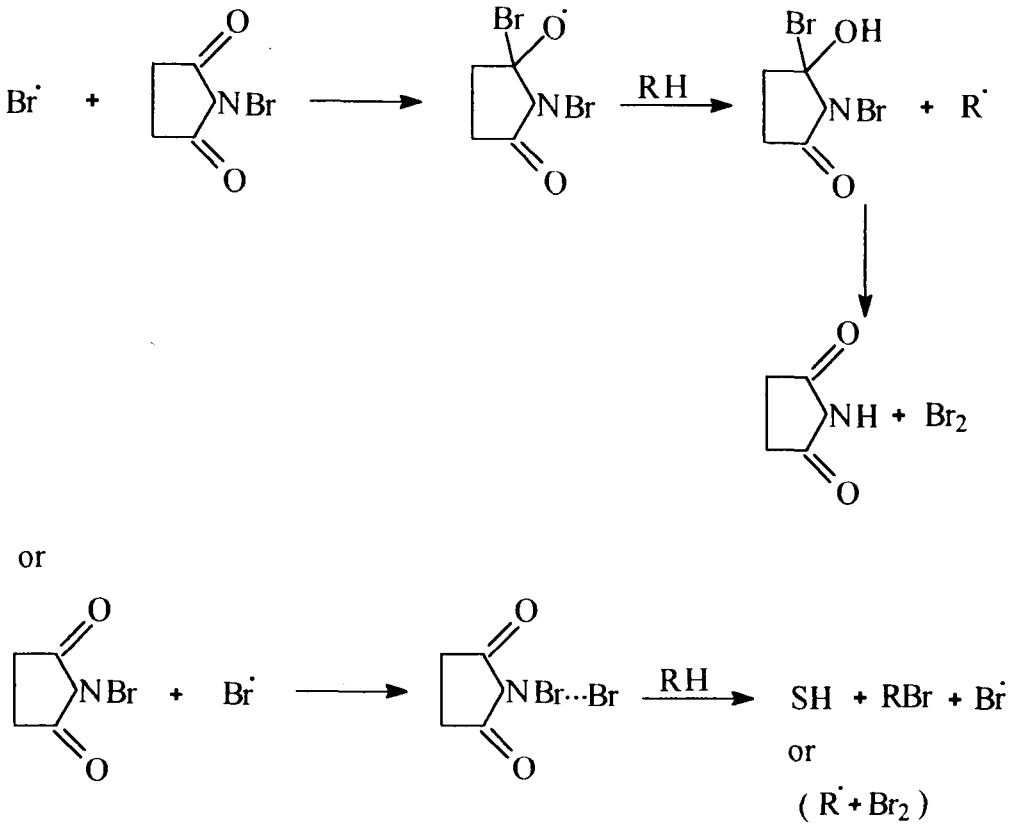
Photodecomposition of NBS was studied by Chow [29] and proposed that the photolysis of acetonitrile solution of NBS in the presence of ethylene oxide and an excess of olefins or benzene in the 30 - 20^{o}C range generates the succinimidyl radical in competition with the bromine atom

reactions. The succinimidyl radical preferentially attacks a π bond to give 1-succinimidyl 2-bromoalkanes rather than abstracting alkyl hydrogens. The photo additions indicated that the succinimidyl group attached itself to the less substituted carbon and bromine to more substituted carbon of the double bond. On the basis of addition reactivity of the succinimidyl radical to olefinic and benzene π - bonds, Chow suggested that this radical is highly electrophilic, which in turn hints that it has σ rather than π electronic configuration. He also proposed that photodecomposition of NBS in the presence of olefins and benzene containing no allylic hydrogen occurs by the succinimidyl radical addition to give straight forward addition products whereas in presence of olefins containing readily abstractable allylic hydrogen, it is complicated by various side reactions involving the bromine atom and bromine.

On the basis of product distribution and kinetic studies of NBS brominations in the presence of dichloro ethylene and bromine, Walling [30] observed it to be simple competing succinimidyl radical and bromine atom chains. On the basis of Kinetic results, he proposed that in presence of dichloroethylene, the rate controlling step is predominantly ring opening of succinimidyl radical which

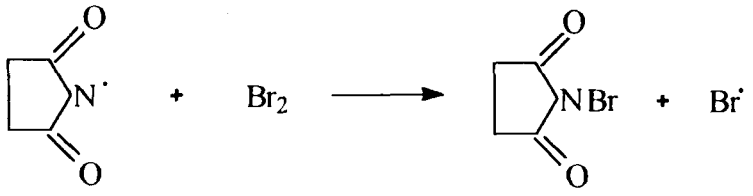
competes favourably with S· attack on solvent. In the presence of Br_2, the rate determining step is the attack of some chain - carrying radical on solvent. Both processes were found to be quite slow, although faster than the reactions of Br· generated from bromine alone. These results, particularly low reactivity of S· together with its required long life, led Walling to postulate that the chain carrier in NBS-Br_2 is neither a succinimidyl radical nor a simple bromine atom but some third specie derived from NBS and Br· (scheme 2.2).

Scheme 2.2



However, they suggested that additional work will identify it more definitely, since the rates of reaction of both the radicals involved appear to be slow, it could be identified by ESR or fast spectroscopic technique.

In another development, the competitive NBS bromination of cyclopentane versus cyclohexane was studied by Tanner et al. [31] and they found that the reaction proceeds by a mechanism dominated by either a bromine atom chain, a succinimidyl chain or a mixed chain. They suggested that the dominance of each of the major chain-carrying processes depends upon the solvent used, to some degree upon the reactivity of the substrate and upon the additives (molecular bromine or ethylene) used to moderate or enhance one or the other chain processes. They also proposed that at higher concentration of NBS in acetonitrile, when the reaction is carried out at low conversions, a succinimidyl radical would be the dominant chain-carrying species but as the reaction proceeds and the concentration of free bromine increases, the product distribution changes to resemble that found for molecular bromine and the change in mechanism may be enhanced by the transfer process,



Tanner et al. proposed that with NBS-Br_2 reagent, the cycloalkanes undergo halogenation by utilising the bromine atom chain, while with (NBS-olefin) reagent, the succinimidyl radical is the dominant chain - carrying species. It was proposed that the another factor which affects the chain carrier is the solubility of the reagent. Because of high solubility of the reagent in the solvents methylene chloride and acetonitrile, the concentration of NBS remains high and the succinimidyl chain remains dominant while in solvents where the NBS is insoluble, only the bromine atom chain can proceed since radical transfer with solid NBS is slow. They concluded that " if two states of radical exist, with this system they are chemically indistinguishable or that the system is not as clearly understood as inferred ".

Tanner [32] further re-examined several examples of Skell's " graded series " using his concentrations of reactants and arrived at the following conclusions :

(i) $CHCl_2Br$/BPI ratios in NBS-CH_2Cl_2-CH_2CCl_2 reactions are essentially the same in the presence of 2,3-dimethyl butane, cyclohexene and butadiene as in the presence of neopentane. These are contrary to the results reported by Skell [33] where the ratios reported appear to be the results of faulty analysis

and incorrect identification of products.

(ii) Most of the NBS is actually consumed by reaction with these substrates, and the formation of significant amounts of polybrominated products is consistent with the participation of Br· chains.

(iii) Reactions in the presence of even 2.5 M benzene yielded BPI as well as N- phenylsuccinimide. Polybrominated products are produced, consistent with Br· chains, but the reactions are messy. BPI, polybrominated products and unidentified materials (which make up the majority of the reaction products) were not found previously [33] and constitute the basis for the re - interpretation of the previous postulations.

(iv) The NBS bromination of chloroform in the absence of oxygen gives BPI under all conditions and high yields in the presence of vinylidine chloride, confirming Wallings conclusions [30]. The results are contrary to Skell's previous report [21] and his suggestion that Walling's results were due to the presence of oxygen.

(v) Photolysis of NIS-I_2 in chloroform gives β - iodo propionyl isocyanate as the major product.

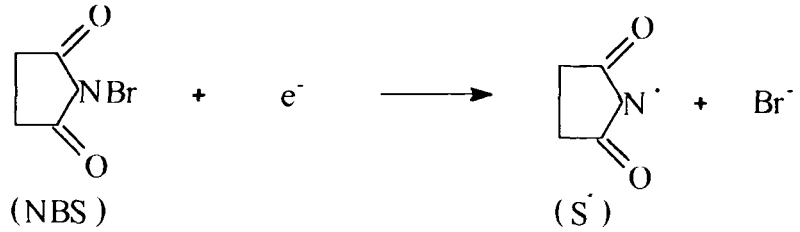
This observation constitutes a new piece of evidence contrary to the formation of π - radical.

(vi) None of the results provided evidence for two states of succinimidyl radical in preference to simple competing S· and Br· chains.

Direct photolysis of NBS in the absence and presence of bromine and its bromine atom initiated decomposition were investigated by Chow et al. [34] by selective irradiation of NBS or Br_2 and by critically examining the BPI yields and the relative selectivity of intermolecular H-abstraction from cyclohexane and dichloromethane. They suggested that photodecomposition of NBS + Br_2 system involves the succinimidyl radical and bromine atom in a fast equilibrium and as the radical - propagating species, without the need to invoke another radical. The succinimidyl radical generated from direct photolysis of NBS is proposed to be a vibrationally excited hot specie which undergoes much faster ring opening than the ground state species.

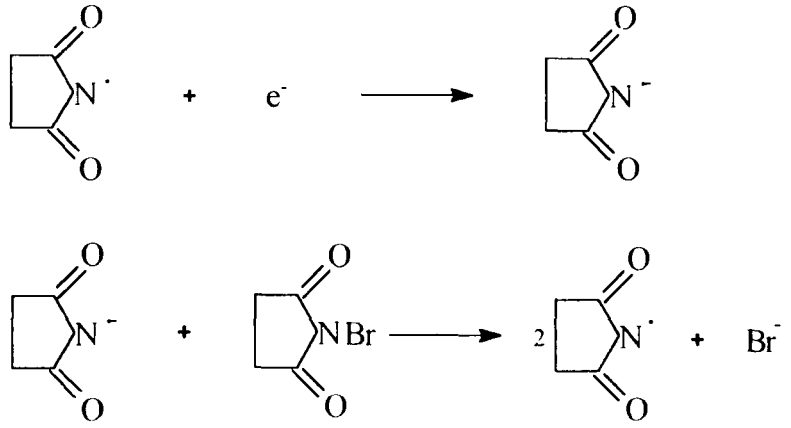
Eberson [35] studied the NBS mechanism and reaction rates by electrochemical reduction. He observed that the electrochemical reduction of NBS in acetonitrile at a platinum cathode generates the succinimidyl radical in an

overall process for which n value is one (n is the number of faradays of charge passed per mole of reaction).

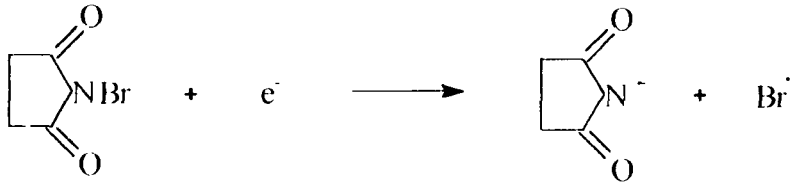


(NBS) (S·)

The succinimidyl anion generated by two electron reduction of NBS is an intermediate in the process and its electron transfer reaction with NBS generates the radical.



Eberson demonstrated the intermediacy of the succinimidyl anion by trapping experiments in which the anion is captured by alkylating agents to give N-alkylsuccinimides. He also suggested that since nitrogen is more electronegative than bromine, reaction shown below represent alternative path for generation of S^-



$$Br^{\cdot} + e^{-} \longrightarrow Br^{-}$$

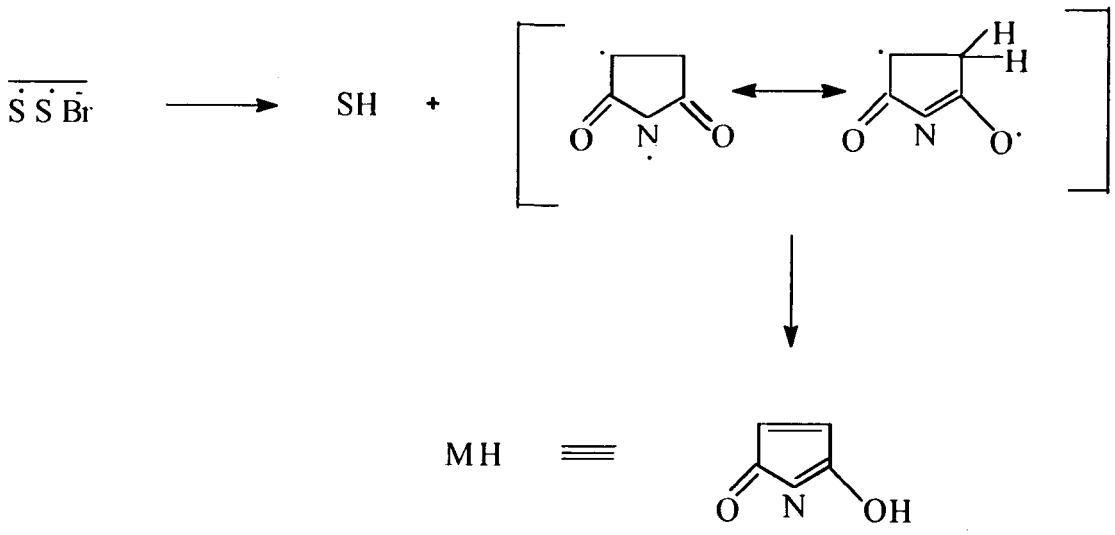
In continuation of this work, Eberson and his co-workers [36] studied the electrochemical reduction of NCS and suggested that the electrochemical reduction of NCS in acetonitrile parallels the reduction of NBS. The succinimidyl anion generated by a two electron reduction of NCS is an intermediate; homogenous electron transfer from the succinimidyl anion to NCS generates the succinimidyl radical which is a precursor for the products formed. The succinimidyl anion can be trapped with methyl tosylate yielding N- Methylsuccinimide but in the absence of the alkylating, agent electron transfer from S^{-} to NCS generates the succinimidyl radical. However, the reduction of NCS by the succinimidyl anion, added as a quaternary ammonium succinimide, in a homogenous chemical system is significantly different from the comparable reaction with NBS.

They proposed that the major products in the reaction of both NBS and NCS are succinimide and low molecular weight succinimide polymer in which the succinimide units are joined by both C - N and C - C linkages. They proposed that $S\cdot$ from SX/S^{-} reaction has the character of $S^{\bullet}_{\pi}$ with its reactions limited to H- abstraction and initiation of

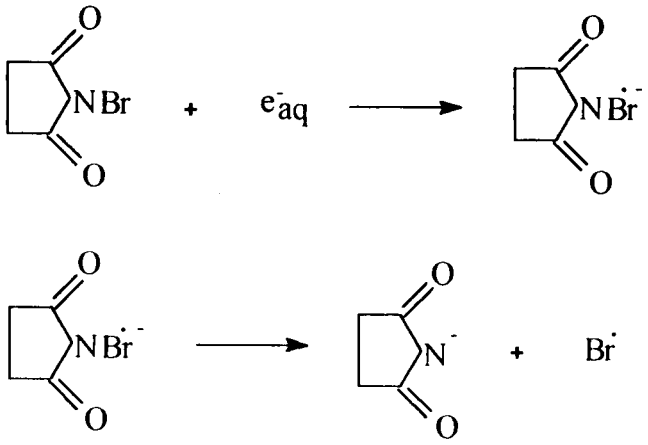
maleimide polymerisation. They did not find any indication of ring opened products, which is a characteristic property of $S^{\bullet}_{\sigma}$.

Eberson et al. [37, 38] further studied the polymal - eimide formation in electron transfer reaction between NBS and succinimidyl anion, which gives predominantly succinimide (SH, ca. 66%) and small percentage (ca.10%) of polymeric material. By NMR spectral comparison with authentic specimens, polymer was shown to be polymaleimide type. The reaction between NCS and S^- also gave polymaleimide (ca. 40%) in addition to SH (ca. 47 %). They proposed that initial electron transfer step between NBS and S^- forms a cage radical anion /radical pair. Nitrogen - bromine bond cleaves within the cage, producing a pair of succinimidyl radicals, $S^{\cdot}$, which reacts with disproportionation to yield succinimide (SH) and maleimide (MH). The latter then undergoes radical polymerisation to give polymaleimide, which is itself a strong indication of electron transfer mechanism.

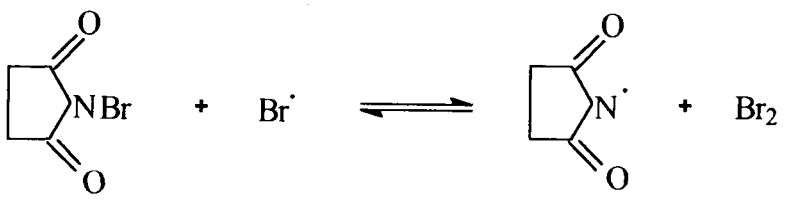
$$S^- + NBS \rightleftharpoons [\, S^-NBS \,] \xrightarrow{ET} \overline{\dot{S}\,\dot{S}\,\bar{B}r}$$



The development of the red-yellow colour as the reaction proceeds is attributed to oligomer formation from polymerisation of MH. In order to further elucidate the mechanism pulse radiolysis study was done by Eberson et al. [39]. One of the major achievement by this study is the fact that $NBS^{\cdot -}$ undergoes cleavage to give S^- and $Br^{\cdot}$. This fragmentation mode is unexpected because the opposite fragmentation into $S^{\cdot}$ and Br^- was taken for granted.



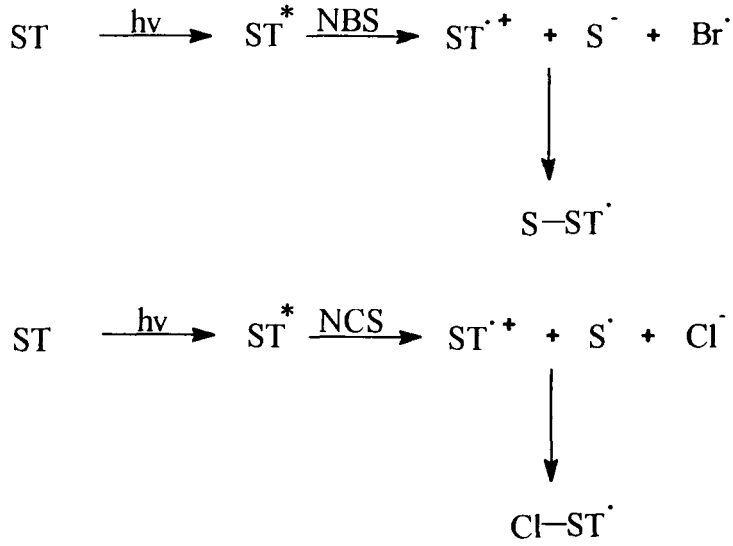
Eberson et al. [40] further studied the reduction of NCS by pulse radiolysis in water. NCS was reduced in a one electron step to yield the succinimidyl radical S·, via the intermediacy of the radical anion NCS $\cdot^{-}$. The rate of ring opening was measured to be 8 x 10^4 s^{-1}. By equilibration with $Cl_2\cdot^{-}/2Cl^{-}$, one electron reduction potential of S· was determined to be 2.22 ± 0.02 V versus NHE. From this value and other data they calculated N - H bond strength in succinimide to be 118 ± 3 K cal/mol. They suggested that the fraction of S· in water might deviate significantly from that in non - hydroxylic solvents due to hydrogen bonding to the N - atom. They further proposed that since the bond dissociation energy, BDE (N - Br) is larger by about 19 K cal/mol than BDE (Br - Br) in molecular bromine, any S· formation via the suggested equilibrium



can safely be ruled out in all chemically realistic situations.

They concluded that the gross properties of S· (such as spectroscopic and thermodynamic) reflect predominant

(more than 99 %) π - state, its reactivity may be that of the lowest excited σ state attenuated by the Boltzmann factor. In order to get more clear information about the radical reaction, Eberson [41] further studied N-halosuccinimide reactions by ESR employing spin trapping. He proposed that photochemically induced formation of succinimidyl spin adducts are most likely formed via the radical cations of the spin traps, formed by reaction between the excited state of spin trap (ST) and the N-halosuccinimide which he called it as " inverted spin trapping " [42].



Eberson proposed that in the case of NBS, it leads directly to $ST^{\cdot+}$ S^- ion pair which collapses to the spin adduct. While in case of NCS, any Cl-ST· formed will react rapidly with SH/S^- formed by further H- abstraction / redox

transformation of S· and thus gives S-ST· adduct. He suggested this mechanism on the basis of the experimental observation that both chloro and succinimidyl spin adducts are detected during the course of photolysis reaction. He also observed total absence of any spin-adduct that can reasonably be assigned to the ring-opened radical from S·, the β - isocyanatocarbonylethyl radical adduct.

Eberson proposed that the photoinduced formation of succinimidyl spin adducts is strongly influenced by the redox properties of the species involved and that the radical cations of spin traps are likely to be involved in most, if not all, succinimidyl spin trapping observed. However, he concluded that " photoinitiated spin trapping will seldom be traceable to an unambiguous mechanism ".

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OBJECTIVE

The recent development of the so called Single Electron Transfer (SET) chemistry is gaining ground very fast. Many organic reactions which were previously classified as polar reactions actually involves radical intermediates formed by a process initiated by SET from the nucleophile to the substrate. Yet despite the growing evidence that SET processes are far more widespread than originally thought, the relationship between SET and polar pathway remain obscure. In inorganic chemistry it is very well accepted and understood that electrons are transferred one at a time. The basic question arises why in some cases electrons should move in pairs and in some cases it should be transferred one at a time. Chemical community seems to be coming around to accept SET pathway as a major one but still some reluctance is there. One of the reason could be that their are not enough reactions with a clear SET mechanism. The other reason could be that their are still some fundamental questions that need to be addressed before SET gains a wider acceptance e.g., (i) What are the factors that determine whether a particular reaction proceeds via SET or a polar pathway ? (ii) What is the precise relationship between the two ? (iii) Do the SET and polar pathways represent discrete route or is there a

mechanistic spectrum bridging these two mechanistic extremes ?. Therefore, one of the objective of the present study would be to answer some of the questions at least to some extent if not in totality.

We feel that in this endeavor ESR spectroscopy (its full potential is yet to be realised) can play an important role. We have made an extensive application of ESR using spin trapping to study the SET aspects of N-Halosuccinimides. The mechanism of N- Halosuccinimide reactions have been the subject of number of investigations however, a definite reaction mechanism could not be established. The controversy over the nature of the chain propagating species have been widely recognised and still continues to attract attention. The areas of disagreement involve both experimental results and their interpreta - tions. Skell et al. claimed two types of succinimidyl (S_σ and S_π) as chain carriers in addition to Br·, in the decomposition of NBS under a wide variety of conditions. He also claimed that ring opened product of succinimidyl radical as one of the intermediate in the reaction. Tanner and co - workers postulated their results as mixed chain reaction of single succinimidyl radical and Br·. Walling et al. initialy recognised the involvement of two radical intermediates along with Br· but recently arrived at same

conclusion as Tanner. All these postulations are mainly derived from end product analysis, kinetic studies, and theoretical considerations.

This work aims to investigate the N- Halosuccinimide chemistry by detecting mainly intermediate species formed during the reaction. It is an attempt to elucidate the mechanism, the effect of environmental factors and of added substances of potential catalytic / inhibitory action on the reaction mechanism. The suggestion that the succini - midyl radical undergoes ring opening is also investigated.

This study is the first of its kind where, nitrones are used in a dual role. The purpose of the nitrone to use for example, as a reductant was to ensure that if at all an electron is donated by it then it will become a cation and the electron captured specie will undergo dissociation and one of the product will be an anion. The probability of anion being trapped by a nitrone cation would be certainly higher then the probability of free radical being trapped by neutral nitrone and thus we may succeed in identifying some of the primary products of ET process. The identifi - cation of primary products always imparts some authenticity to the mechanism, rather than mechanism derived from end products.

CHAPTER III

EXPERIMENTAL

CHEMICALS

All the chemicals used were of the highest available quality. N- Bromosuccinimide (NBS), N- Chlorosuccinimide (NCS), N- Iodosuccinimide (NIS), Succinimide (SH) and N- Methylsuccinimide (NMS) were purchased from Aldrich and were purified by the procedure reported in the literature. NBS, NCS and NIS were stored over calcium chloride in a dessicator with protection from light. Spin traps, PBN and DMPO were obtained from Sigma Chemical Co. and were used as such. Purity was confirmed by recording IR and NMR spectra. All the solvents used in the spectral measurements were of spectrograde quality. For ESR measurements solvents were dried by standard procedures. For UV spectroscopic study, the spectral transmissions of solvents were checked against highly purified water.

UV STUDIES

All UV measurements were carried out with Beckman DU 650 spectrophotometer, resolution 0.1 nm and band width 1 nm. Matched pair of quartz cells with path length 1 cm were used. The wavelength calibration of the instrument was checked against Holmium oxide filter and intensity calibration was checked against standard solution of K_2CrO_4

in 0.1N NaOH. For spectral measurements standard solutions of the order of 10^{-3} M were prepared and necessary dilutions were made. All solutions were prepared only prior to recording the UV spectra.

ESR STUDIES

First derivative ESR measurements were recorded on Varian E- 109, X- band spectrometer, with 100 KHz field modulation. A 9.6 GHz, microwave frequency generator was used. All ESR measurements were made at room temperature (20 $\pm$ 2^{o} C). Field calibration of the ESR Spectrometer was frequently checked with standard samples of di-tert. Butyl nitroxide or standard marker supplied by Varian.

In spectral recording, optimum level of microwave power was used to avoid saturation effect. In some cases where spectral overlapping was intense, spectras were recorded at low microwave power. Optimum modulation level of amplitude was selected to avoid line broadening. In most of the spectra field sweep of $\pm$ 40 G or $\pm$ 80 G was chosen. Some spectra were always recorded at higher field sweep to see any specie with a very different g value. In early stages of the reaction when reactants were just mixed, scanning time employed was low (2 minutes) in order to detect any short lived specie, otherwise it was 4 - 8

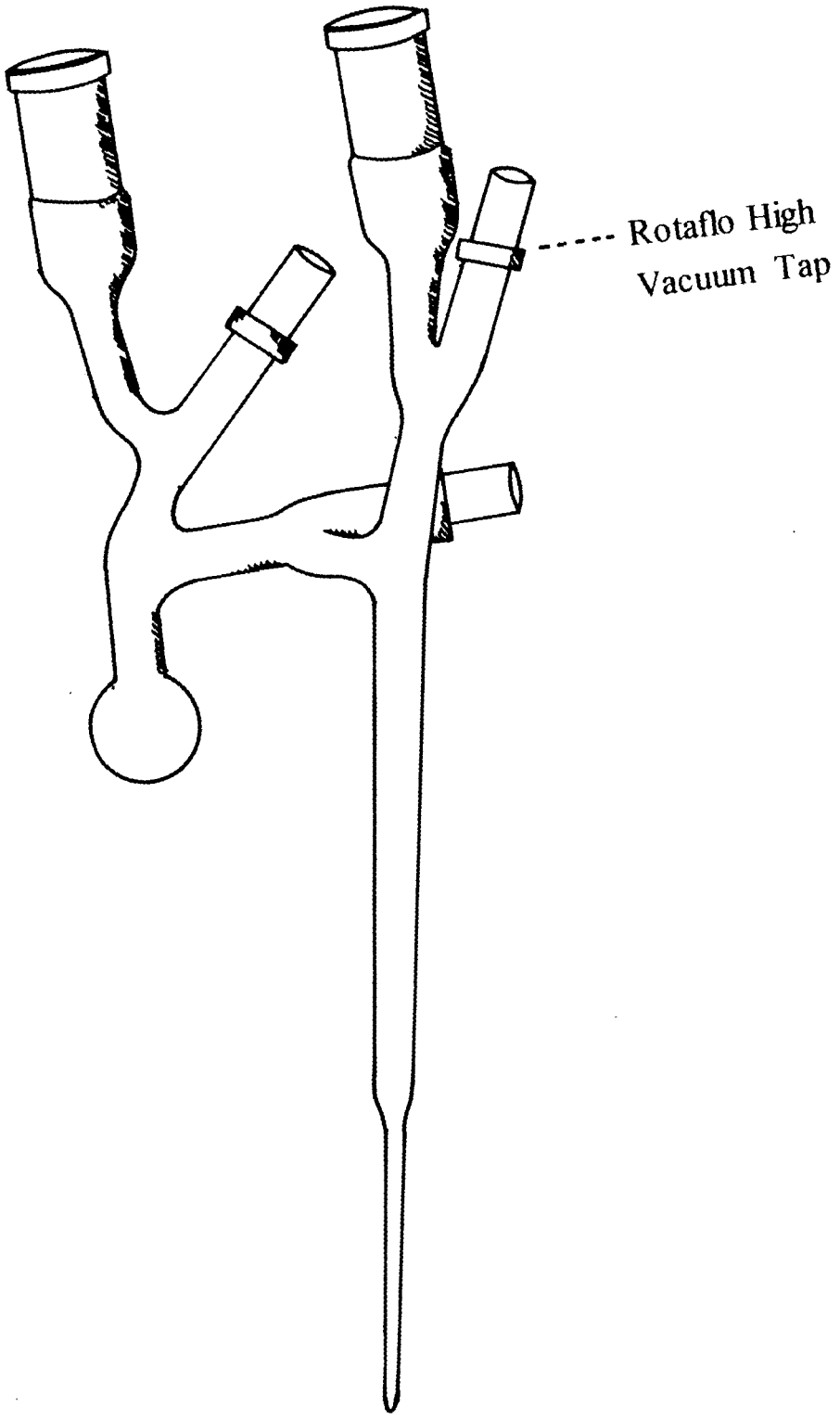
minutes. In spectra where secondary or tertiary hyperfine splittings was very low, a component of the spectra was scanned at a small field range with slow scan speed. A best combination of receiver gain and time constant was chosen to achieve good signal to noise ratio.

Solvents with low dielectric constant were preferred, unless required to study the higher dielectric effect on the reaction mechanism. The total volume in the cell was ca. 0.5 ml. All hyperfine measurements reported are an average of more than one set of values and their accuracy are within the range of $\pm$ 0.2 G. g values were calculated with respect to DPPH (α , α - diphenyl- β - picrylhydrazyl) as standard marker and the accuracy is within $\pm$ 0.0003.

EXPERIMENTAL DETAILS

All the ESR experiments were carried out in a specially designed cell of Quartz, as shown in Fig. 3. All reacting solutions were thoroughly degassed by repeated freeze and thaw cycle to a vacuum of 0.02 Torr. Photolysis experiments were carried out in situ with medium pressure mercury lamp. The beam was focussed on the sample by the help of a Pyrex convex lense with a cut off of 280 nm. Scanning was continuous and started immediately on mixing degassed solutions. The concentration of the substrates

Fig. 3



ESR CELL

were of the order of ca. 10^{-3} molar. Different batches of spin traps were used and the results were essentially same. Low concentrations of the spin traps and substrates were used to minimise the participation of secondary reactions. After mixing, the cell was left in the cavity of the spectrometer to avoid accidental exposure to stray light. In some cases spectra were recorded even after 24 hours to see the growth of any specie which could be helpful in interpreting the mechanism. All experimental observations reported are fully reproducible.

COMPUTER SIMULATION

All the spectral assignments were confirmed by simulating the spectra using the parameters obtained from the experimental spectra, by an in house developed simulation programme. The programme is given in the appendix.

CHAPTER IV

RESULTS & DISCUSSION

N - CHLOROSUCCINIMIDE

This work is an attempt to study the Single Electron Transfer (SET) reactions involving N- Chlorosuccinimides. These are strong electron acceptor (very low redox potential) because of the presence of halogen atoms and electronegative succinimidyl ring. Their electron captured dissociative mechanism involving ions and / or free radicals have been studied. The effect of environmental factors e.g., different solvents, polar, apolar and hydroxylic and of added substrates of potential catalytic and / or inhibitory action, on the reaction mechanism is also explored.

All SET reactions were carried out under mild conditions and external source was used only when needed to promote electron transfer. In this study nitrone (N-tert. butyl α - phenyl nitrone; PBN) is used in a dual role as an oxidant / reductant and a spin trap under various conditions. The role of nitrone as a spin trap is well established and documented. However, it is not established whether it is relatively an efficient donor or acceptor. Therefore, we set out to establish this property. Acids are well known powerful electron acceptor while bases are powerful electron donors. When nitrone solution in water was mixed with varying concentrations of HCl in water Fig. 4, a sharp isosbestic point at 265 nm was observed.

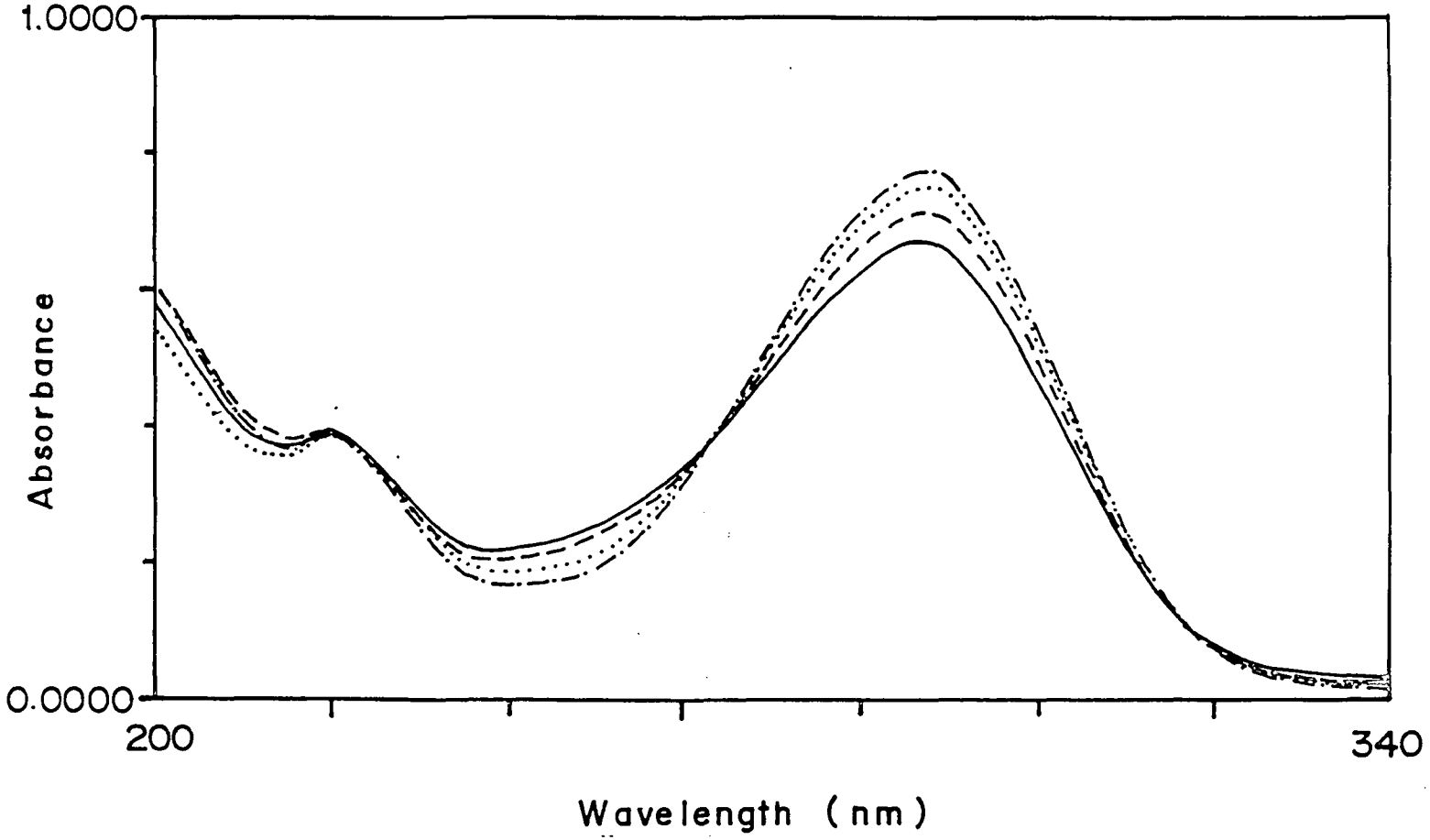


Fig. 4 : UV spectra of PBN (10^{-5} M) with different concentrations of HCl (0.002 M) —·—·—; PBN alone ; ····, PBN : HCl (I:I) ; - - - -, I:II ; ——, I:IV

This indicate that a charge transfer (CT) complex is formed between HCl and PBN. Similarly, when PBN solution in water was mixed with varying concentrations of NaOH in water Fig. 4.1, no such isosbestic point is observed indicating clearly that no charge transfer complex is formed. This establishes that certainly PBN is a better electron donor then acceptor.

As discussed earlier, for an electron transfer to take place two criteria must be met :

(i) Thermodynamic requirement must be met. The redox potential of the donor must be high as compared to that of the acceptor.

(ii) Donor and acceptor must form some sort of charge transfer complexes as these are precursor to the electron transfer processes. The ionisation potential of the donor must be low and electron affinity of the acceptor must be high.

CT complexes should involve single equilibria, otherwise multi equilibria complicate mechanistic interpretation. Therefore, it became imperative for us to look first into the possibility of CT complex formation. Though, number of techniques are known but we have used UV spectroscopy.

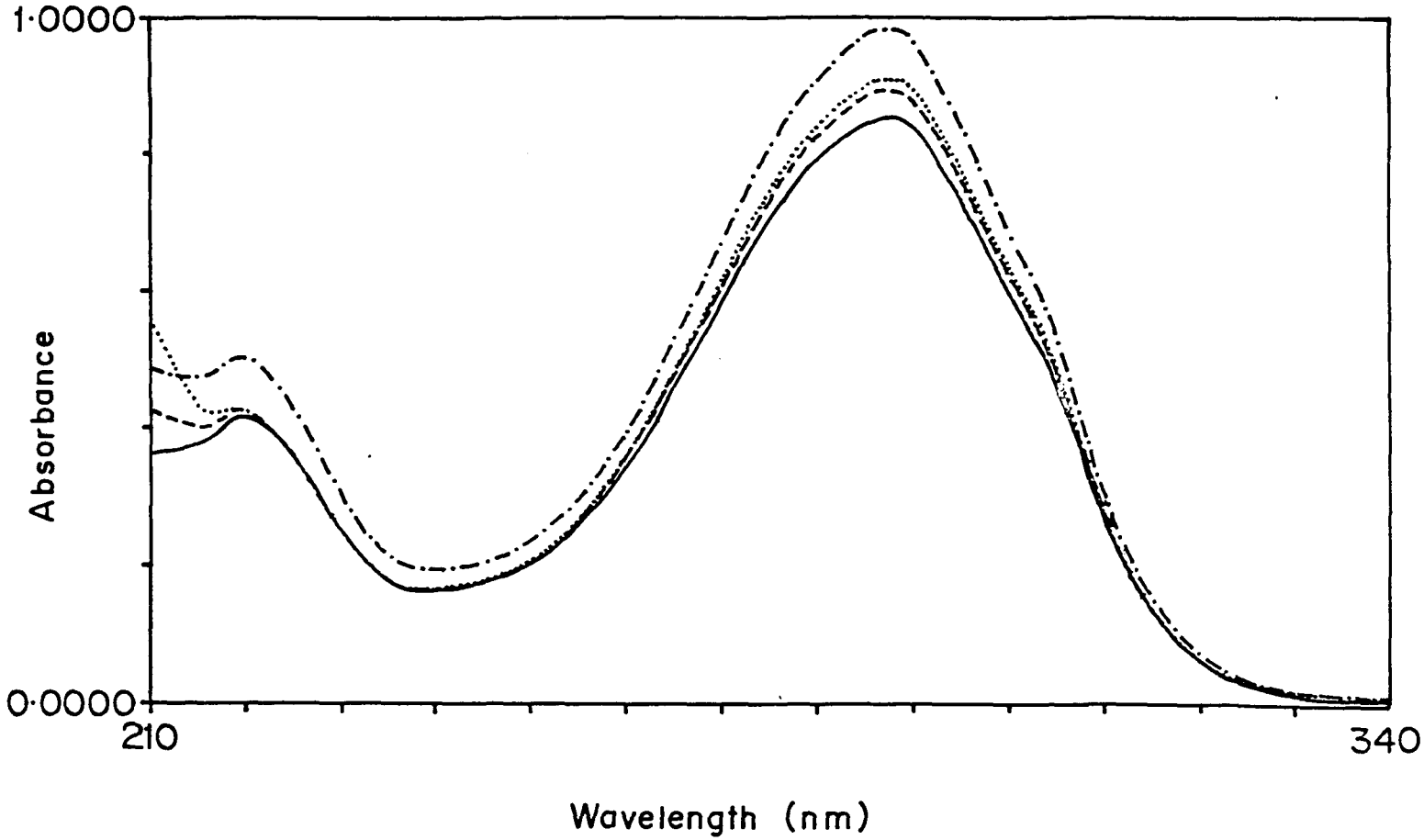


Fig. 4.1 : UV spectra of PBN (10^{-5}) with different concentrations of NaOH (0.002 M) -·-·-, PBN alone; ·····, PBN : NaOH (I:I) : ----, I:II ; ——, I:IV

N- Chlorosuccinimide (NCS) and PBN system

UV STUDY

In our system there are only two components, nitrone (PBN) as an electron donor and NCS as electron acceptor. As a representative plot Fig. 4.2 shows the UV spectra of the mixtures of NCS and PBN in 1,4- Dioxan in different relative proportions. A clear and fairly sharp isosbestic point is observed at 259 nm which does not shift with the change in the relative concentration of the constituents, indicating the presence of a single equilibrium. Similar isosbestic points were observed in other solvents also. Thus CT complex is formed suggesting the feasibility of SET reaction between NCS and PBN. The results of ESR studies are described below.

ESR STUDY

All the experiments were essentially carried out under oxygen free environment as oxygen being : (i) powerful oxidising agent (ii) capable of forming CT complexes (iii) paramagnetic and (iv) high reactivity towards free radicals etc., it can influence the reaction mechanism significantly.

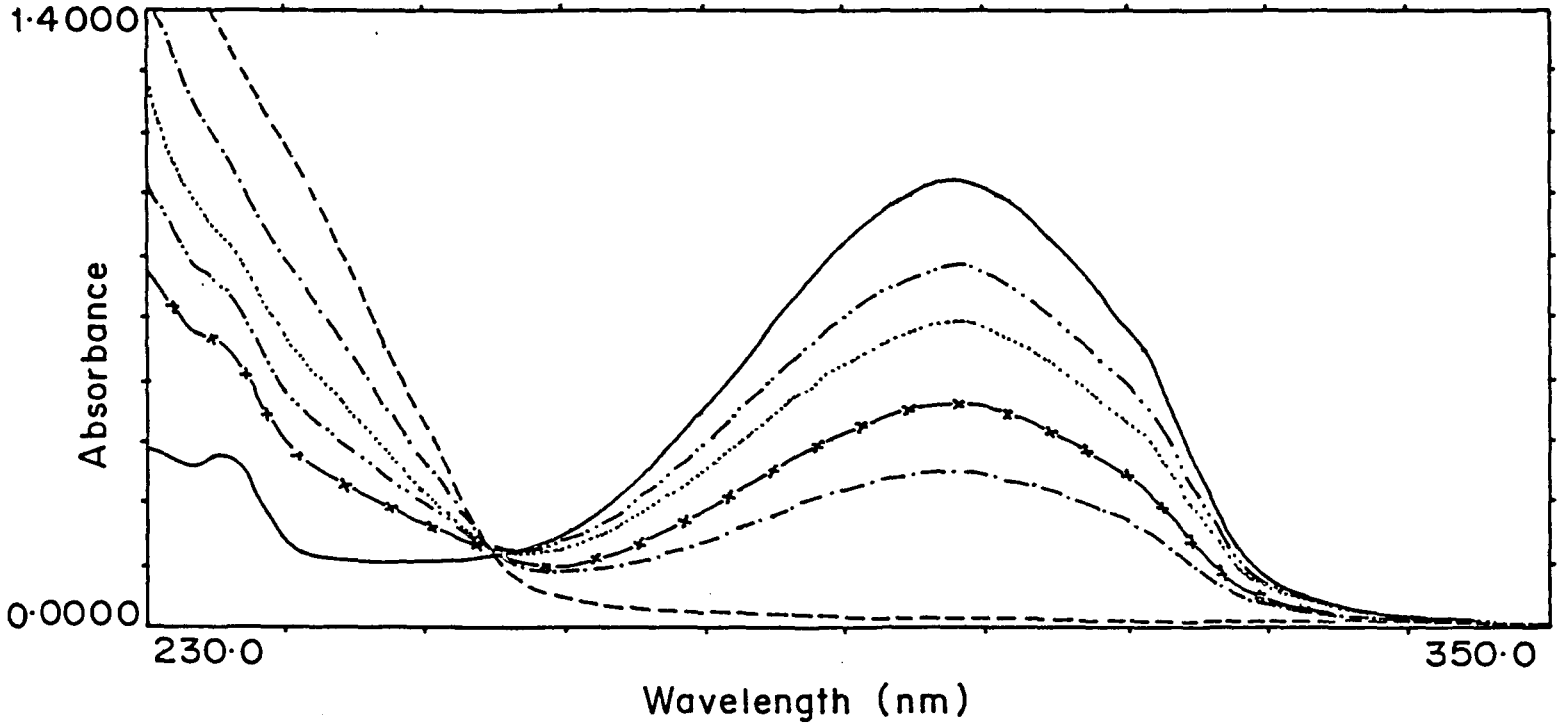


Fig. 4.2 : UV spectra of PBN and NCS in 1,4 - Dioxan

——, PBN alone (6.14×10^{-5}) ;

– – –, NCS alone (6.14×10^{-5}) ;

—·—·, NCS & PBN in I:I ; ·····, I:II ; —x—x—, II:I ;

—··—··, I:III

N- Chlorosuccinimide and Nitrone in Benzene

On mixing degassed solutions of NCS and PBN (1:1) in benzene, the spectra Fig. 4.3 was observed immediately and consists of two spin adducts, say A and B. The adduct A, showed a set of eight overlapping quartets with intensity ratio 1 : 1 : 2 : 2 : 2 : 2 : 1 : 1. The observed spectra can be analysed as follows : The primary nitrogen (^{14}N) splits into a triplet of intensity ratio 1 : 1 : 1 with 12.60 G splitting. Each of these lines splits into a quartet suggesting interaction with a nuclei of spin I = 3/2 where some of the components overlap resulting in a spectra of eight set of signals. There are clearly two set of eight line spectra, suggesting the presence of two isotopes in different isotopic abundance. The intensity ratio is 3 : 1. The hyperfine coupling for the larger set of signals is 6.20 G and for the smaller one is 5.12 G. The evidence for the chloro adduct is clear because the ratio of the splitting constants agrees with the ratio of their magnetic moments : ($\mu\ ^{35}Cl = 1.061$, $\mu\ ^{37}Cl = 0.883$) and even the intensity ratio agrees with their isotopic abundances (75 % and 25 % respectively). Each of these line further splits up into a doublet with a splitting of 0.75 G, showing the presence of hydrogen atom in the adduct. The g value calculated is 2.0074. The splitting

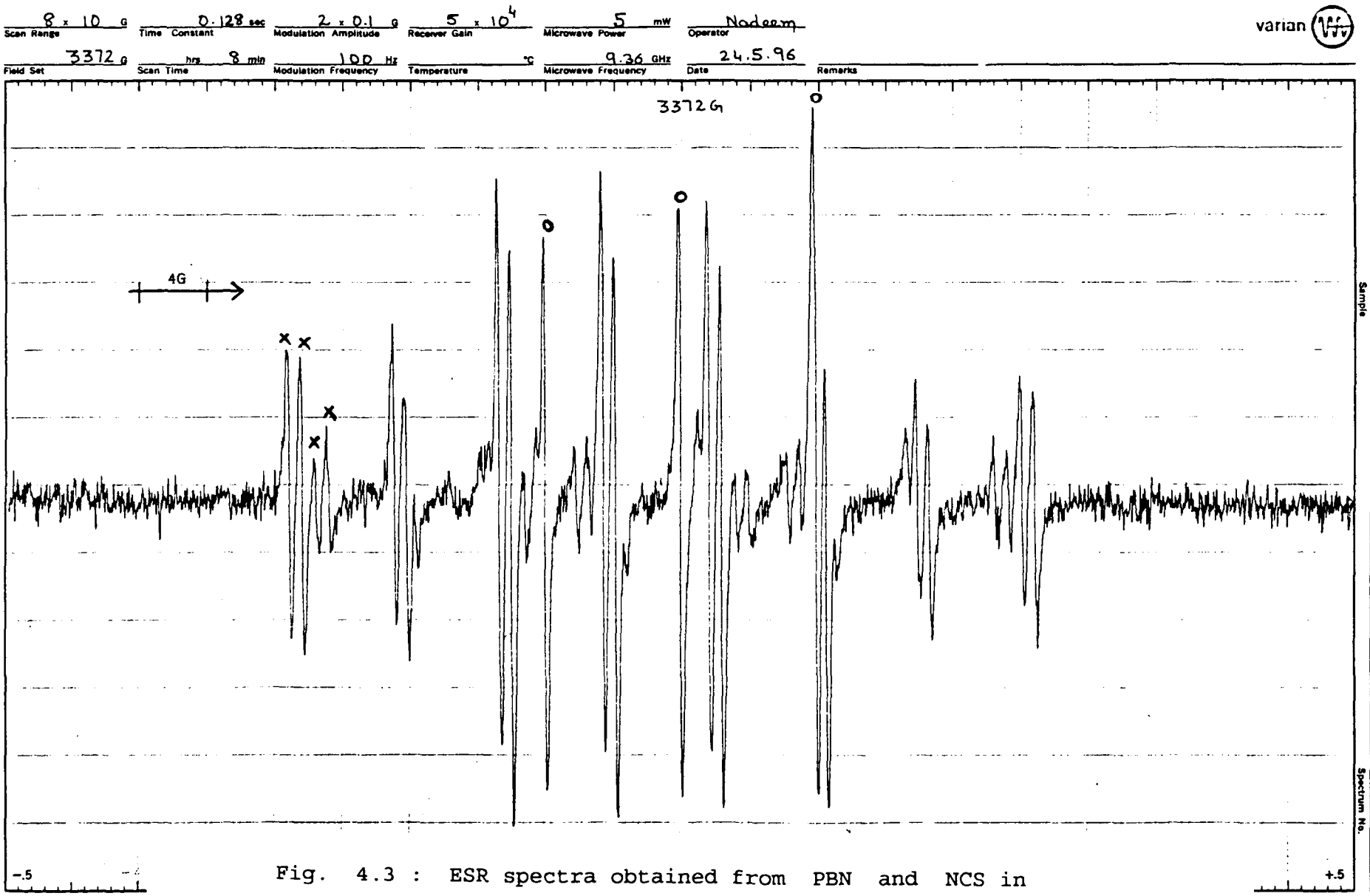


Fig. 4.3 : ESR spectra obtained from PBN and NCS in benzene. × , Cl-PBN· adduct ; o , PBNOX.

pattern and the hyperfine couplings suggest that it is a chloro adduct of PBN (Cl-PBN·). The simulated spectra Fig. 4.4 matches with the experimental spectra. The hyperfine values measured for Cl-PBN· adduct agrees well with those reported [1]. The spin adduct B, showed only a triplet (3 x 1), suggesting splitting from only one ^{14}N atom with hyperfine splitting, a_N = 8.00 G and g = 2.0066. This range of hyperfine splittings are typical for acyl nitroxide type of radicals. We therefore, assign the adduct to benzoyl tert.-butyl nitroxide radical $C_6H_5CON(O\cdot)Bu^t$, (commonly denoted as PBNOX). The measured hyperfine parameters agrees with the reported value [2]. The reaction was monitored continuously. The signal corresponding to chloro adduct disappeared in ca. 30 minutes while a continuous increase in intensity of PBNOX was observed and was the only signal left after ca. 30 minutes of the reaction. However, another triplet (3 x 1) with larger nitrogen hyperfine splitting a_N = 15.62 G, g = 2.0058, was observed after few hours along with PBNOX and is assigned to di- tert. butyl nitroxide (DTBN) [$(Bu^t)_2NO\cdot$] [3]. It could be recorded with ^{13}C satellite lines with hyperfine splitting of $a^{13}C$ = 4.12 G. DTBN was the only signal left after ca. 24 hours of the reaction.

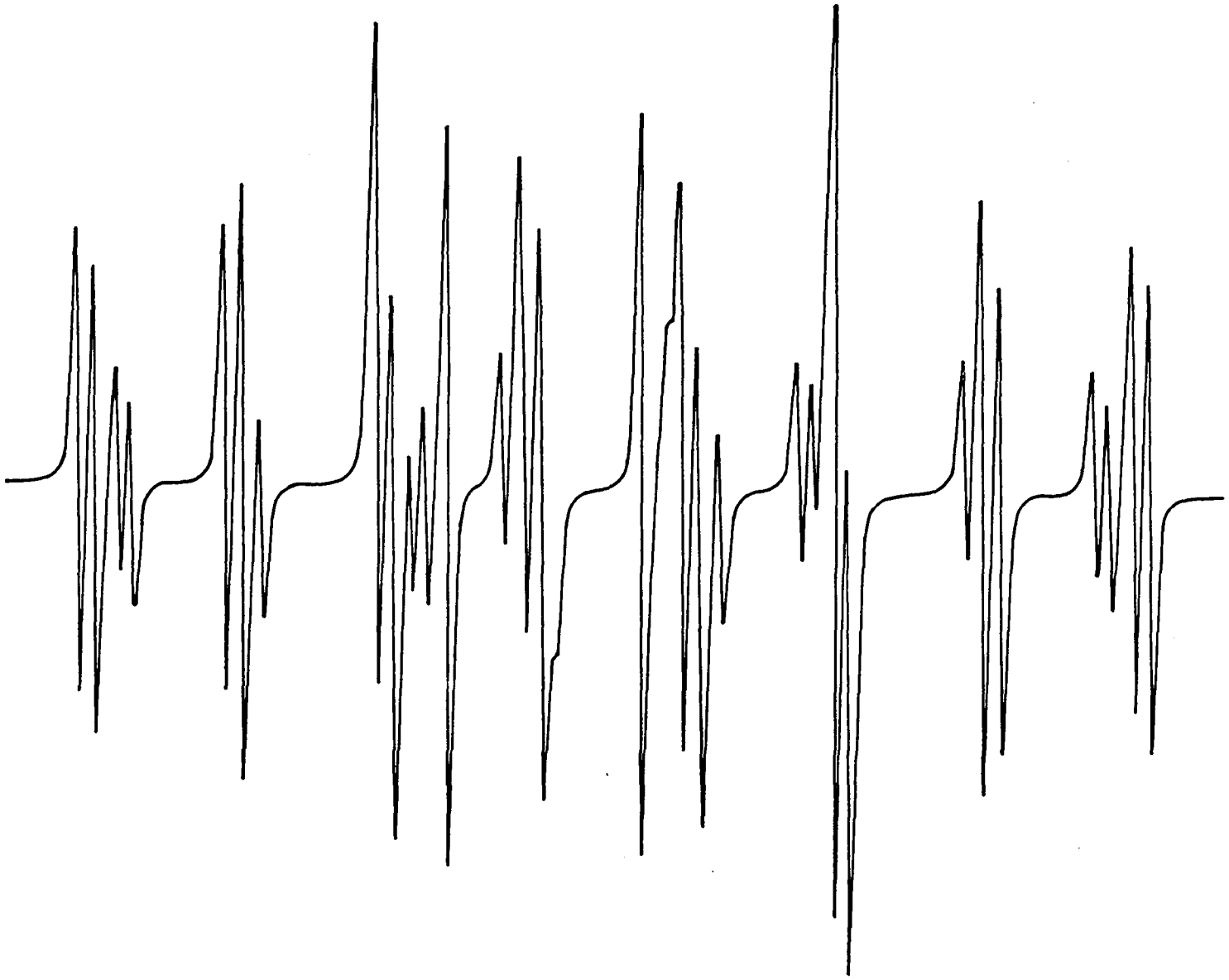


Fig. 4.4 : Computer simulated spectra of 4.3. Cl-PBN·adduct

L.W = 0.35 ; PBNOX L.W = 0.48, ΔG = 1.2.

Series of experiments were carried out at varying concentration ratios of substrate to spin trap. Reactions carried out at concentration of NCS to PBN (2:1),were marked by signals corresponding to chloro adduct and PBNOX. Reactions performed at other higher concentration ratios of NCS yielded similar results. Reactions performed at concentration 2 : 1 PBN to NCS, weak signals of chloro adduct along with PBNOX were observed initially. Another weak signal developed after ca. one hour of the reaction due to some other specie, let us call it adduct " C ". However, in reaction of PBN to NCS (4 : 1), the immediate spectra observed corresponds to PBNOX. After ca. 40 minutes another spectra identical to " C " developed along with PBNOX. However, the spectra was overlapped by intense signals of PBNOX. The adduct " C " could be observed only at high gain of the instrument as shown in Fig. 4.5.

The spectra could be analysed as : A primary splitting due to nitrogen (hyperfine splitting a^{14}_{N} = 14.43 G) into a triplet of intensity ratio 1 : 1 : 1, then each line of this triplet splits into a doublet (a^{β}_{H} = 6.15 G) because of β -H, each of these lines again splits up into a triplet of intensity ratio 1 : 1 : 1 ($a^{14}_{N'}$ = 1.00 G). This splitting pattern suggests that some nitrogen centered radical has been trapped by PBN. The spectra appears to

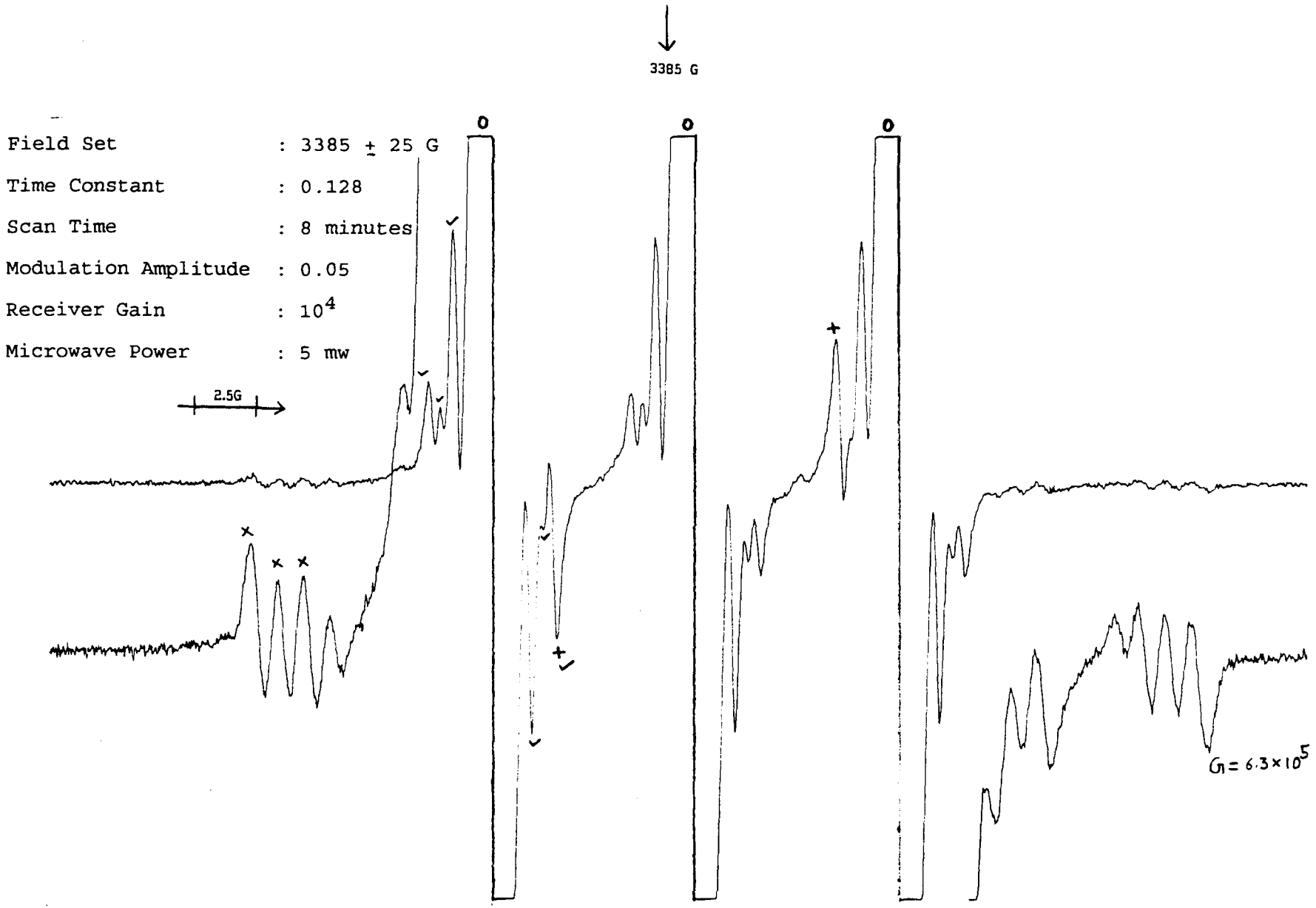


Fig. 4.5 : ESR spectra obtained in benzene at high concentration of PBN. x , S-PBN· ; o , PBNOX. ✓, ^{13}C ; + , ^{15}N isotope splitting from PBNOX.

be succinimidyl radical (S·) adduct of nitrone (PBN), S-PBN·. Literature survey revealed that succinimidyl adduct of PBN has similar couplings and splitting pattern as observed by us [4]. Therefore, our preliminary assignment seems to be correct. Triplets of DTBN were observed along with PBNOX after ca. 6 hours of the reaction. However, DTBN was the only signal left at the end of the reaction. In reactions where PBNOX signals were intense, it was accompanied by another set of triplet of doublets (3 x 2) with hyperfine splittings a_N = 13.12 G, a^{β}_{H} = 1.50 G. This is a characteristic splitting arising from the interaction of one nitrogen and one hydrogen atom. We tentatively assign it to benzoyloxyl radical adduct of nitrone (C_6H_5COO-PBN·) [5].

In order to confirm our assignment, blank experiments were carried out. Dibenzoylperoxide being a well known source of benzoyloxyl radicals [6], reactions were carried out between PBN and dibenzoylperoxide. On mixing degassed solutions of PBN and traces of dibenzoyl peroxide, the spectra Fig. 4.6 with hyperfine splittings : a_N = 13.12 G and a^{β}_{H} = 1.50 G was observed. These hyperfine parameters are in agreement with our assignment of benzoyloxyl radical adduct of PBN.

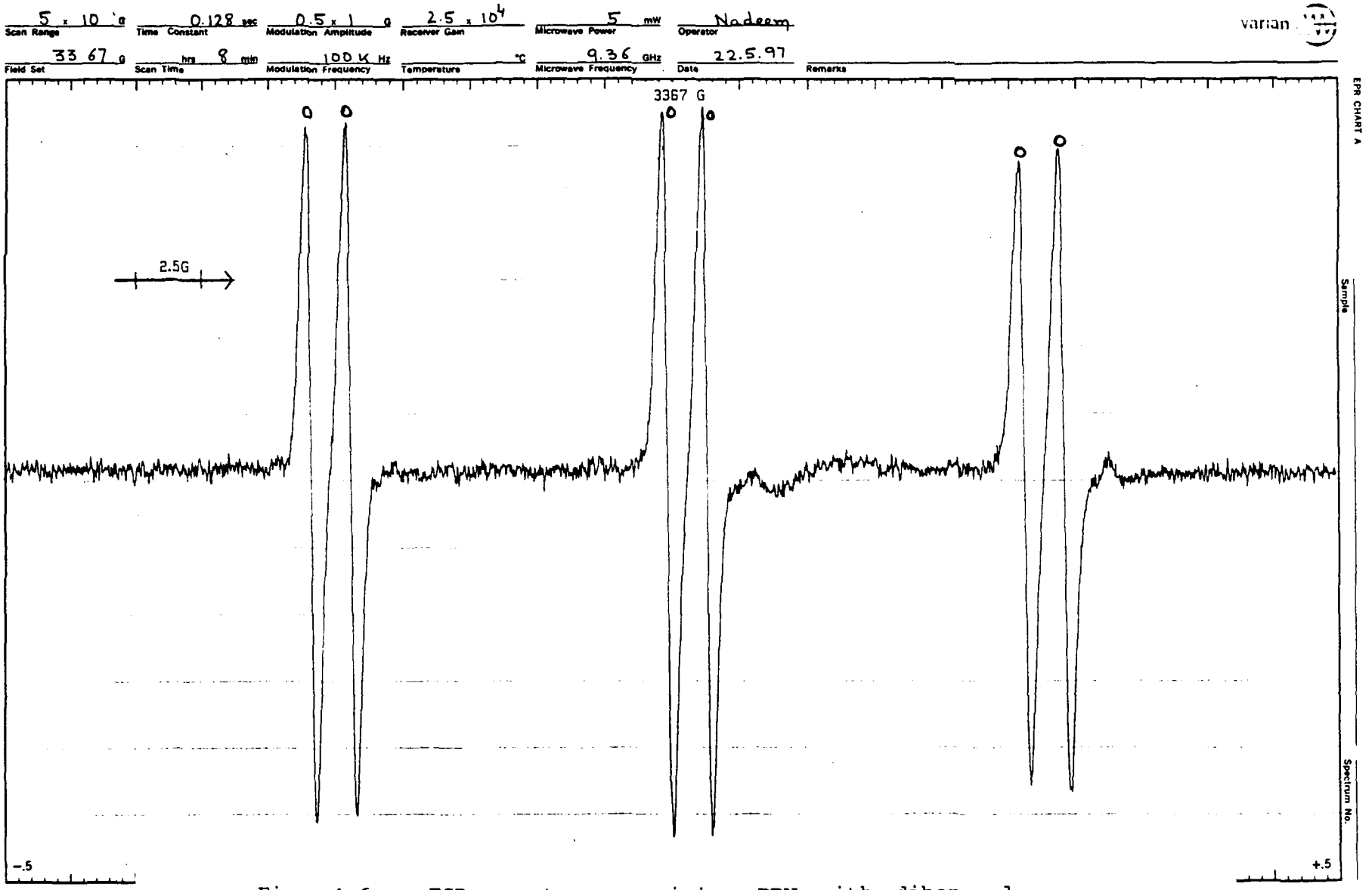
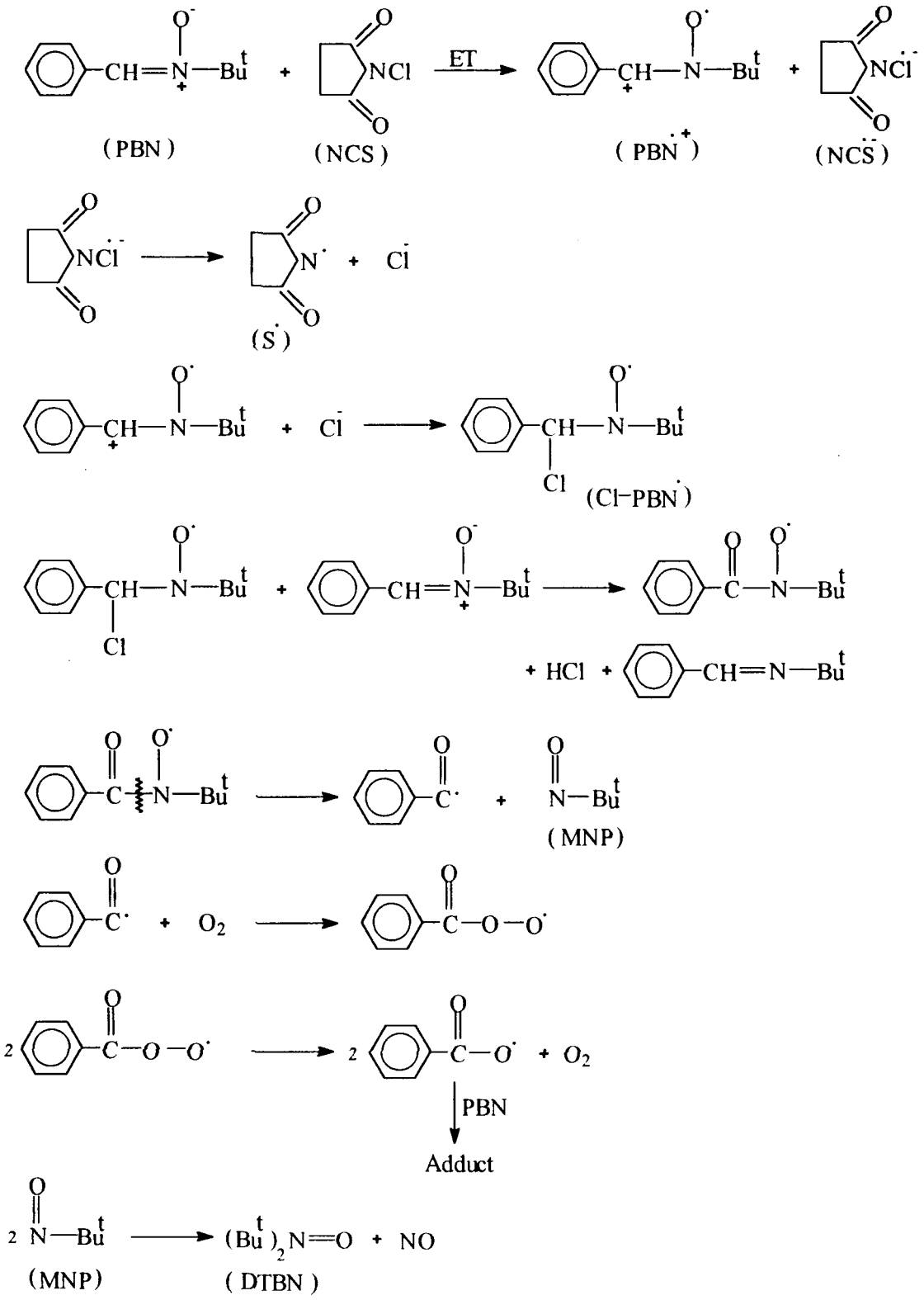


Fig. 4.6 : ESR spectra on mixing PBN with dibenzoyl peroxide in benzene. o , C_6H_5COO-PBN· adduct.

On the basis of experimental results and redox properties of substrates (E^{O} PBN = 1.5 V and E^{O} NCS = 0.3 V) [7], we propose the mechanism shown in Scheme 4. The reaction is initiated in all probability by an electron transfer from nitrone (PBN) to NCS resulting in the formation of nitrone cation ($PBN^{\cdot +}$) and NCS radical anion ($NCS^{\cdot -}$). $NCS^{\cdot -}$ dissociates to give succinimidyl radical ($S^{\cdot}$) and corresponding chloride ions (Cl^{-}). This postulation is also in conformity with the electronegativity difference between nitrogen and chlorine (3.0 versus 3.2) [8]. We suggest that chloro adduct of PBN (Cl-$PBN^{\cdot}$) is formed by the reaction of $PBN^{\cdot +}$ and Cl^{-} (inverted spin trapping). In reactions where the concentration of NCS was either comparable or higher to PBN, the spectra was dominated by the Cl-$PBN^{\cdot}$ adduct along with PBNOX while in reactions where the concentration of NCS was lower than that of PBN, PBNOX was the major specie observed.

We propose that in reactions carried out at higher concentration ratios of PBN to NCS, some of the neutral PBN is still left in the system. The stoichiometry of the reaction is 1 : 1 which means that comparable concentration of PBN is used with NCS in electron transfer processes and some of the neutral molecule of PBN are still available to

Scheme 4



trap succinimidyl free radicals and are detected only when its concentration reaches the ESR detection limit. Formation of di-tert. butyl nitroxide (DTBN) in later stages of the reactions may be due to the β -cleavage of PBNOX to give tert. nitroso butane (MNP) which is well known to produce DTBN as shown in Scheme 4. However, formation of MNP from β - cleavage of chloro adduct of PBN cannot be ruled out. We propose that benzoyl radicals formed by β - cleavage of PBNOX reacts with traces of oxygen giving benzoyl peroxyl radicals. This undergoes bimolecular reaction yielding benzoyloxyl radicals which is subsequently trapped by PBN giving benzoyloxyl radical adduct as shown in Scheme 4.

As mentioned above, oxygen sometime plays a critical role through number of ways in influencing the reaction mechanism. This work was repeated in presence of oxygen (i.e without degassing). The sequence of the spectra observed was Cl-PBN· adduct followed by PBNOX. However, well resolved splitting of the chlorine isotopes were not observed due to extensive line broadening. No substantial change in the intensity of the PBNOX was observed. This indicate that oxygen has either very little or no effect on the electron transfer process atleast in this system. This also establishes that the origin of PBNOX is not due to

oxidation by oxygen. Several paths have been proposed for the transformation of chloro adduct of PBN to PBNOX [9]. The mechanism proposed by Janzen [9] seems satisfactory and is shown in scheme 4.

In sets where PBNOX concentration was high, signals due to ^{13}C and ^{15}N isotopes could be recorded Fig. 4.7. The hyperfine splittings measured from the observed spectra are ; a^{14}_{N} = 8.00 G, a^{α}_{13-C} = 4.80 G, a^{β}_{13-C} = 3.87 G, a^{γ}_{13-C} = 2.75 G and a^{15}_{N} = 11.25 G. The simulated spectra Fig. 4.8 agrees with the experimental one. To the best of our knowledge it is the first such spectra of PBNOX where the satellite signals from ^{13}C in all the different positions are clearly revealed. Such examples are rare for conformational studies with the help of ESR spectroscopy.

The stability of a spin adduct will be higher where the delocalisation of the unpaired electron density is extensive over the molecular frame work. Hydrogen bonding, charge transfer complex formation etc., are such possible paths. With this idea in mind we added traces of N-methylsuccinimide to the system, no new adduct was observed but there was a dramatic increase in the stability of the Cl-PBN· adduct and was stable upto ca. 3 - 4 hours. Similar results were obtained on addition of succinimide in the system.

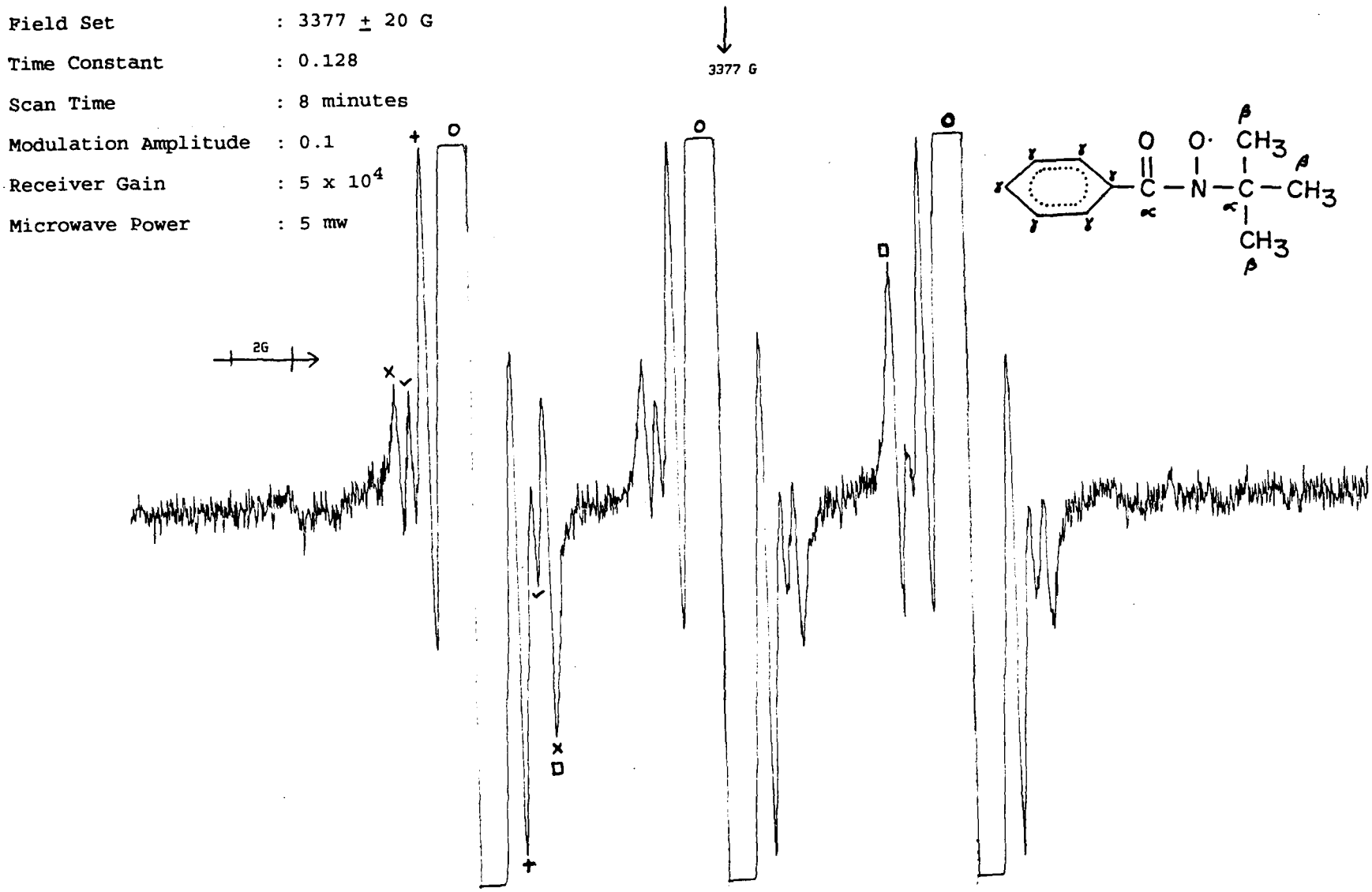


Fig. 4.7 : ESR spectra of PBNOX obtained in benzene.

O , PBNOX ; X , α - ^{13}C ; ✓ , β - ^{13}C ;

+ , γ - ^{13}C ; D - ^{15}N

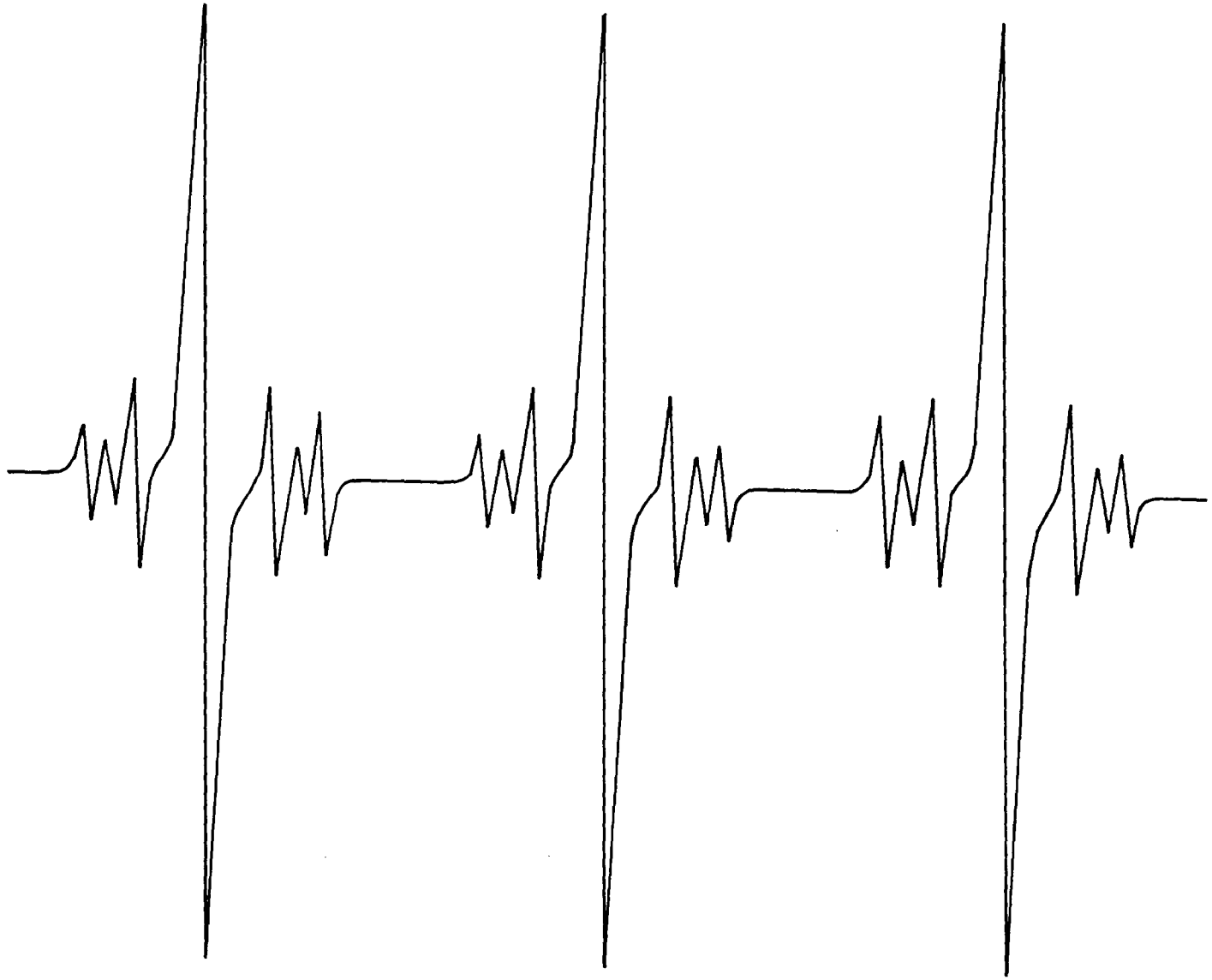


Fig. 4.8 : Computer simulation of 4.7 using hyperfine parameters calculated from experimental spectra. PBNOX L.W = 0.4 and ^{13}C L.W = 0.2, $\Delta G = 0$

Thus, we attribute the stability of Cl-PBN· adduct as probably due to the formation of some charge transfer type of bonding between the unpaired electron on oxygen of the spin adduct with nitrogen of the N- methyl or N- H group of succinimides. If this is really feasible, then the unpaired electron has got two N-O type of bonds and delocalisation becomes more effective. This is the most plausible explanation we can suggest for such phenomenon. To the best of our knowledge this is the first such example. We feel that this idea could be used for increasing the stability of the spin adducts in other systems too.

The other mode to enhance stability, is to vary the structure of the spin traps itself because the stability of the spin adducts not only depends on the radical structure but also on the spin trap used. Hence, reactions were carried out with 5,5 - Dimethyl- 1 - Pyrroline N- Oxide (DMPO), a cyclic and quite effective spin trap.

The immediate spectra observed when the reactions were carried out at concentration 1 : 1, showed unstable and weak signals which could not be analysed. At concentration of NCS to DMPO 2 : 1, signals with poorly defined features were obtained prior to loss of signal. Reactions carried out at concentration of NCS to DMPO (1 : 2),

yielded similar results. However, reactions carried out at concentration ratio of NCS to DMPO 1 : 3, two set of signals say " A " and " B " (very low intensity) were observed initially. Over a period of ca. 30 minutes signal " A " grew in intensity while " B " disappeared. Signal " A " consists of lines of splitting pattern 3 x 3 x 2 (similar to S-PBN·), a characteristic spectra of some nitrogen centered radical adduct of DMPO Fig. 4.9. The hyperfine splittings measured are a_N = 14.00 G, a^{β}_{H} = 20.30 G and $a_{N'}$ = 2.01 G (from succinimidyl nitrogen). On this basis signal " A " is assigned to succinimidyl adduct of DMPO (S - DMPO·). The simulated spectra Fig. 4.10 is in good agreement with the experimental spectra. The hyperfine splittings are in agreement with those reported for tetramethylsuccinimide adduct of DMPO [10]. This adduct decayed in ca. one hour. However, when the reaction was carried out at concentration of NCS to DMPO (1 : 5), the succinimidyl radical adduct of DMPO (S-DMPO·) was quickly replaced ca. 20 minutes, by another set of septet signals with intensity ratio 1 : 2 : 2 : 2 : 2 : 2 : 1 as shown in Fig. 4.11. This is a characteristic spectra arising due to interaction of an unpaired electron with one nitrogen and two equivalent H- atoms of the adduct where some of the inner components overlap resulting in a septet. The hyperfine splittings measured are ; a_N =

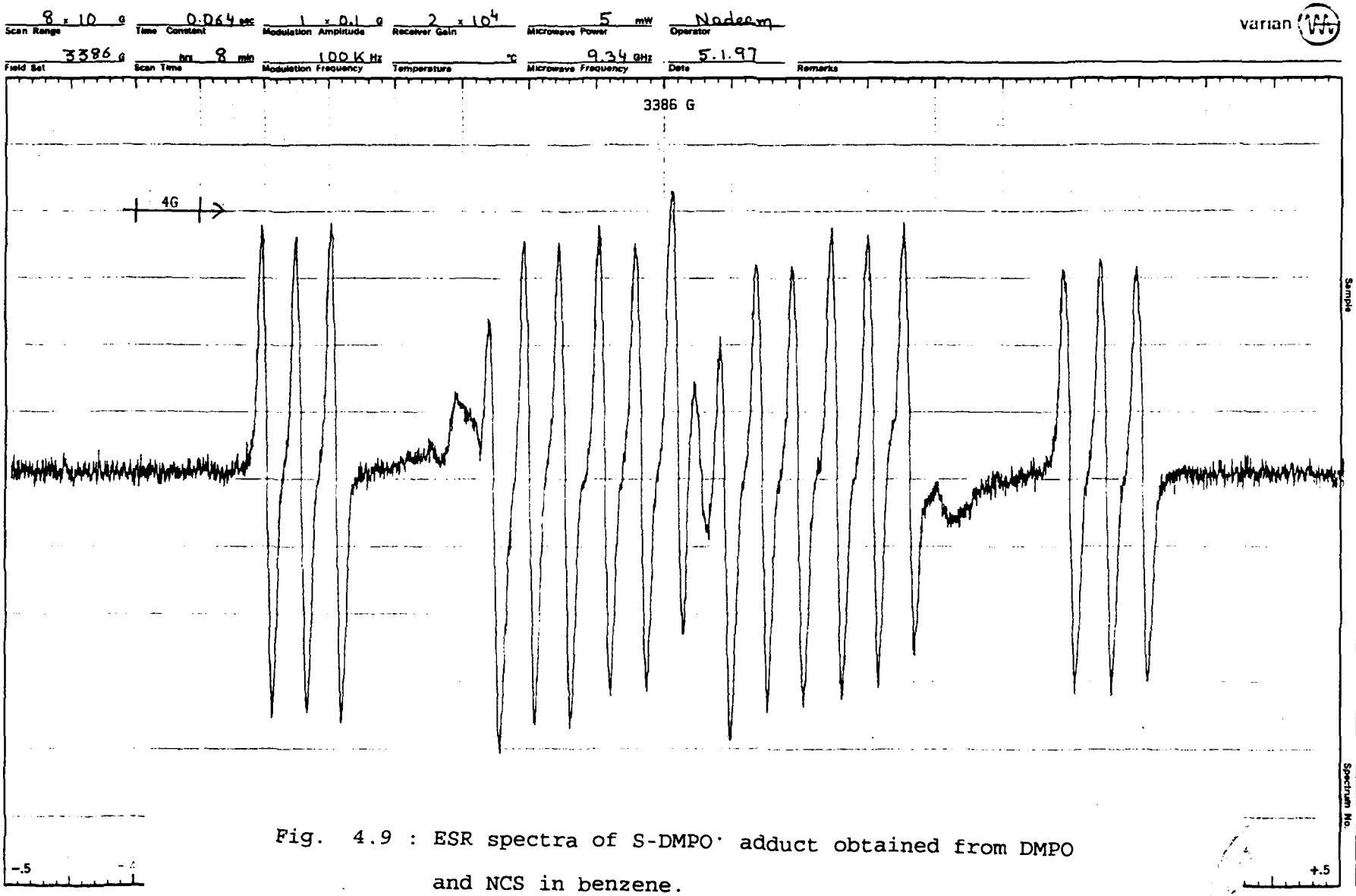


Fig. 4.9 : ESR spectra of S-DMPO· adduct obtained from DMPO and NCS in benzene.

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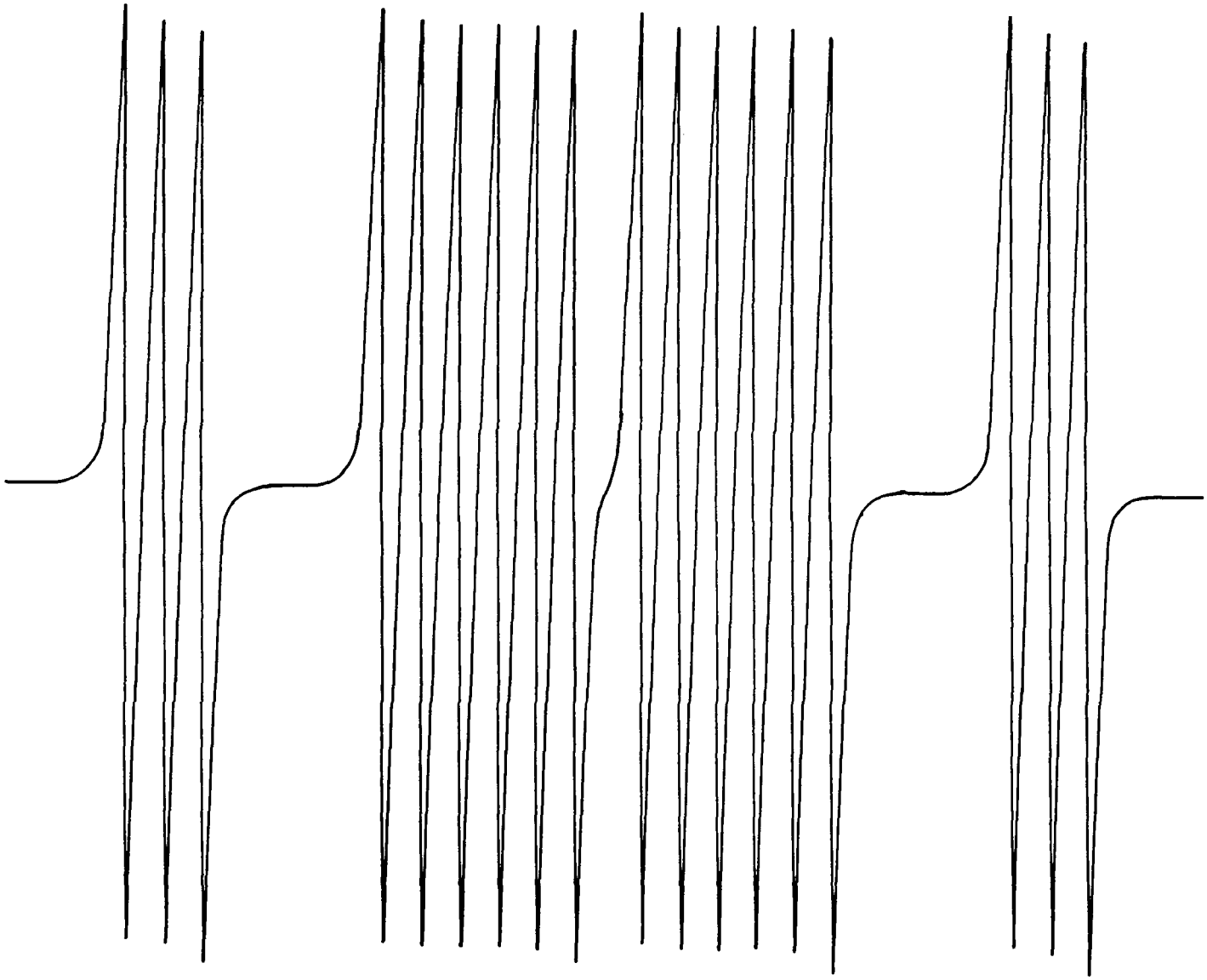


Fig. 4.10 : Computer simulation of 4.9 using hyperfine parameters calculated from the experimental spectra. L.W = 0.8.

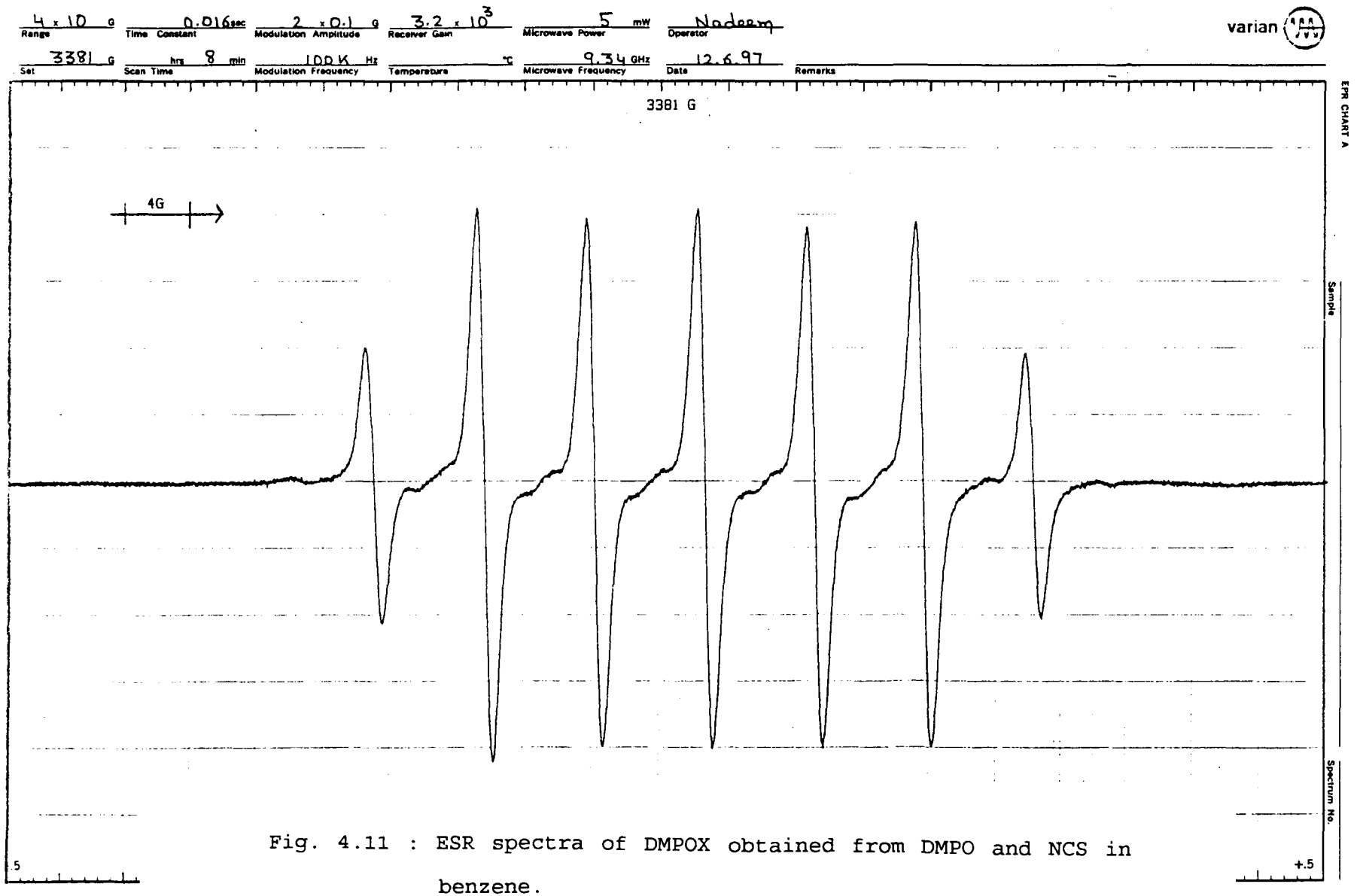


Fig. 4.11 : ESR spectra of DMPOX obtained from DMPO and NCS in benzene.

6.60 G, a^{β}_{H} = 3.25 G (2H). Analysis of the splitting pattern and hyperfine splittings suggests it to be DMPOX (5,5- dimethyl -2 - pyrrolidone - 1 - oxyl) and is identical to the reported one [11]. The hydrogen splitting originate from C- 3 carbon atom of the DMPOX. The simulated spectra Fig. 4.12 agrees with the experimental spectra.

On the basis of these experimental results we suggest the mechanism shown in Scheme 4.1. The reaction is initiated by electron transfer from DMPO to NCS resulting in the formation of DMPO radical cation ($DMPO^{\cdot +}$), succinimidyl radical ($S^{\cdot}$) and chloride ions (Cl^{-}) as shown in the scheme. The immediate adduct which was expected is chloro adduct of DMPO (Cl-$DMPO^{\cdot}$). However, inspite of our best efforts we could not see the chloro adduct of DMPO. Literature survey showed no record of data for the chloro adduct for DMPO [12]. It appears that this adduct is highly unstable. The appearance of succinimidyl adduct of DMPO at higher concentration of DMPO can be explained simply by the fact that after an initial act of electron transfer, large number of neutral DMPO molecules are still left to trap succinimidyl free radicals. The mechanism involved in the formation of DMPOX is well reported in the literature [11].

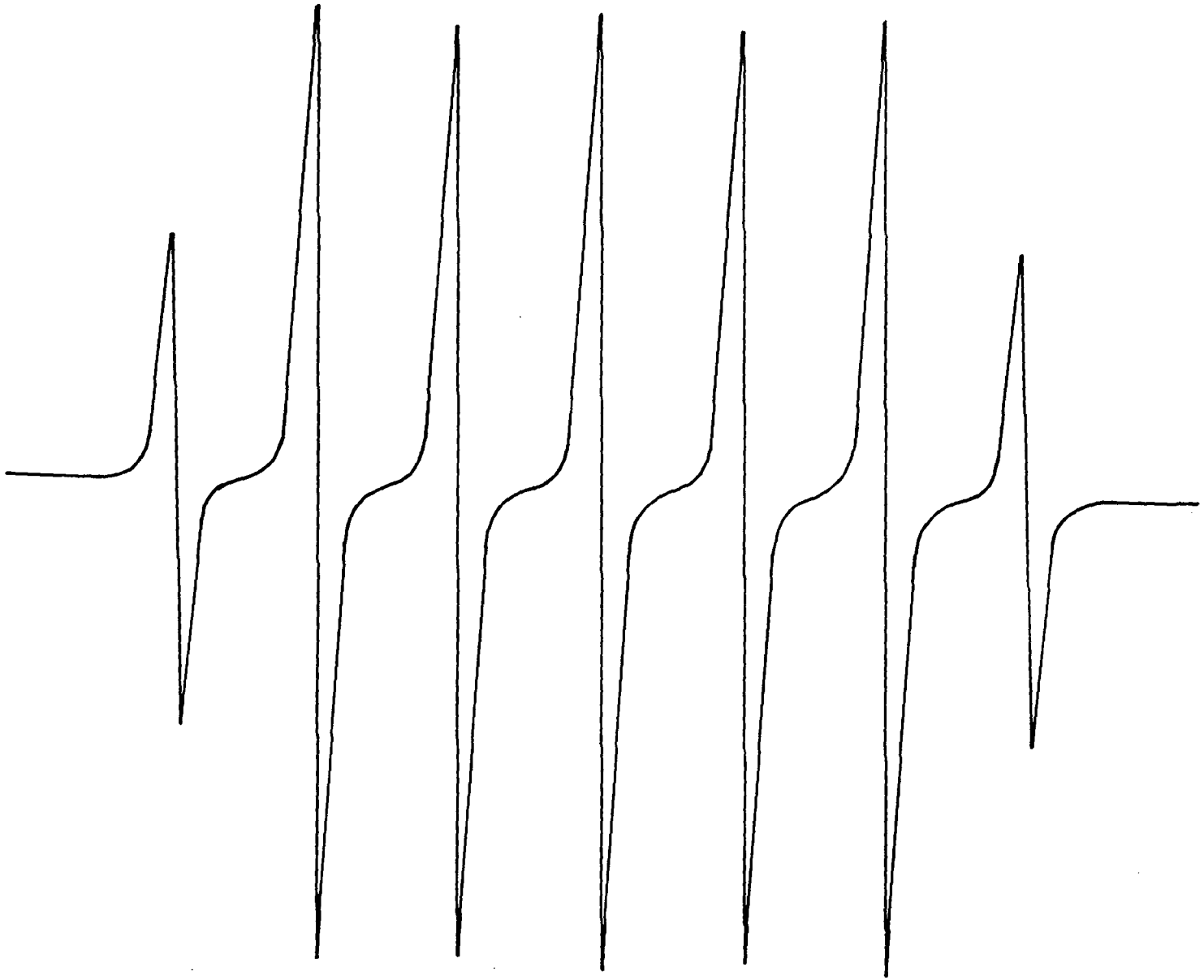
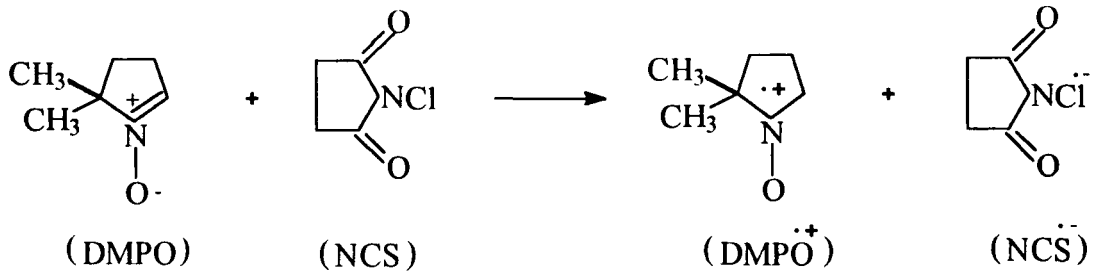
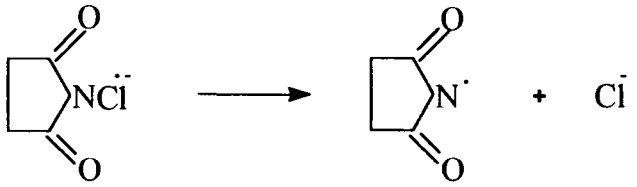


Fig. 4.12 : Computer simulated spectra of 4.11 using parameters calculated from the experimental spectra L.W = 0.5.

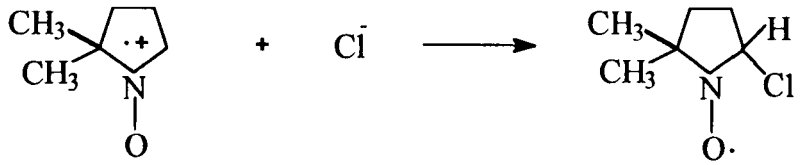
Scheme 4.1



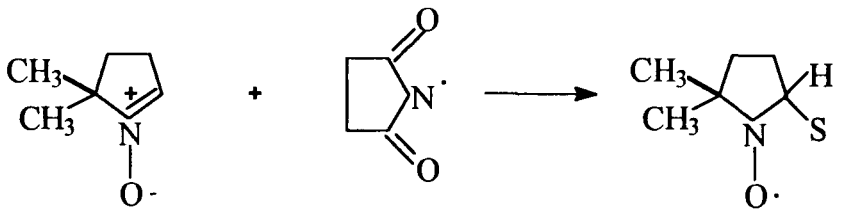
(DMPO) (NCS) ($DMPO^{\cdot+}$) ($NCS^{\cdot-}$)



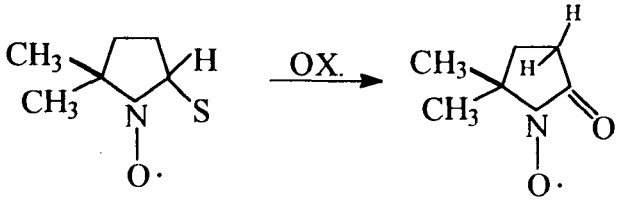
($S^{\cdot}$)



(Cl—$DMPO^{\cdot}$)



($S^{\cdot}$) (S—$DMPO^{\cdot}$)



(DMPOX)

DMPO is more difficult to oxidise than PBN by 0.2 - 0.3 V, at least as judged by their anodic potentials in cyclic voltammograms [11]. Even with strong oxidising agent like Hexachloro Osmate (V), it has been established [11] that such a potential difference reduced the incidence of inverted spin trapping from a defined list of nucleophiles. The appearance of succinimidyl adduct of DMPO shows that NCS is a better oxidant.

The appearance of succinimidyl adduct of PBN and DMPO both in benzene suggests that it prefers to add to spin trap rather to benzene and does not support the reported proposals [2], that succinimidyl radical is trapped by benzene.

In the light of all these experimental observations and absence of any adduct with the characteristics expected for ring opened product of succinimidyl radical ($\cdot CH_2CH_2CONCO$, β - isocyanatocarbonyl ethyl radical), we propose that the reaction involves possibly only two chain carriers : succinimidyl radical and chloride ion in this system. No change in the intensity of the chloro adduct of PBN on adding bicyclopentadiene (a radical scavenger) in the system, also supports this postulation. In order to avoid the possibility of any solvent participation in the radical reaction for e.g., addition of the radicals across the

double bond of the solvent as suggested in case of benzene, the reaction was studied in variety of solvents with different properties.

N- Chlorosuccinimide and Nitrone in n- Hexane

On mixing degassed solutions of NCS and PBN in 1 : 1 concentration weak signals of chloro adduct with hyperfine splittings a_N = 12.20 G, a^{35}_{Cl} = 6.30 G, a^{37}_{Cl} = 5.00 G, a^{β}_{H} = 0.8 G and g = 2.0075 were observed initially. The hyperfine parameters are similar to that observed in benzene. These signals were accompanied by another triplets (3 x 1) with hyperfine splitting a_N = 7.87 G and g = 2.0067 assigned to PBNOX [2]. The chloro adduct signals were short lived ca. 10 minutes while PBNOX was the only signal left. The reactions were carried out at varying concentration ratios of NCS to PBN. At a concentration of NCS to PBN (2 : 1), the results were same. Similar results were obtained at other higher concentration ratios of NCS. At concentration of NCS to PBN (1 : 2) the reaction was marked by intense PBNOX signals and a triplet of doublet with hyperfine splittings a_N = 13.40 G, a^{β}_{H} = 1 50 G, which has been assigned to benzoyloxyl radical adduct of PBN. After few hours another triplet with hyperfine splitting ; a_N = 15.10 G

and g = 2.0060 along with a^{13}_C satellite lines with a^{13}_C = 4.20 G assigned to DTBN was observed Fig. 4.13. The simulated spectra Fig. 4.14 matched well with the experimental spectra. Similar results were obtained at other higher concentration ratios of PBN. Under the conditions discussed above, we did not see any succinimidyl adduct which could be due to low stability. The chloro adduct was not observed even in reactions done in presence of N- methylsuccinimide and / or succinimide. Reactions carried under photolytic conditions at 1 : 1 concentration showed PBNOX and Cl-PBN· which disappeared in ca. 15 minutes and spectra due to DTBN apeared.

The formation of DTBN could not be assigned to a single mechanism. Its formation from β - cleavage of PBNOX and / or Cl-PBN· is possible. With DMPO the immediate spectra observed at 1 : 1 concentration showed unstable and very poorly resolved signals which could not be analysed. Reactions at other concentrations of NCS showed similar results. Reactions carried out at higher concentration ratio of DMPO to NCS (4 : 1), showed succinimidyl adduct of DMPO with a_N = 14.20 G, a^{β}_H = 20.21 G and $a_{N'}$ = 2.20 G (from succinimidyl nitrogen atom) [10]. However, this adduct was short lived (ca. 10 minutes) and was replaced by DMPOX with hyperfine values a_N = 6.6 G, a^{β}_H = 3.3 G

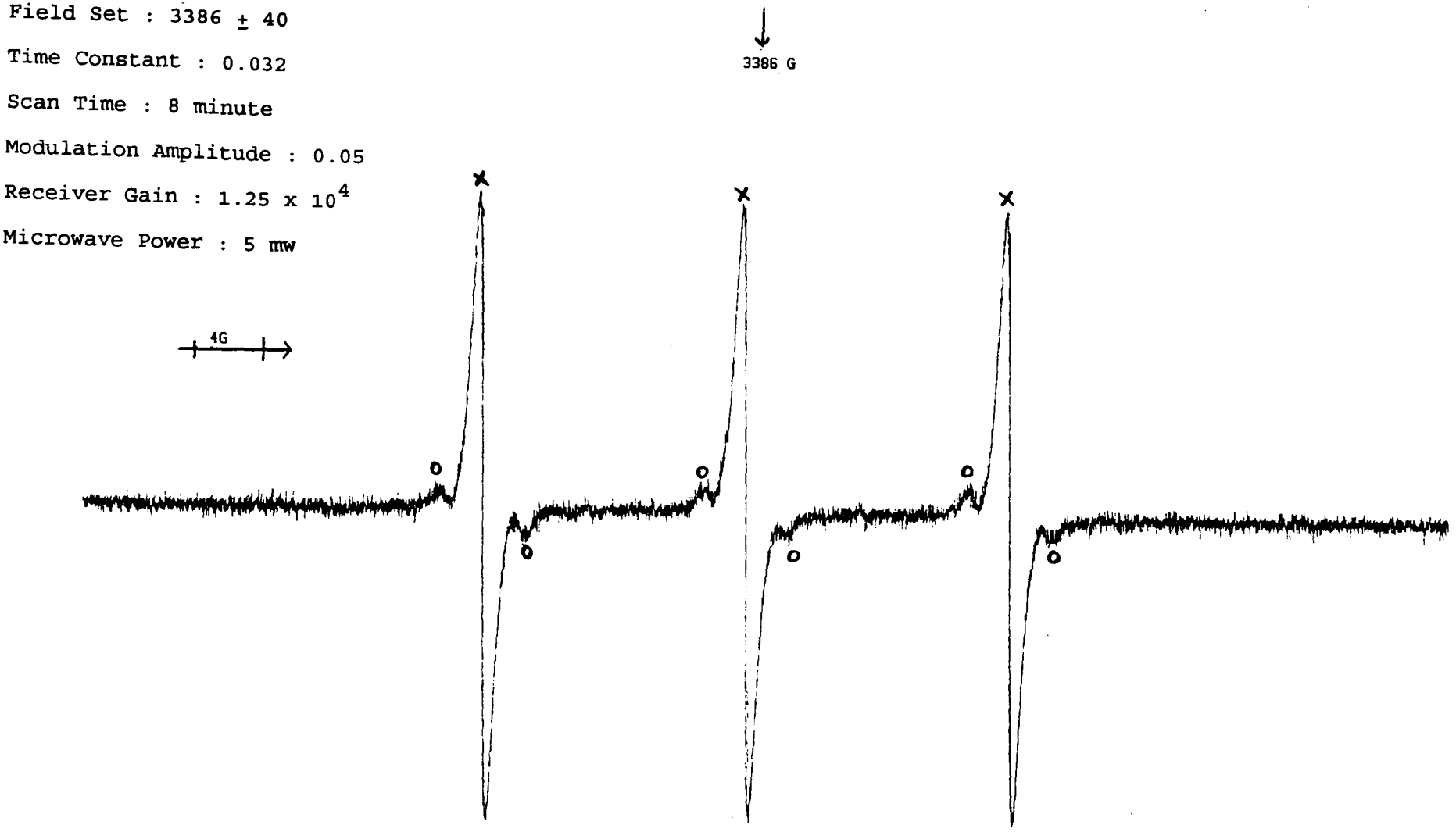


Fig. 4.13 : ESR spectra obtained from PBN and NCS in n- Hexane

X , DTBN ; O , ^{13}C

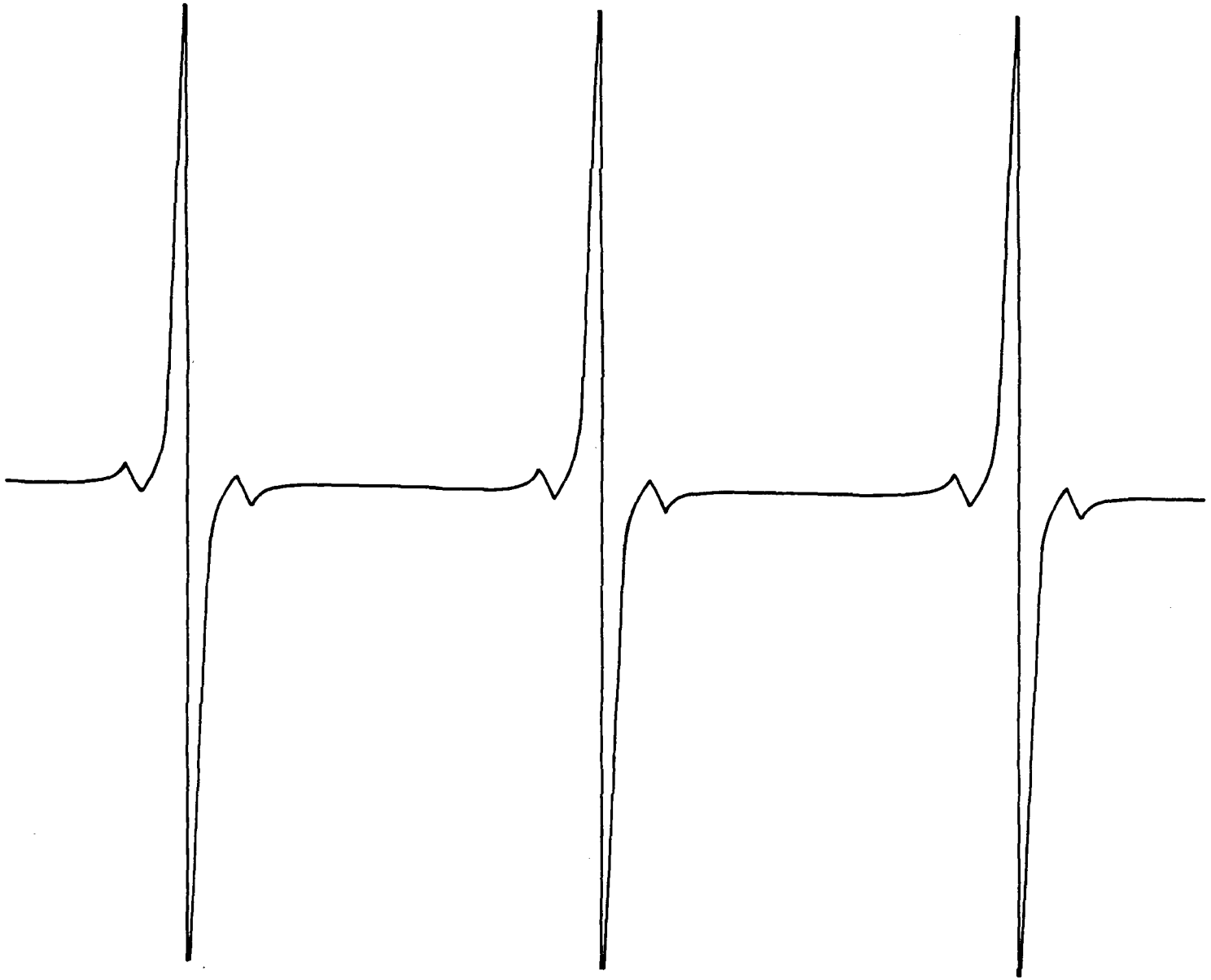


Fig. 4.14 : Computer simulated spectra of 4.13 using parameters measured from experimental spectra L.W = 0.6,

(2H) [11]. Similar results were obtained at other concentration ratios of DMPO to NCS.

We did not observe any ring opened adduct of succinimidyl radical and the results shows the presence of only succinimidyl radicals ($S^{\cdot}$) and chloride ions (Cl^{-}) in the system.

N- Chlorosuccinimide and Nitrone in Acetonitrile

Reactions in acetonitrile were extremely fast. The immediate spectra observed at comparable concentration showed only PBNOX with a_N = 8.12 G and g = 2.0065. The reaction was studied at varying relative concentrations of NCS to PBN. Reactions carried out at concentration 2 : 1, showed only triplets of PBNOX with well defined satellite signals of ^{13}C and ^{15}N isotopes with hyperfine splittings a_N= 8.12 G, $a^{\alpha}_{13\text{-}C}$ = 4.87 G, $a^{\beta}_{13\text{-}C}$ = 4.00 G, $a^{\gamma}_{13\text{-}C}$ = 2.75 G, a^{15}_{N} = 11.5 G. However, reactions carried out at higher concentrations of PBN to NCS (2 : 1), an additional triplet of DTBN with hyperfine splitting a_N = 15.75 G and g = 2.0060 was observed in later stages of the reaction. Similar results were obtained at other concentration ratios of NCS and PBN.

Reactions in the presence of succinimide and/or N-

methylsuccinimide did not show any sign of chloro adduct. It seems high dielectric constant of the solvent does not favour charge transfer type of interaction observed in benzene. Similar mechanism shown in Scheme 4 is proposed. We suggest that the absence of chloro and / or succinimidyl adduct is due to high instability of the adducts in this solvent while PBNOX being stable is observed in all the runs.

Next we studied the reaction under photolytic conditions. At concentration 1 : 1 NCS to PBN, the system was photolysed after ca. 5 minutes of mixing and photolysis was carried out continuously. The spectra observed in the first five minutes showed signals only due to PBNOX, after ca. 5 minutes another triplet of doublet appeared with hyperfine splittings a_N = 13.37 G and a^{β}_{H} = 1.52 G which has been assigned to benzoyloxyl radical adduct of PBN. After ca. 10 minutes another spectra corresponding to chloro adduct of PBN (Cl-PBN·) appeared along with PBNOX and benzoyloxyl radical adduct. The hyperfine splittings of the Cl-PBN· measured from the observed spectra are a_N = 12.60 G, a^{35}_{Cl} = 6.29 G, a^{37}_{Cl} = 5.12 G and a^{β}_{H} = 0.75 G. However, this adduct disappeared in ca. 10 minutes while PBNOX was the only signal left.

In an another set where the reaction mixture was photolysed immediately on mixing, the spectra corresponding to Cl-PBN· along with weak signals of PBNOX was observed initially. The chloro adduct disappeared in ca. 20 minutes on continuous photolysis and was replaced by another set of signals with splitting pattern 3 x 3 x 2 as shown in Fig. 4.15. The measured hyperfine splittings are ; a_N = 14.37 G a^{β}_{H} = 5.25 G, $a_{N'}$ = 1.62 G (from succinimidyl nitrogen). This splitting pattern has been assigned to succinimidyl radical adduct of PBN (S-PBN·) [4]. The simulated spectra Fig. 4.16 is in good agreement with the experimental spectra. This adduct was also unstable and was replaced by benzoyloxyl radical adduct of PBN which also disappeared leaving only PBNOX behind. On the basis of these experimental results we suggest the mechanism shown in Scheme 4.2.

We feel that under photolytic conditions, electron transfer from PBN to NCS is highly efficient. The succinimidyl radicals formed after the cleavage of NCS radical anion, abstracts H- atom from the solvent yielding succinimide and $\cdot CH_2CN$. Cl-PBN· reacts with succinimide (which may be in the excited state) yielding HCl and succinimidyl adduct of PBN. We suggest this reaction pathway as one of the possible mode where succinimidyl

Field Set	: 3385 ± 25 G
Time Constant	: 0.250
Scan Time	: 4 minutes
Modulation Amplitude	: 0.4
Receiver Gain	: 10^5
Microwave Power	: 5 mw

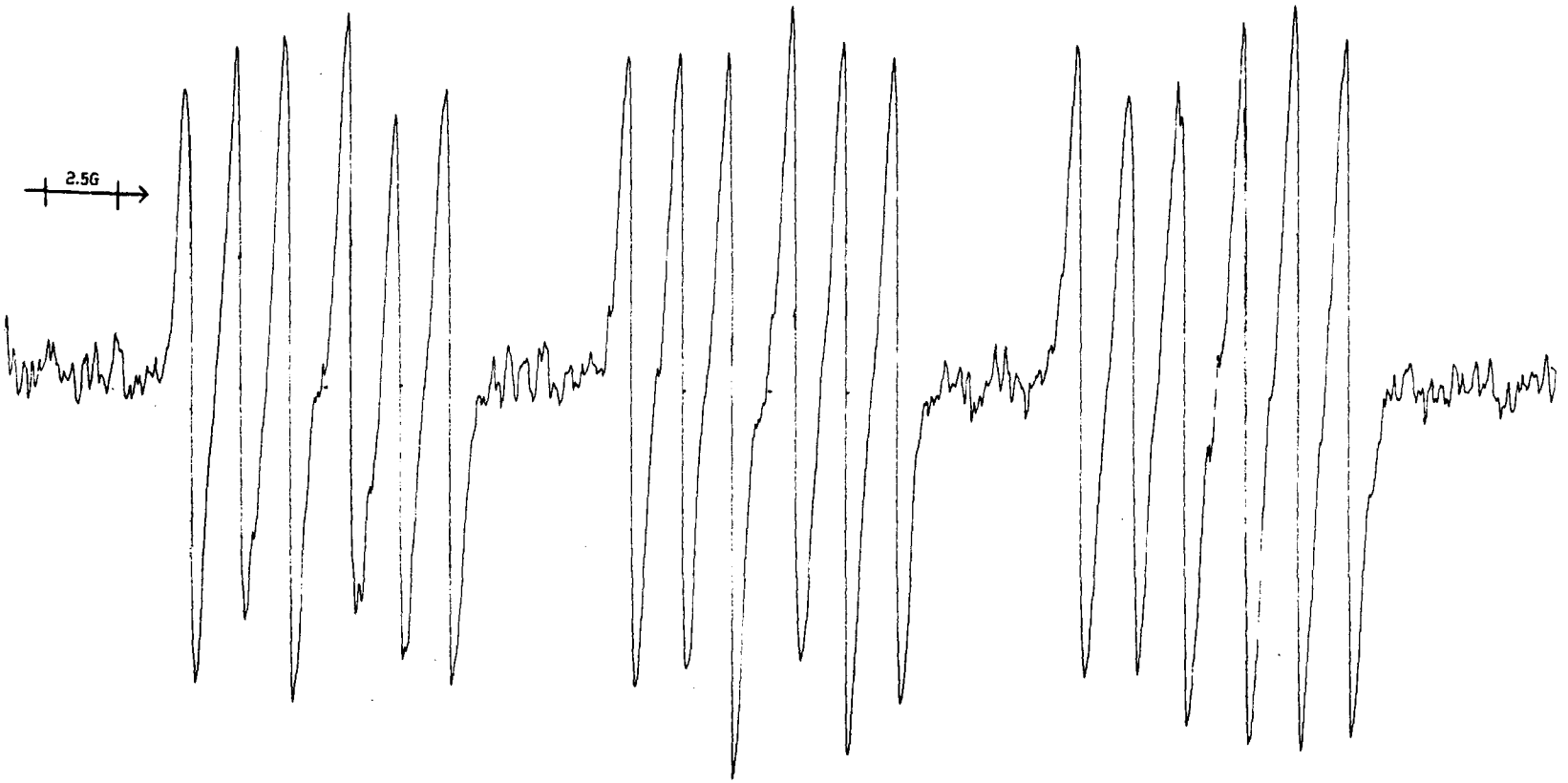


Fig. 4.15 : ESR spectra obtained from PBN and NCS during photolysis in CH_3CN.

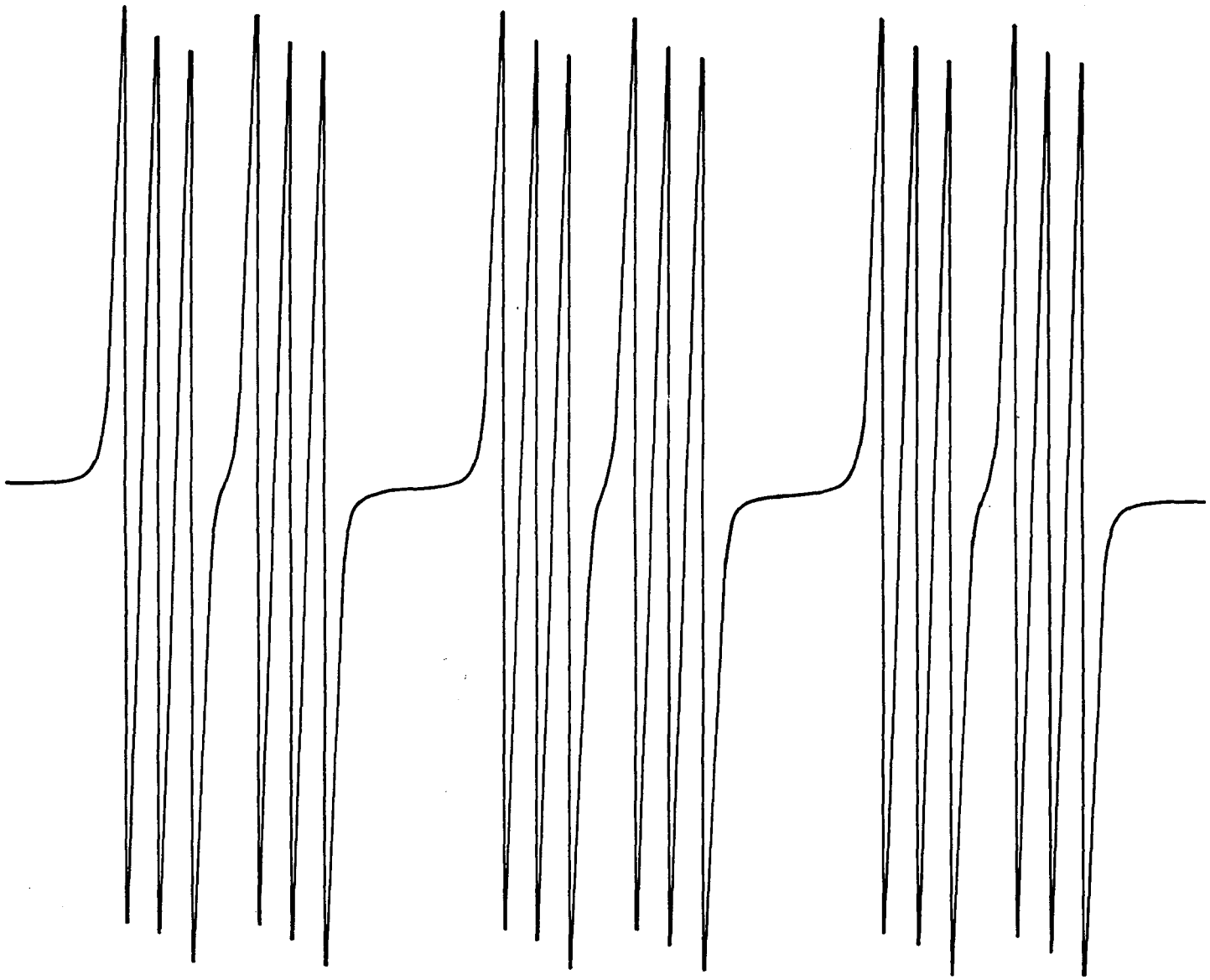
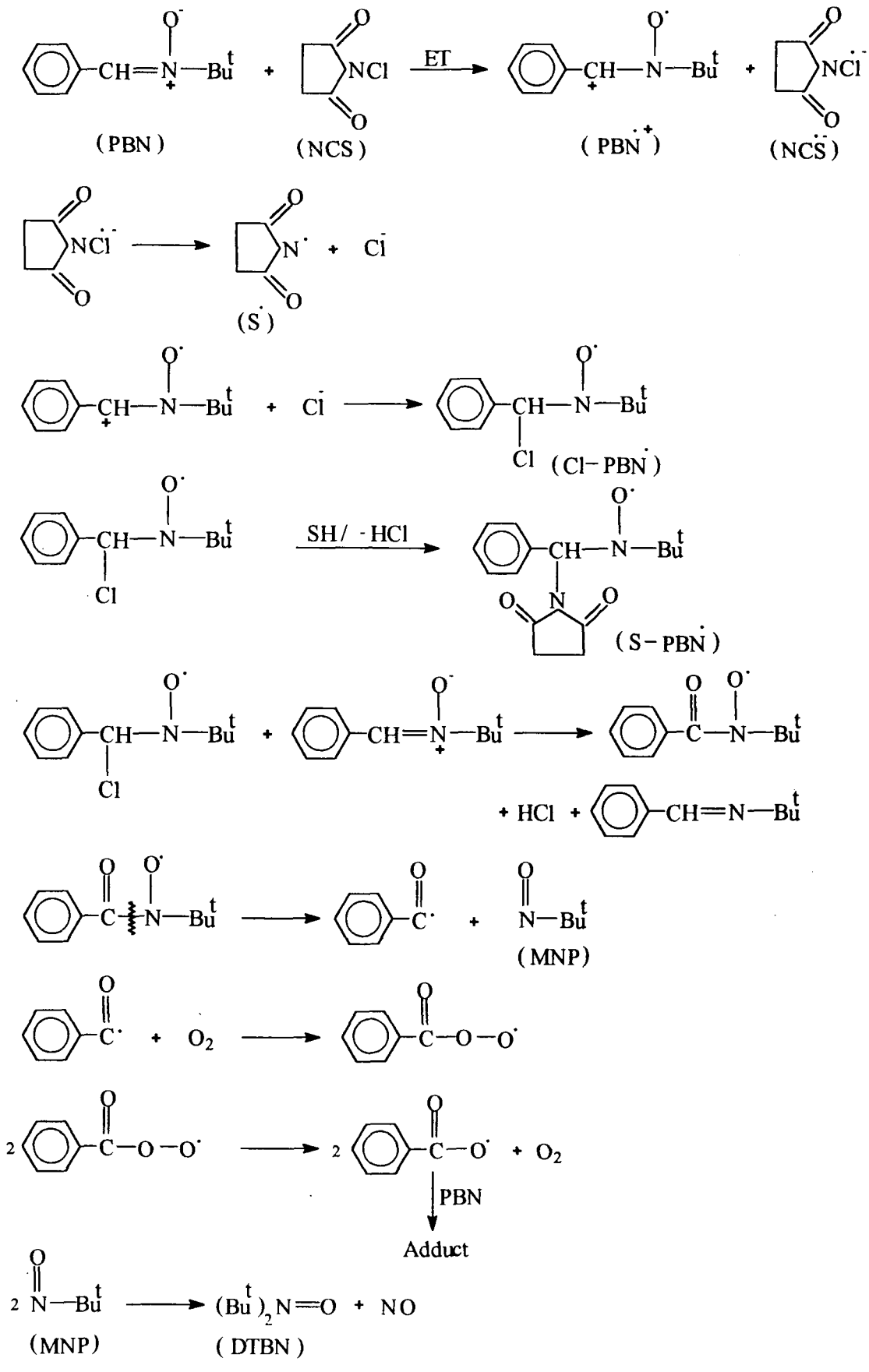


Fig. 4.16 : Computer simulated spectra of 4.15 using hyperfine parameters calculated from the experimental spectra, L.W = 0.4.

Scheme 4.2



adduct appeared only after the decay of chloro adduct. $\cdot CH_2CN$ may undergo some reaction e.g., dimerisation and are therefore not observed. The SET study under these two different situations where : (i) photolysis was started after ca. 5 minutes of mixing the reactants and (ii) photolysis was started immediately on mixing the reactants can be explained as follows. In case (i), the electron transfer converts most of the NCS to Cl-PBN$\cdot$ which being unstable, is converted to PBNOX (observed with very high intensity) and not much of the Cl-PBN$\cdot$ is left when photolysis is started while in case (ii) the Cl-PBN$\cdot$ adduct formed seems to react with succinimide in the excited state and appears to follow a different pathway to give S-PBN$\cdot$. This postulation is supported by the observance of PBNOX in low intensity in case (ii).

The chloro adduct is observed only under conditions of continuous photolysis. These results support that spin adducts with good leaving groups e.g. Cl^-, can be observed under conditions of continuous generation (e.g., photolysis) or in low permitivity solvents e.g., benzene [13].

We failed to see succinimidyl adduct in the presence of DMPO. DMPOX was the only signal observed in all the runs with hyperfine splittings a_N = 7.00 G and a^{β}_H = 3.60 G

(2H). These experimental observations suggest that the system consists of S· and Cl^- as chain carrier with no sign of any ring opening of succinimidyl radicals (S·).

N- Chlorosuccinimide and Nitrone in Dichloromethane

Mixing of NCS and PBN solutions in 1 : 1 concentration showed two set of signals Fig. 4.17. One triplet of doublet with hyperfine splittings a_N = 14.62 G, a^{β}_{H} = 2.25 G and g = 2.0060, parameters similar to that of an alkyl type radical adduct of PBN and another was PBNOX with hyperfine values a_N = 8.00 G, g = 2.0065 G. The former signal decayed out in ca. 2 hours while a continuous increase in PBNOX intensity was observed and was the only signal left at the end. On the basis of hyperfine splittings the triplet of doublet is assigned to $CHCl_2$-PBN· adduct. The simulated spectra Fig. 4.18 is in agreement with the experimental one. The hyperfine splitting agrees with reported [14] values. Reaction performed at higher concentration of NCS to PBN 2 : 1, showed only PBNOX and $CHCl_2$-PBN· adducts. PBNOX was the only adduct left at the end of the reaction. Reactions done at other concentrations showed similar adducts. We did not see any chloro and / or succinimidyl adduct in all these runs. At higher concentration of PBN to NCS 2 : 1, PBNOX was the

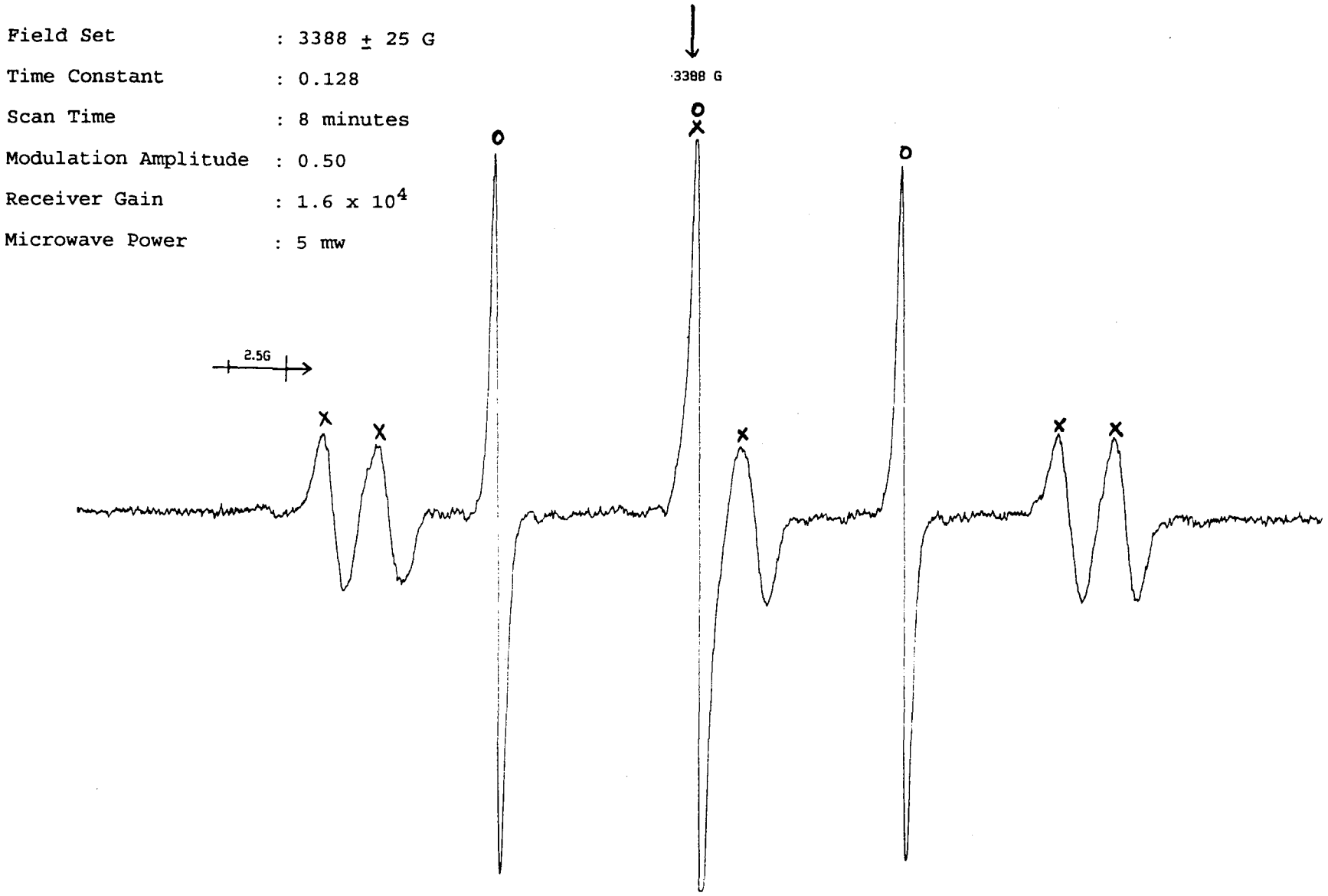


Fig. 4.17 : ESR spectra obtained from PBN and NCS in CH_2Cl_2.

X , $CHCl_2$-PBN· adduct ; O , PBNOX.

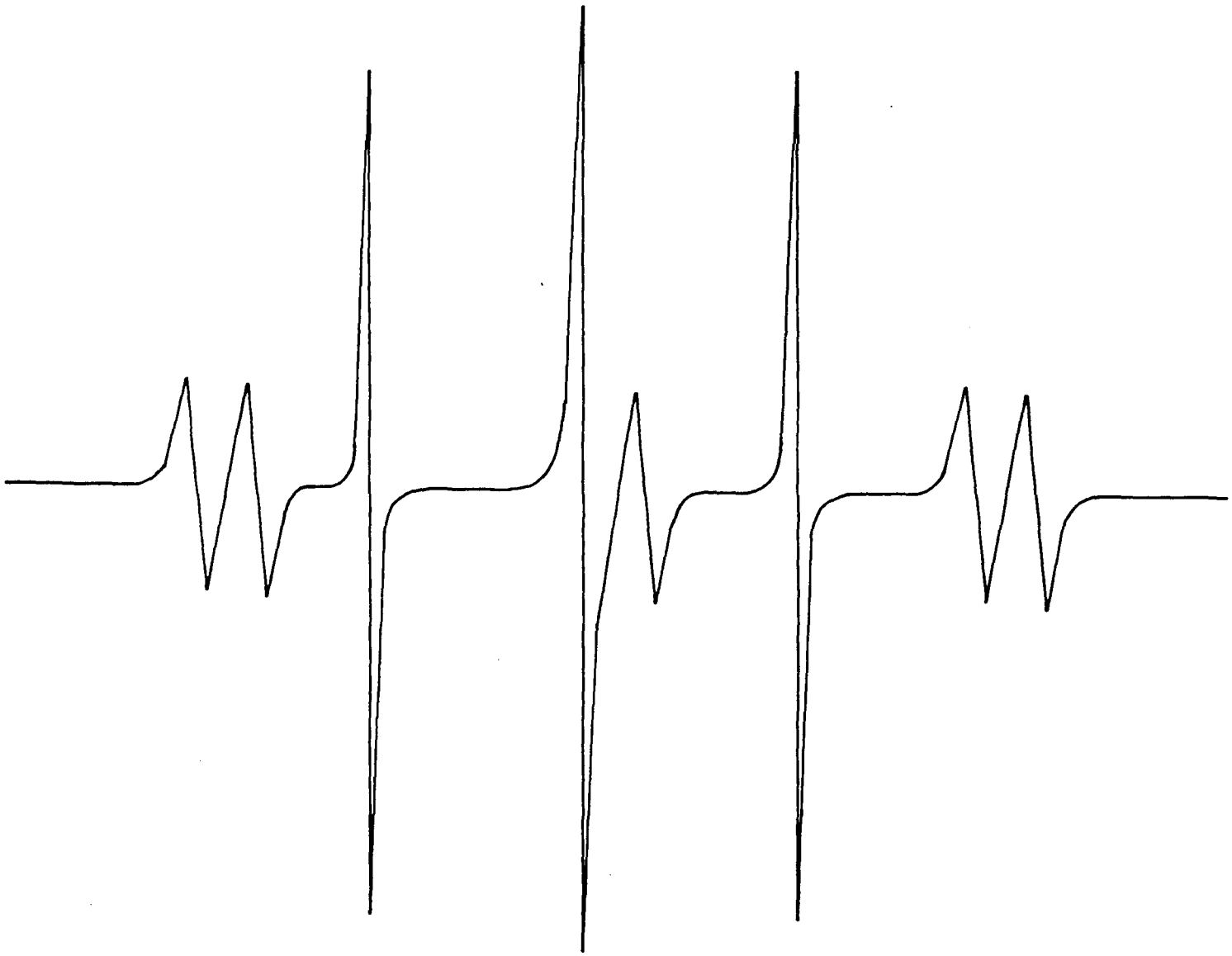


Fig. 4.18 : Simulated spectra of 4.17. $CHCl_2$-PBN· L.W = 0.8

PBNOX L.W = 0.4, ΔG = - 1.2.

only specie observed. At other higher concentrations of PBN to NCS, DTBN with hyperfine splittings, a_N = 15.70 G and g = 2.0060 was observed in later stages of the reaction.

The suggested mechanism is formulated in Scheme 4.3. After the primary act of ET, respective species as shown in the scheme are initially formed. We suggest that $CHCl_2$-PBN· adduct is formed due to H-abstraction from the solvent by the succinimidyl radicals and subsequent trapping by PBN. We suggests that in $\cdot CHCl_2$, the two chlorine atoms make the carbon atom electron deficient which make this radical reactive towards PBN as compared to $\cdot CH_2CN$ radicals.

The reaction was repeated in dichloromethane with 10 % benzene. The immediate spectra observed was that of Cl-PBN· adduct and PBNOX. The Cl-PBN· decayed in ca. 20 minutes while PBNOX was the only signal left. This confirms our earlier postulations that Cl-PBN· adduct is more stable in benzene. Under photolytic conditions the immediate spectra observed was Cl-PBN· with hyperfine splittings ; a_N = 12.56 G, a^{35}_{Cl} = 6.20 G, a^{37}_{Cl} = 5.21 G, a^{β}_{H} = 0.75 G. This spectra was replaced by : (i) S-PBN· with a_N = 14.50 G, a^{β}_{H} = 5.43 G and $a_{N'}$ = 1.25 G (ii) benzoyloxyl adduct of PBN with a_N = 13.25 G, a^{β}_{H} = 1.50 G and (iii) PBNOX

Scheme 4.3

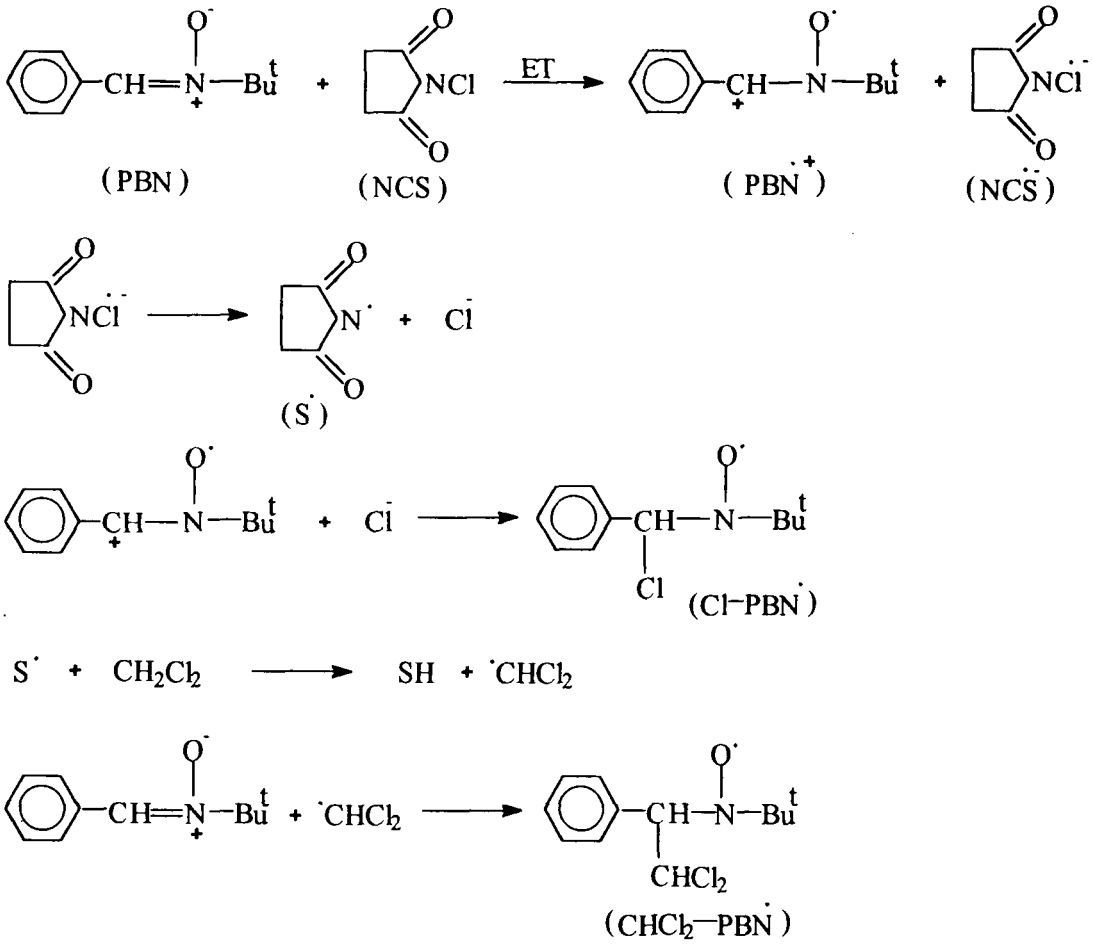


Fig. 4.19. The spectra simulated Fig. 4.20 agrees with the experimental one. After ca. 30 minutes of continuous photolysis PBNOX along with DTBN with hyperfine splittings a_N = 15.70 G and g = 2.0060, accompanied by ^{13}C satellite lines with hyperfine splitting a^{13}_{C} = 4.37 G were left.

Under photolytic conditions the mechanism is similar to that proposed in case of acetonitrile. The observance of chloro adduct under photolytic conditions and / or in 10 % benzene in dichloromethane lends support to the postulation made in case of acetonitrile. Again we did not see any sign of ring opened specie and our assertion that $S^{\cdot}$ and Cl^{-} are the chain carriers is consistent.

N- Chlorosuccinimide and PBN in Alcohols

Alcohols have an important property of solvating the anions and can remove them from the reaction site. Therefore, SET reactions of NCS in alcohols were studied.

N- Chlorosuccinimide and PBN in Ethanol

The immediate spectra Fig. 4.21, recorded at 1 : 1 concentration showed a triplet of doublet with hyperfine splittings ; a_N = 14.60 G, a^{β}_{H} = 2.80 G along with another set of signals with splitting pattern 3 x 3 x 2 and

Field Set : 3381 ± 25 G

Time Constant : 0.064

Scan Time : 4 minutes

Modulation Amplitude : 0.50

Receiver Gain : 2.5×10^3

Microwave Power : 5 mw

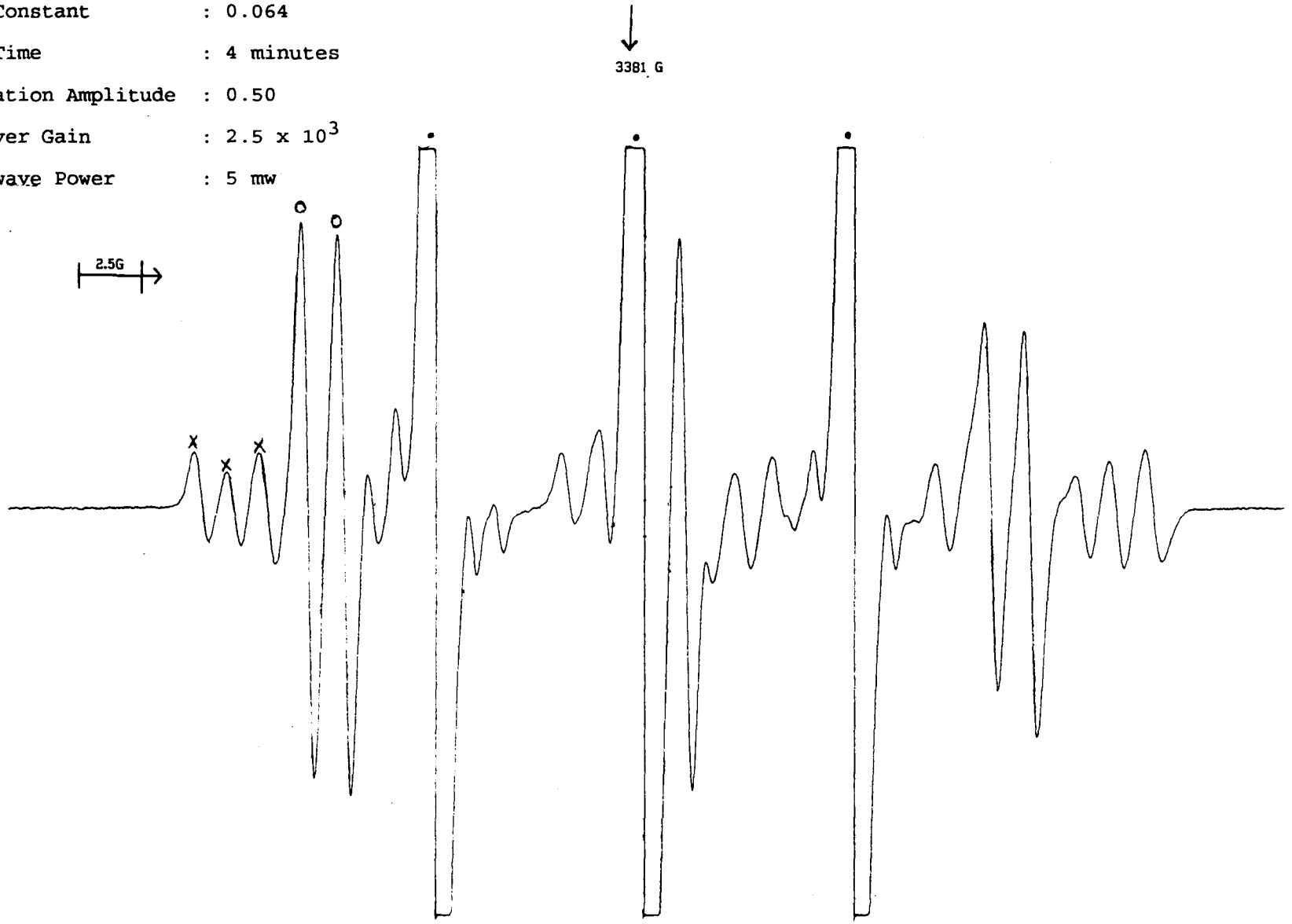


Fig. 4.19 : ESR spectra obtained from PBN and NCS during photolysis in CH_2Cl_2. X , S-PBN· ; O , $CHCl_2$-PBN· ; • , PBNOX.

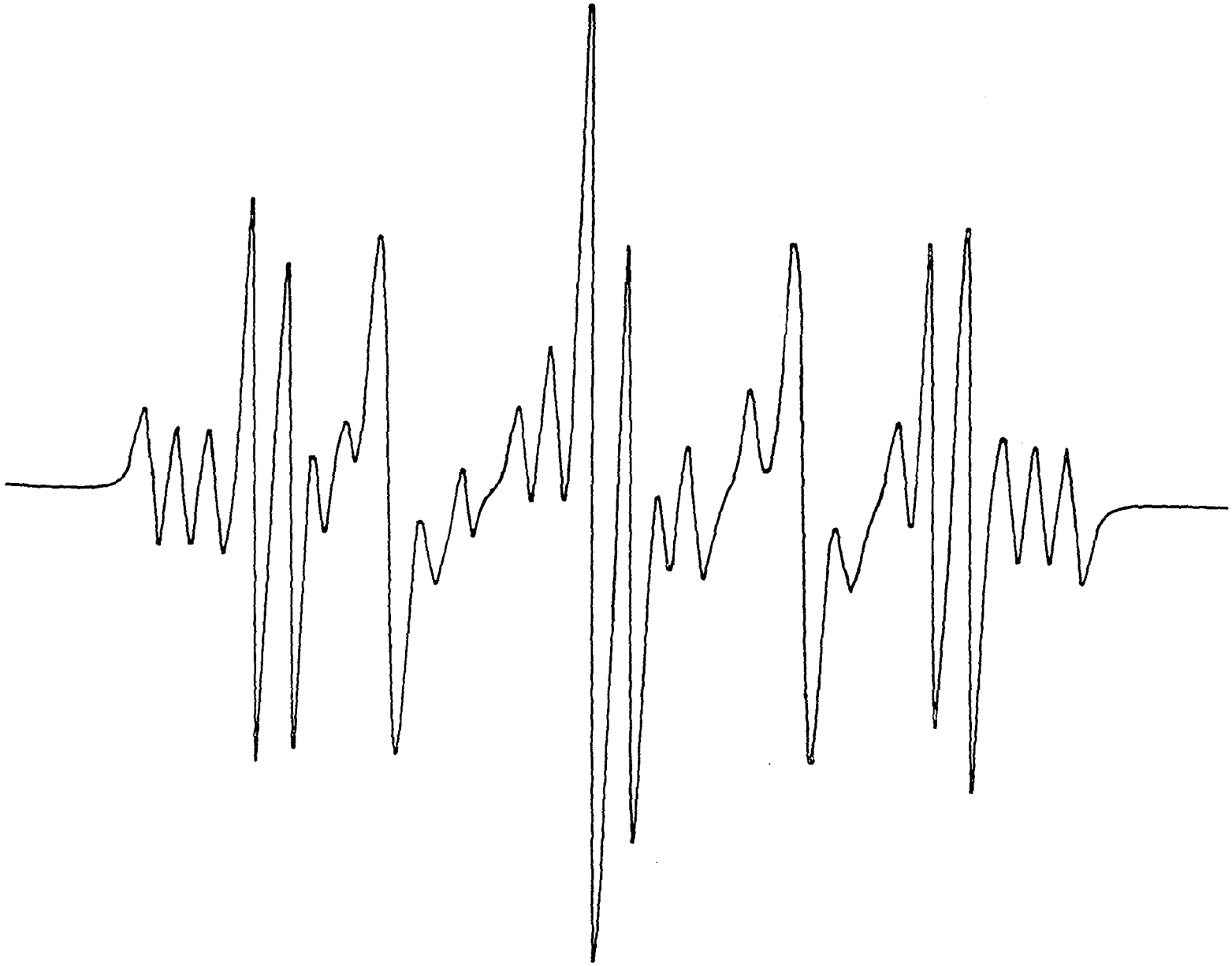


Fig. 4.20 : Computer simulated spectra of 4.19. S-PBN· L.W = 0.7 ; ·$CHCl_2$ L.W = 0.5 ; PBNOX L.W = 0.6; $\Delta G = -0.6$

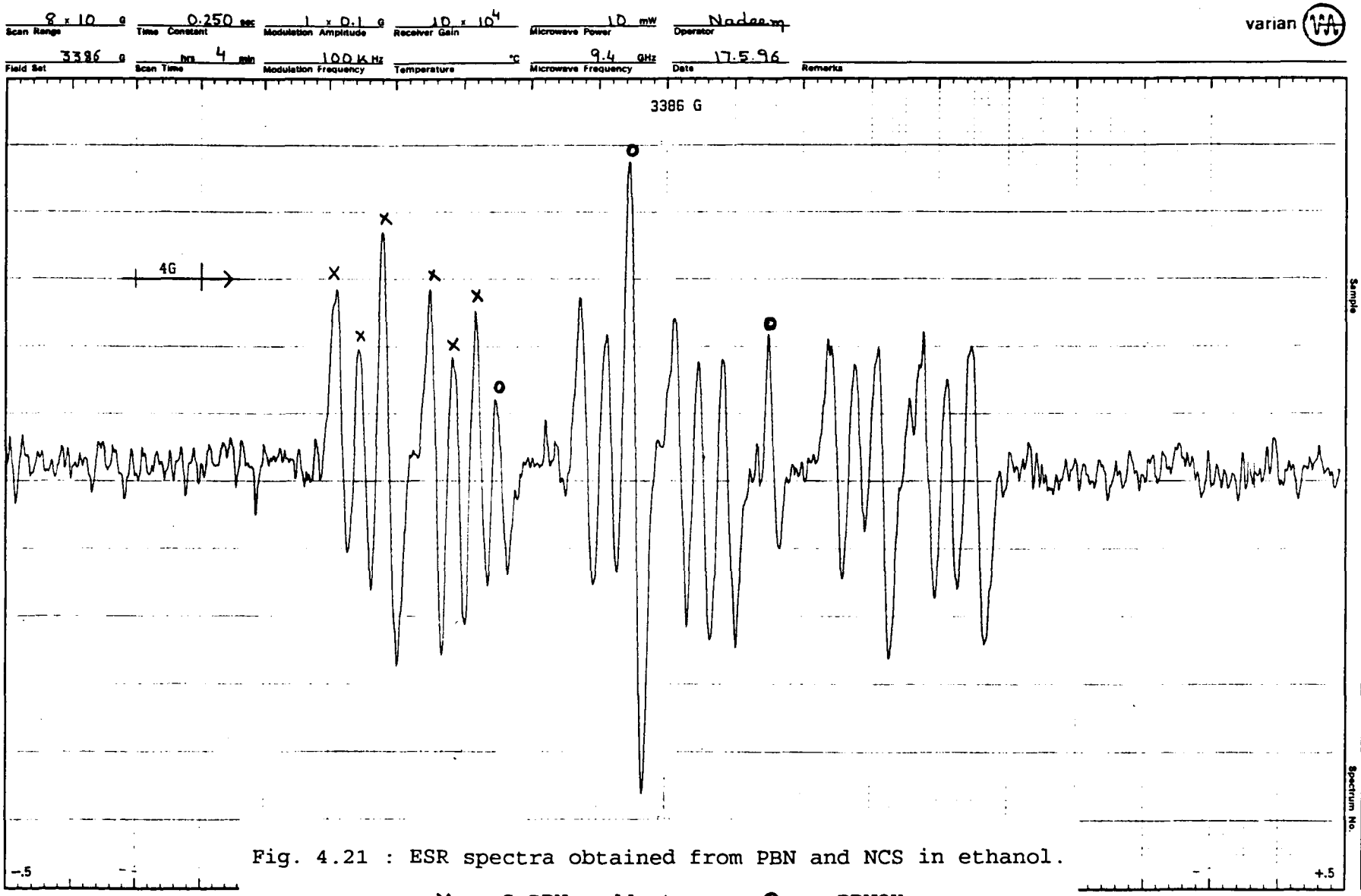


Fig. 4.21 : ESR spectra obtained from PBN and NCS in ethanol.

X , S-PBN· adduct ; O , PBNOX.

hyperfine couplings ; a_N = 14.70 G, a^{β}_{H} = 5.62 G, $a_{N'}$ = 1.37 G. These adducts were accompanied by weak triplets of PBNOX with hyperfine splittings a_N = 8.00 G and g = 2.0066. The spectra with 3 x 3 x 2 splitting has been assigned to S-PBN· adduct. The magnitude of hyperfine splitting suggests, the triplet of doublet is most probably due to solvent derived radical adduct of PBN (CH_3CH_2O-PBN·). Hyperfine couplings agree with the reported values [15]. The simulated spectra Fig. 4.22 matches with the experimental one. The solvent derived adduct decays out in ca. 15 minutes while succinimidyl adduct increases in intensity but after some time it was replaced by triplet of triplets (3 x 3) Fig. 4.23 with hyperfine values, a_N = 16.64 G, $a_{N'}$ = 1.80 G. The triplet of triplets can be analysed as follows : primary nitrogen gives lines of intensity 1 : 1 : 1. Each of these lines further splits up into triplet (1 : 1 : 1), signifying the presence of another nitrogen. This spectra can be interpreted as succinimidyl radical adduct of MNP (S-MNP·) which is confirmed by simulation Fig. 4.24. The hyperfine splittings are in good agreement with the literature values [16].

Experiments were repeated at different relative concentrations of NCS and PBN. At NCS to PBN (1 : 2), the growth and intensity of the S-PBN· adduct was low but

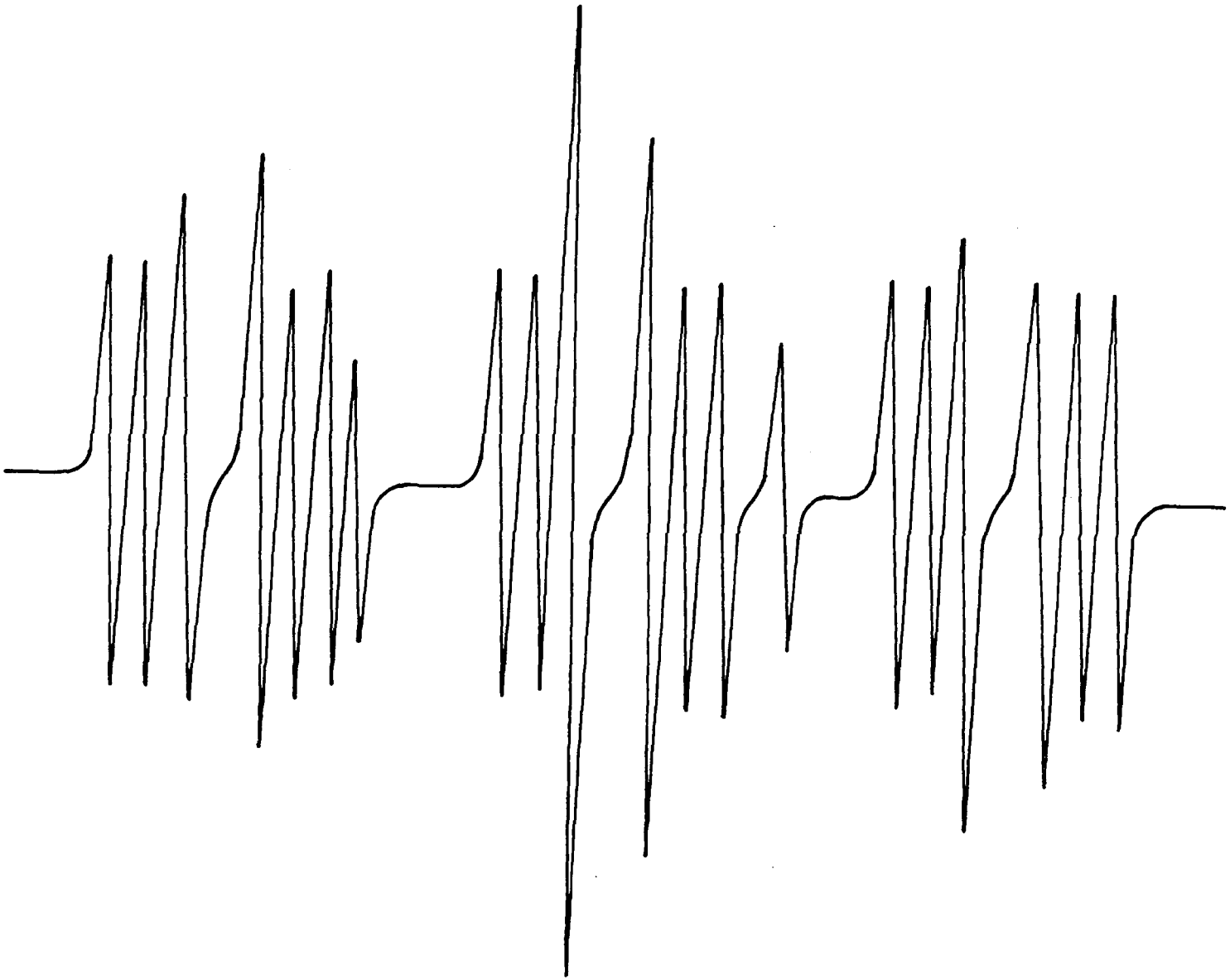


Fig. 4.22 : Simulated spectra of 4.21. S-PBN· L.W = 0.5, PBNOX L.W = 0.6, ΔG = - 1.52.

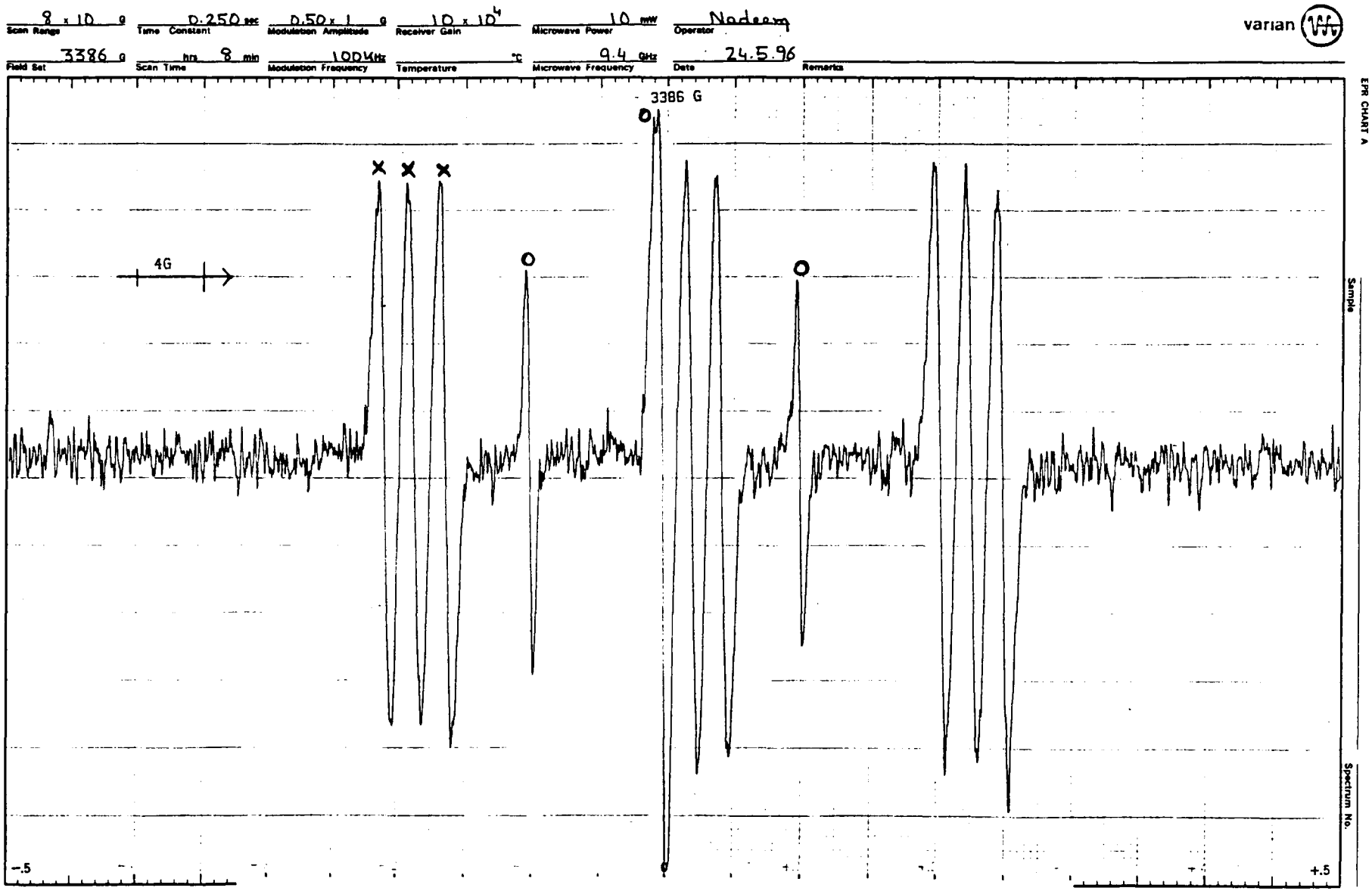


Fig. 4.23 : ESR spectra obtained from PBN and NCS in ethanol.

× , S-MNP· adduct ; O , PBNOX.

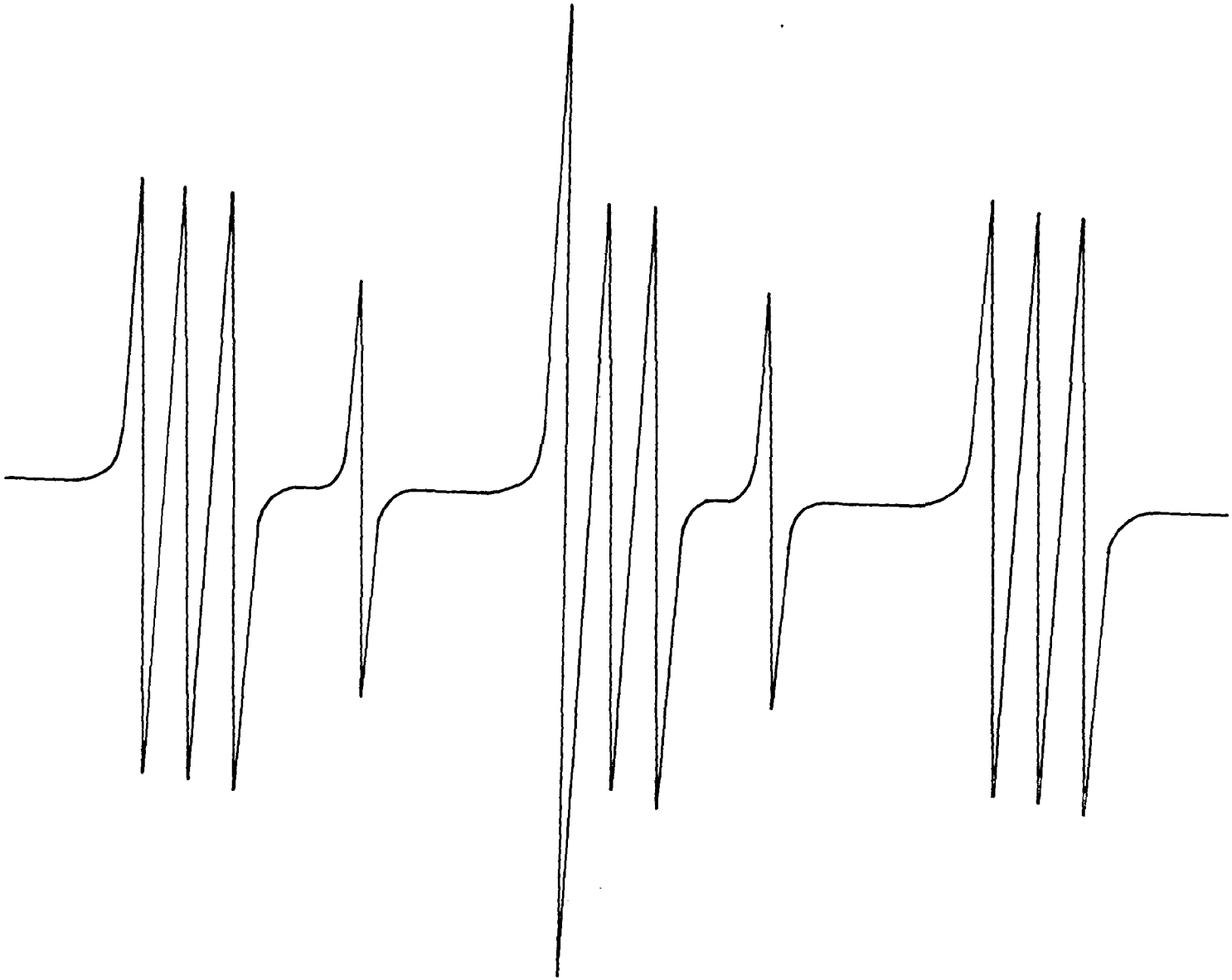
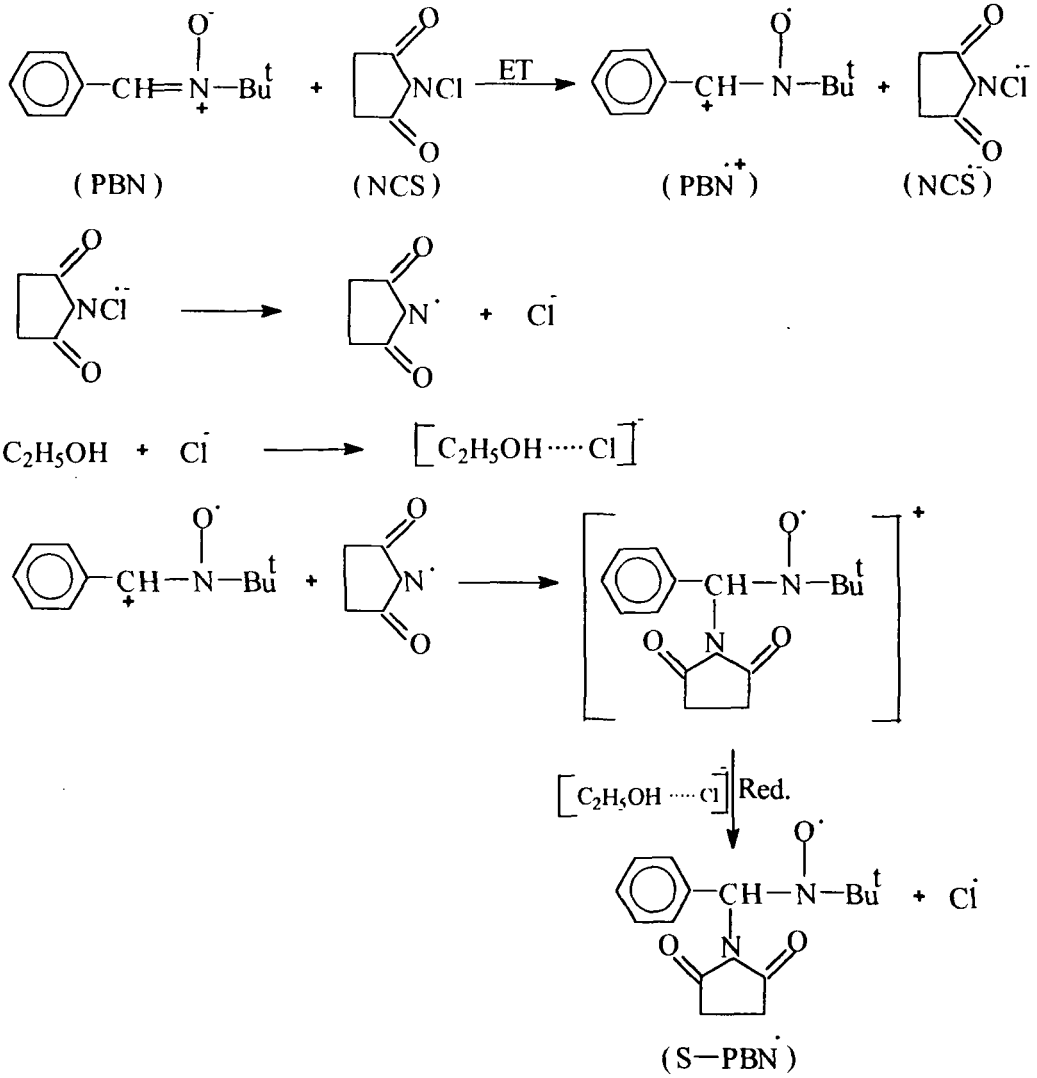


Fig. 4.24 : Simulated spectra of 4.23. S-MNP· L.W = 0.7, PBNOX L.W = 0.5, Δ G = - 1.8.

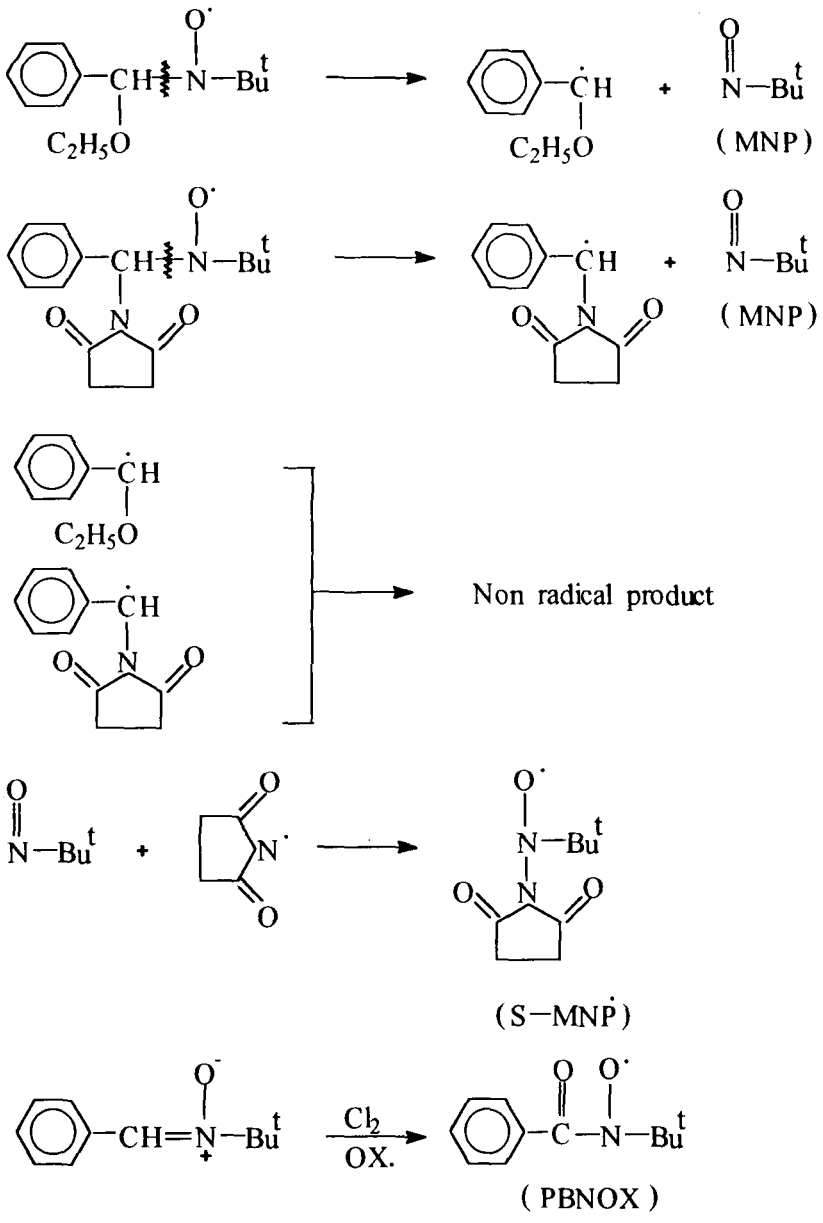
the spectra was basically similar. Similar results were observed at other higher concentration ratios of PBN. In experiments with higher concentration of NCS to PBN (2 : 1), there was fleeting appearance of the triplet of doublet along with S-PBN· adduct in the beginning of the reaction but was quickly superseded by the signals due to succinimidyl radical adduct of MNP. Thus the intensity and growth of the signals are dependent on the relative concentrations of NCS and PBN.

The mechanism shown in Scheme 4.4 is suggested to account for the experimental results. The electron transfer and subsequent dissociation results in the formation of $PBN^{\cdot +}$, $S^{\cdot}$ and Cl^{-}. The chloride ions produced are immediately solvated by ethanol and removed from the system and hence the reason for the absence of chloro adduct. Solvated complex acts as a nucleophile and reduces $S\text{-}PBN^{\cdot +}$ to S-PBN· which is observed in the reaction. The chlorine atoms may escape from the solvent cage which in turn may either dimerise to produce molecular chlorine or abstract hydrogen from ethanol giving $C_2H_5O\cdot$ radicals which are subsequently trapped by neutral PBN. We also feel that the molecular chlorine thus formed oxidises nitrone to PBNOX as suggested by Janzen et al. [17]. Since, Cl^{-} is effectively removed in the early stages of the reaction,

Scheme 4.4



contd..


Non radical product
(MNP)
(MNP)
(S−MNP·)
(PBNOX)

therefore weak PBNOX signals were observed. S-PBN· adduct formed undergoes β - cleavage as shown in the Scheme yielding tert. nitroso butane (MNP). MNP thus formed immediately traps succinimidyl radicals giving S-MNP· adduct. The formation of MNP from β - cleavage of ethoxy adduct of PBN is also possible.

In order to see how effective solvation is, the reaction was carried out in benzene with 10 % ethanol. The immediate spectra observed was ethoxy radical adduct of PBN rather than Cl-PBN· which was observed in neat benzene. These results establishes that even 10 % ethanol is effective in removing the chloride ions generated in the reaction. However, we did not see the succinimidyl adduct in these runs probably due to change in the reaction mechanism. The reactions were also carried out in different analogues of alcohols, as each alcohol differs from the other.

N- Chlorosuccinimide and PBN in Iso- Propanol

Iso- proponal is an alcohol with some unique property e.g., when benzophenone is irradiated in this alcohol, the conversion of benzophenone to benzpinacol occurs quantitatively. The proton donating ability of this solvent is remarkable. With this information in mind we

studied our reactions in this solvent.

When the reaction was performed in iso- propanol, the immediate spectra observed at (1 : 1) was triplet of doublet with hyperfine splittings a_N = 14.40 G, a^{β}_H = 2.20 G along with succinimidyl radical adduct of PBN with hyperfine values, a_N = 14.60 G, a^{β}_H = 5.70 G, $a_{N'}$ = 1.20 G. This adduct was replaced (ca. 20 minutes) by a triplet of triplets (3 x 3) with hyperfine splittings a_N = 16.60 G and $a_{N'}$ = 1.80 G, assigned to S-MNP· adduct. This adduct was accompanied by weak signals of PBNOX with hyperfine splittings a_N = 8.00 G, g = 2.0067 and was the only signal left at the end of the reaction. Reactions at varying concentration ratios of NCS and PBN yielded similar results. However the intensity and the appearance of the adducts were dependent on the relative concentrations of NCS and PBN as discussed earlier.

Reaction pathways seems to be similar as proposed in case of ethanol. The system was studied in butanol, iso-butanol and 2-ethoxy ethanol. The results were essentially similar, hence are not being included.

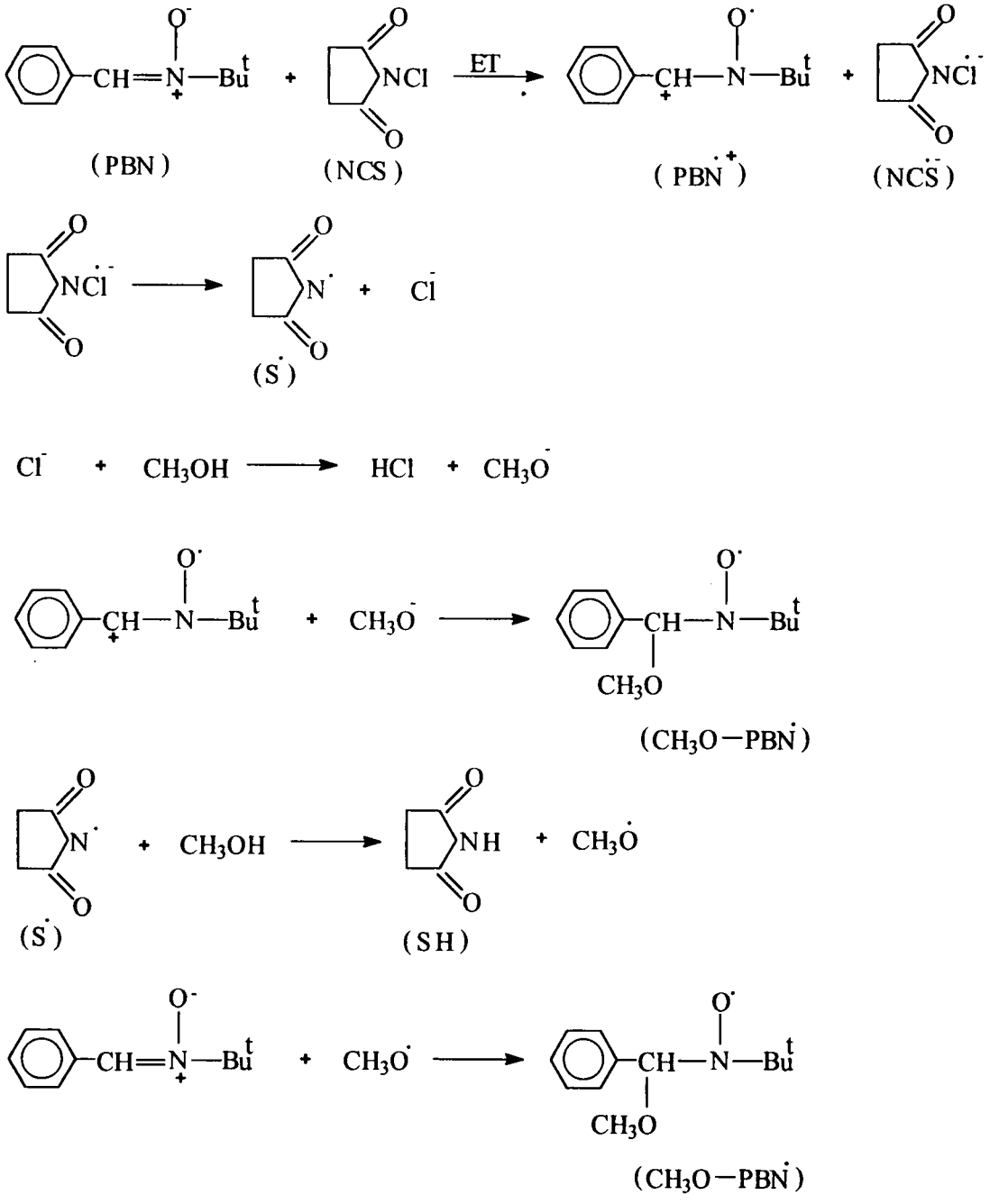
N- Chlorosuccinimide and PBN in Methanol

Methanol has lower solvating capability, higher dielectric constant, higher hydrogen bond donating ability, and lower hydrogen bond accepting ability as compared to other alcohols used in our study [18]. It was therefore, felt that the study in this solvent may provide some additional information about the NCS chemistry not observed so far.

When the reaction was performed in methanol at concentration 1 : 1, we did not see any sign of succinimidyl adduct of PBN and / or MNP. The only signals observed were a triplet of doublet with hyperfine splittings a_N = 14.40 G, a^{β}_H = 3.00 G, assigned to methoxy adduct of PBN [19]. This adduct was replaced (ca. 20 minutes) by PBNOX with hyperfine splittings, a_N = 8.10 G, g = 2.0065 and was the only signal left at the end of the reaction. Reactions carried out at other concentration ratios of NCS and PBN yielded similar results. It appears that the pathways leading to the formation of S-PBN$^{\cdot}$ are less favourable in this solvent and the possible difference in the reaction mechanism is shown in Scheme 4.5.

We feel that in this system due to poor solvation of chloride ions, the major reaction pathway is H- abstraction

Scheme 4.5



from CH_3OH giving CH_3O-PBN$^{\cdot}$ adduct as shown in the Scheme. The complete absence of succinimidyl adduct suggest that these radicals may also be involved in H- abstraction reactions leading to the formation of solvent derived adducts which are dominant in methanol. The role of methanol in diverting the reaction pathway is nicely illustrated in this system.

All the results in alcohols again reinforce our proposal that $S^{\cdot}$ and Cl^{-} are the only possible chain carrier with no sign of any ring opened specie. Next reactions were performed in Carbontetrachloride where the possibility of other reactions such as H- abstraction reactions, solvation etc., are minimal.

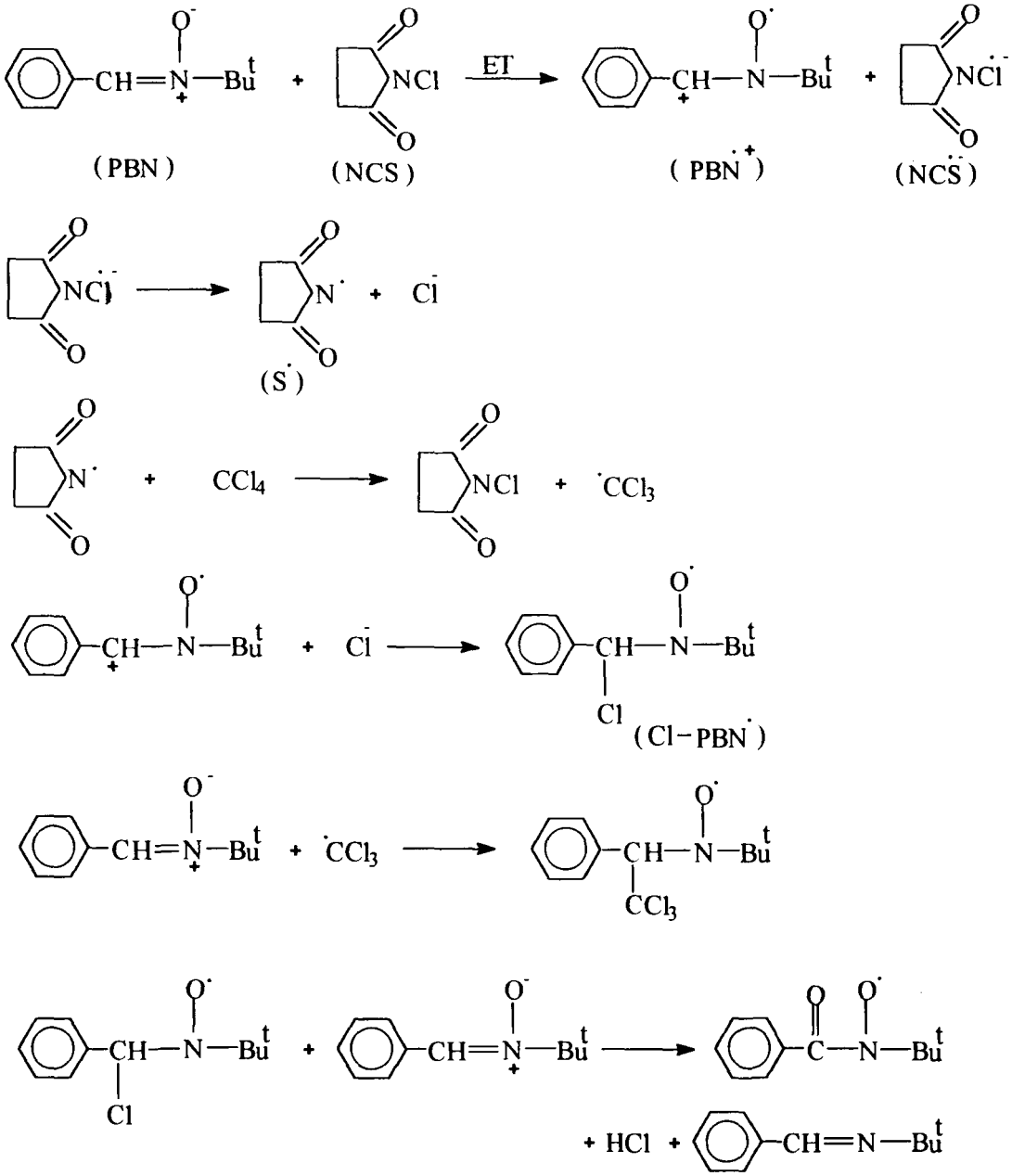
N- Chlorosuccinimide and Nitrone in Carbontetrachloride

The original reaction (bromination by NBS) was discovered by Ziegler in Carbontetrachloride therefore, it became important for us to study this system in CCl_4. Moreover in CCl_4 the possibility of H- abstraction reactions, solvation etc., are minimal.

Immediate spectra recorded on mixing degassed solutions of NCS and PBN in 1 : 1 concentration showed the chloro adduct of PBN with hyperfine splittings a_N = 12.37 G, a^{35}_{Cl}

= 6.18 G, a^{37}_{Cl} = 4.98 G and a^{β}_{H} = 0.81 G along with PBNOX with hyperfine splittings a_N = 7.87 G and g = 2.0066. The chloro adduct decayed in ca. one hour. Another adduct, a triplet of doublet with hyperfine splittings, a_N = 13.80 G and a^{β}_{H} = 1.62 G appeared. The magnitude of hyperfine splitting agrees with the literature value [20] for the adduct CCl_3-PBN·. It is also based on our observation of solvent participation in one way or other in all the reactions studied so far. PBNOX with ^{13}C and ^{15}N isotope splittings as a_N = 8.00 G, a^{α}_{13-C} = 4.70 G, a^{β}_{13-C} = 3.80 G, a^{γ}_{13-C} = 2.70 G and a^{15}_{N} = 11.20 G was left at the end. Reactions repeated at varying concentration of NCS and PBN yielded similar results. Similar results were obtained under photolytic conditions. We suggest that succinimidyl free radicals formed after key step of ET reacts with CCl_4 yielding back NCS and $\cdot CCl_3$ which is trapped by neutral PBN as shown in the Scheme 4.6. In this way the continuous regeneration of NCS is achieved. This could be one of the reason for the longer life time of chloro adduct till all the nitrone present is consumed. In reactions with DMPO, DMPOX was the only adduct observed with hyperfine splittings a_N = 6.8 G and a^{β}_{H} = 3.2 G (2H). Here too we did not observe any ring opened radical product of succinimidyl radicals.

Scheme 4.6



N- Chlorosuccinimide and Nitrone in 1,4- Dioxan

1,4-Dioxan is a unique solvent, its dielectric constant is very low (2.2), yet (i) it participate in hydrogen bonding (moderately) (ii) It can solvate ionic species comparatively lower than alcohols and (iii) participates in charge transfer complexing processes. The major objective of study in this solvent was to see the effect of all the properties mentioned above.

The immediate spectra at equimolar concentration showed two spin adducts (i) Cl-PBN· adduct with a_N = 12.43 G, a^{35}_{Cl} = 6.25 G, a^{37}_{Cl} = 5.25 G, a^{β}_{H} = 0.75 G and (ii) PBNOX with a_N = 8.00 G and g = 2.0066. Decay of Cl-PBN· was followed by the appearance of S-PBN· with hyperfine splittings, a_N = 14.40 G, a^{β}_{H} = 5.75 G and $a_{N'}$ = 1.00 G. This adduct was unstable and was replaced by triplet of triplets (3 x 3) with hyperfine splittings, a_N = 16.25 G and $a_{N'}$ = 1.75 G assigned to S-MNP· adduct. PBNOX with hyperfine couplings ; a_N = 8.00 G, $a^{\alpha}_{13\text{-}C}$ = 4.70 G, $a^{\beta}_{13\text{-}C}$ = 3.80 G, $a^{\gamma}_{13\text{-}C}$ = 2.80 G and a^{15}_{N} = 11.25 G was left at the end. In reaction at higher concentration of NCS to PBN (2 : 1), only an increase in the intensity of chloro and succinimidyl adducts were observed. Similar results were obtained at other concentrations of NCS and PBN. The results can be explained as follows : Primary act of ET

generates S· and Cl^- leading to Cl-PBN· adduct. S· abstracts hydrogen atom from 1,4-Dioxan giving succinimide. The succinimide being nucleophilic [2] reacts with Cl-PBN· adduct replacing chlorine of Cl-PBN· and thus results in the growth of S-PBN· signals with decaying Cl-PBN· adduct. We did not observe any solvent derived radical adduct, one of the possible reason could be its dimerisation. S-PBN· adduct undergoes β - cleavage giving MNP which subsequently traps succinimidyl radical to give S-MNP· adduct.

N- Chlorosuccinimide and Nitrone in DMF

Dimethyl formamide (DMF) is used as a solvent and catalyst in organic synthesis [21]. The understanding of the radical processes is of general interest because of potential side reactions initiated by radicals produced from DMF. Some scant information is available in literature [21] about the free radical chemistry of DMF. So far we have observed solvent derived adducts in our system. We chose this solvent with an objective that besides studying our system, we may get some information regarding the free radical chemistry of DMF itself.

The immediate ESR spectra recorded in reaction carried out at comparable concentrations was due to PBNOX

(triplet, a_N = 8.10 G) and chloro adduct of PBN (a_N = 12.50 G, a^{35}_{Cl} = 6.30 G, a^{37}_{Cl} = 5.20 G and a^{β}_{H} = 0.76 G). The chloro adduct (Cl-PBN·) disappeared in ca. 25 minutes while PBNOX was the only adduct left after ca. 25 minutes with clearly defined splittings of ^{13}C and ^{15}N isotopes. The hyperfine splittings measured from the spectra are a_N = 8.10 G, a^{α}_{13-C} = 4.80 G, a^{β}_{13-C} = 3.80 G, a^{γ}_{13-C} = 2.70 G and a^{15}_{N} = 11.20 G. Reactions were carried out at varying concentrations of NCS to PBN and the results obtained were same. In reaction carried out at higher concentration of PBN to NCS (2 : 1), another triplet appeared along with PBNOX in later stages of the reaction with hyperfine couplings, a_N = 15.70 G and g = 2.0060 Fig. 4.25. Similar triplets were also observed previously and is assigned to di-tert. butyl nitroxide (DTBN). The hyperfine splitting is in agreement with literature value [3]. The spectra simulated Fig. 4.26 using these hyperfine splittings agrees with Fig. 4.25. Similar results were obtained at other higher concentrations of PBN.

In one of the sets traces of 2- methyl 2- nitroso propane (MNP) was added in the system, initially the chloro adduct and PBNOX appeared. However, another set of weak signal which grew in intensity to a well resolved spectra Fig. 4.27, was observed after ca. 30 minutes of the

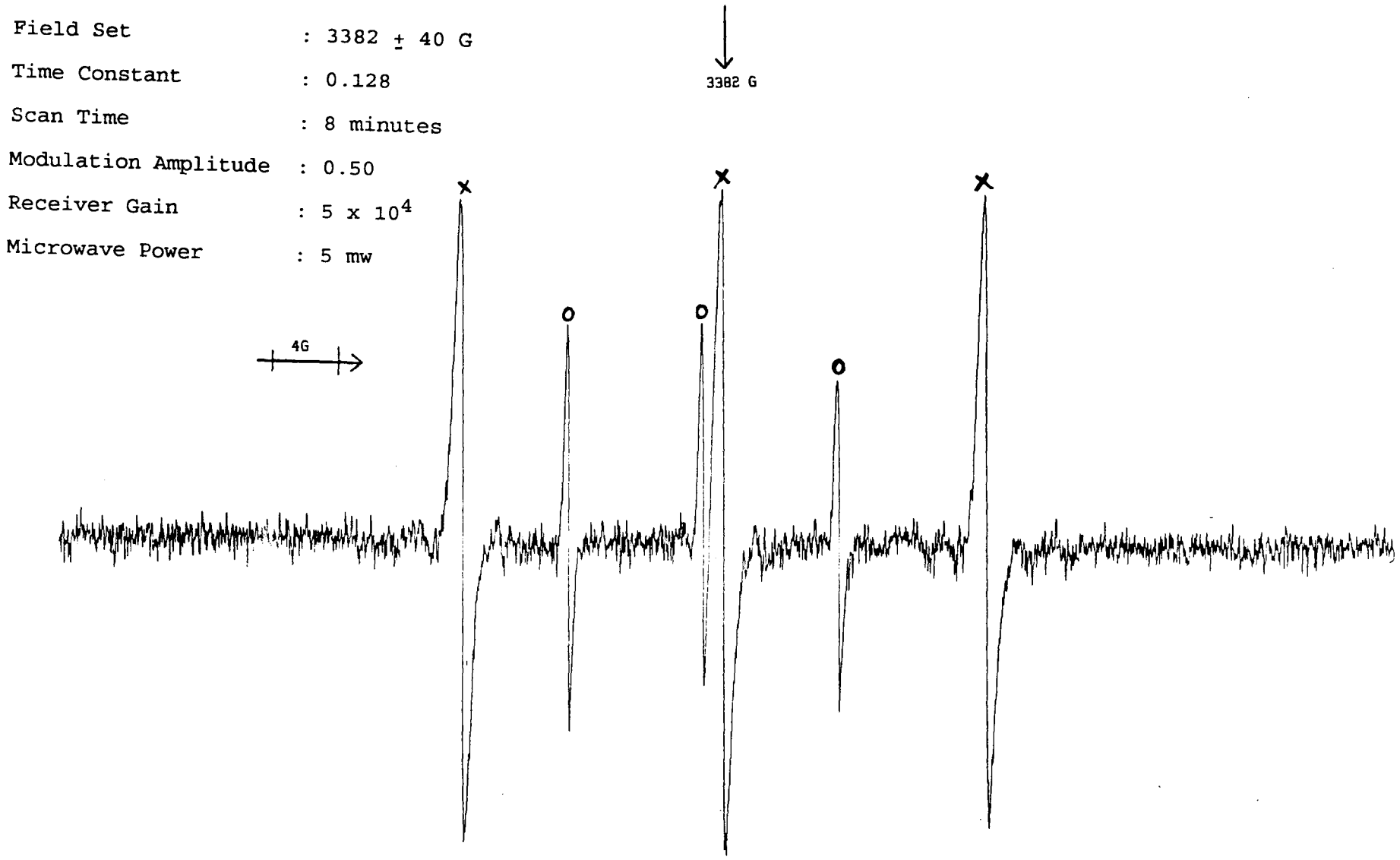


Fig. 4.25 : ESR spectra obtained from PBN and NCS in DMF.

X , DTBN ; O , PBNOX.

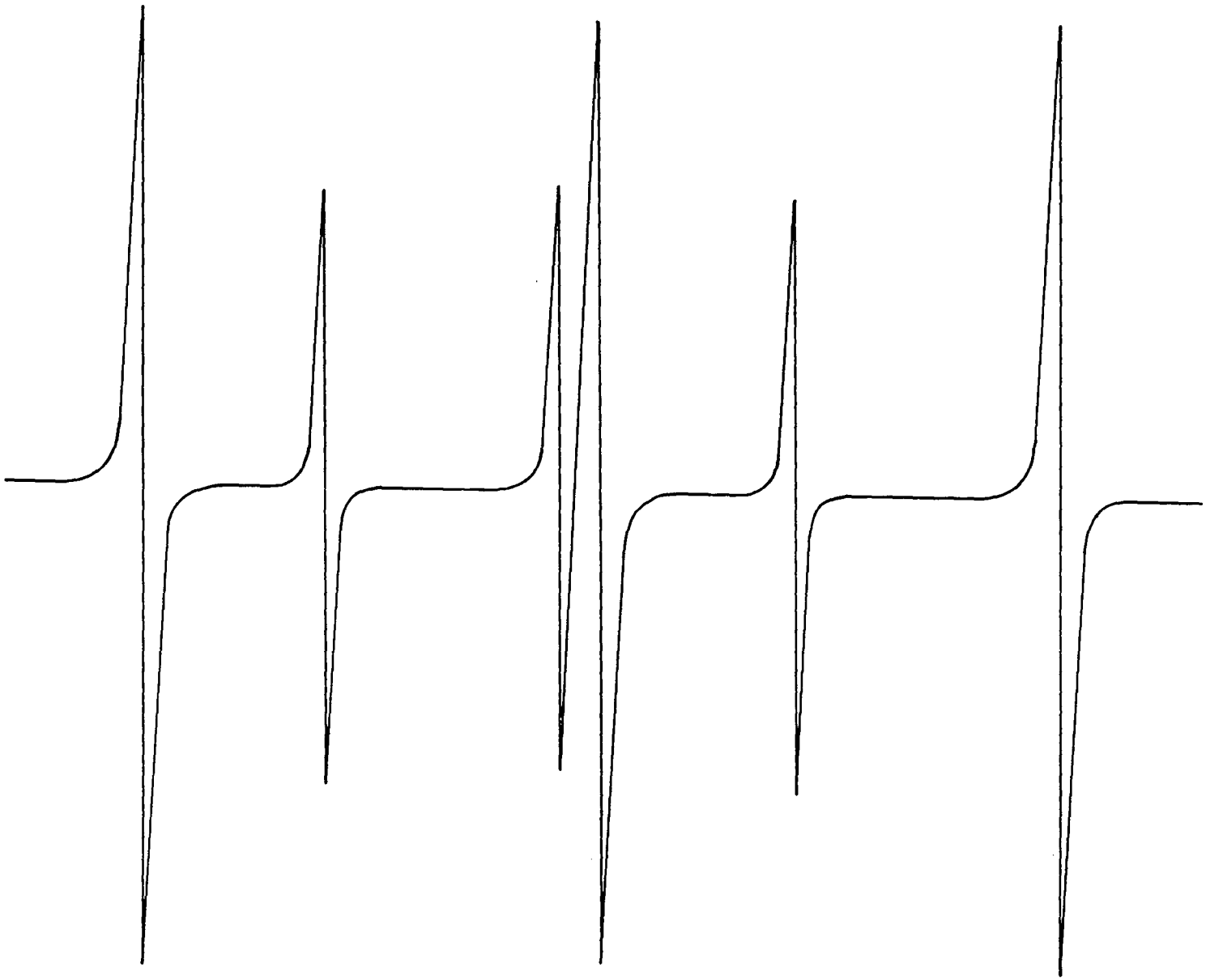


Fig. 4.26 : Simulated spectra of 4.25. DTBN L.W = 0.6, PBNOX L.W = 0.4, ΔG = 0.6.

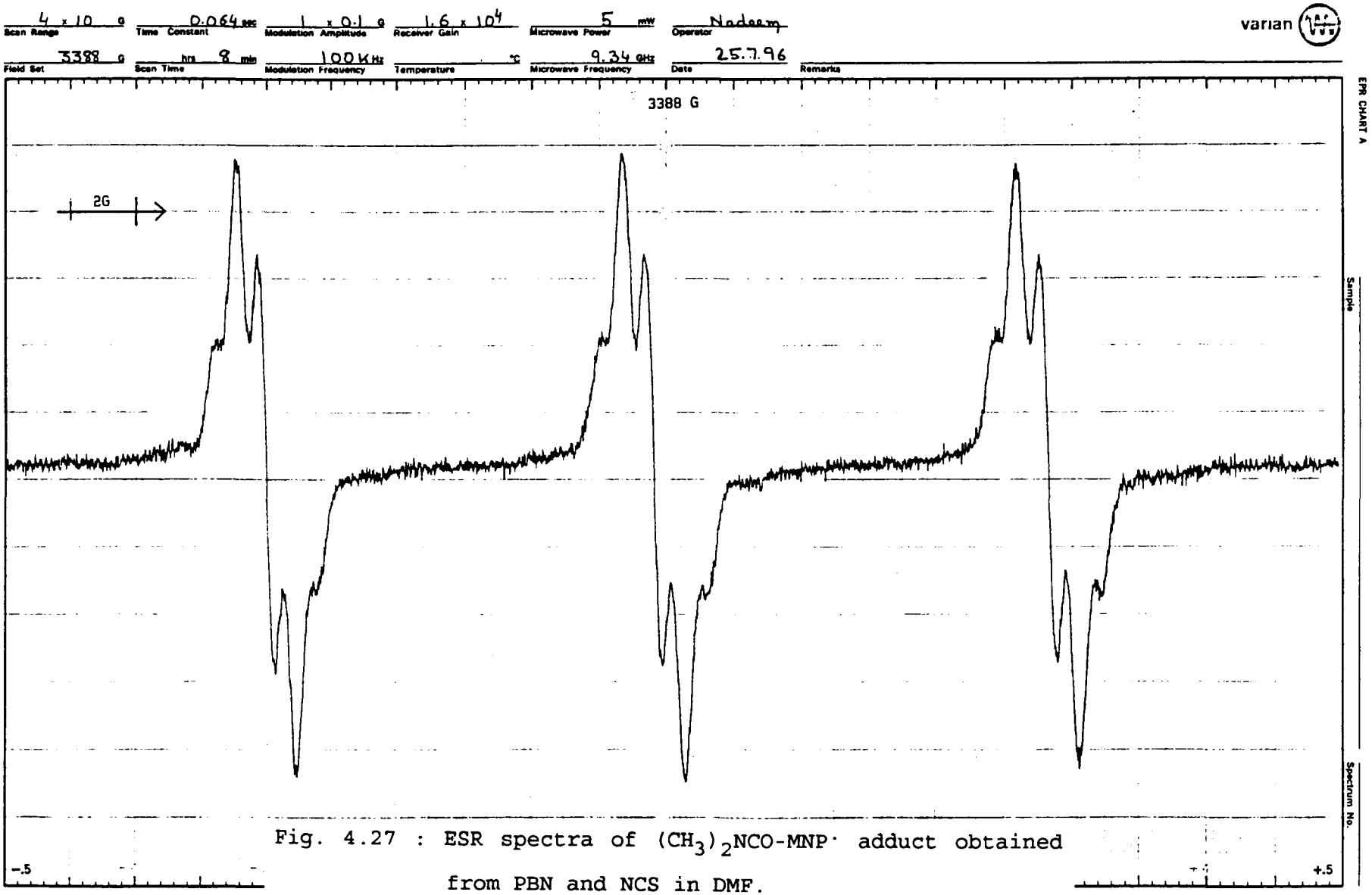


Fig. 4.27 : ESR spectra of $(CH_3)_2NCO$-MNP· adduct obtained from PBN and NCS in DMF.

reaction. When the middle component of the spectra was scanned at scan range of ± 10 G, the finer splittings could be measured accurately. The splitting pattern could be analysed as follows : The primary nitrogen gives a triplet of 1 : 1 : 1 which further splits up into smaller triplets signifying the presence of another nitrogen in the adduct. This further splits up into a splitting pattern 1 : 3 : 3: 1, indicating the interaction with three equivalent H- atoms. The spectra simulated Fig. 4.28 using the hyperfine splittings a_N = 11.75 G, $a_{N'}$ = 0.48 G and a^{β}_{H} = 0.67 G (3 H) matched very well with the observed spectra. On the basis of analysis of the hyperfine splittings it is assigned to adduct formed by H- abstraction from formyl group of DMF and subsequent trapping by MNP. Our hyperfine values are in good agreement with those reported [22]. The observance of interaction from only one methyl protons of the adduct has been reported earlier [22]. It could be due to hindered rotation of the methyl groups across the N - C bond of the adduct. These results thus supports our earlier proposal that succinimidyl radicals are possibly involved in H- abstraction reaction from the solvent.

The proposed mechanism is shown in Scheme 4.7. The mechanism involved in the generation of PBNOX is explained

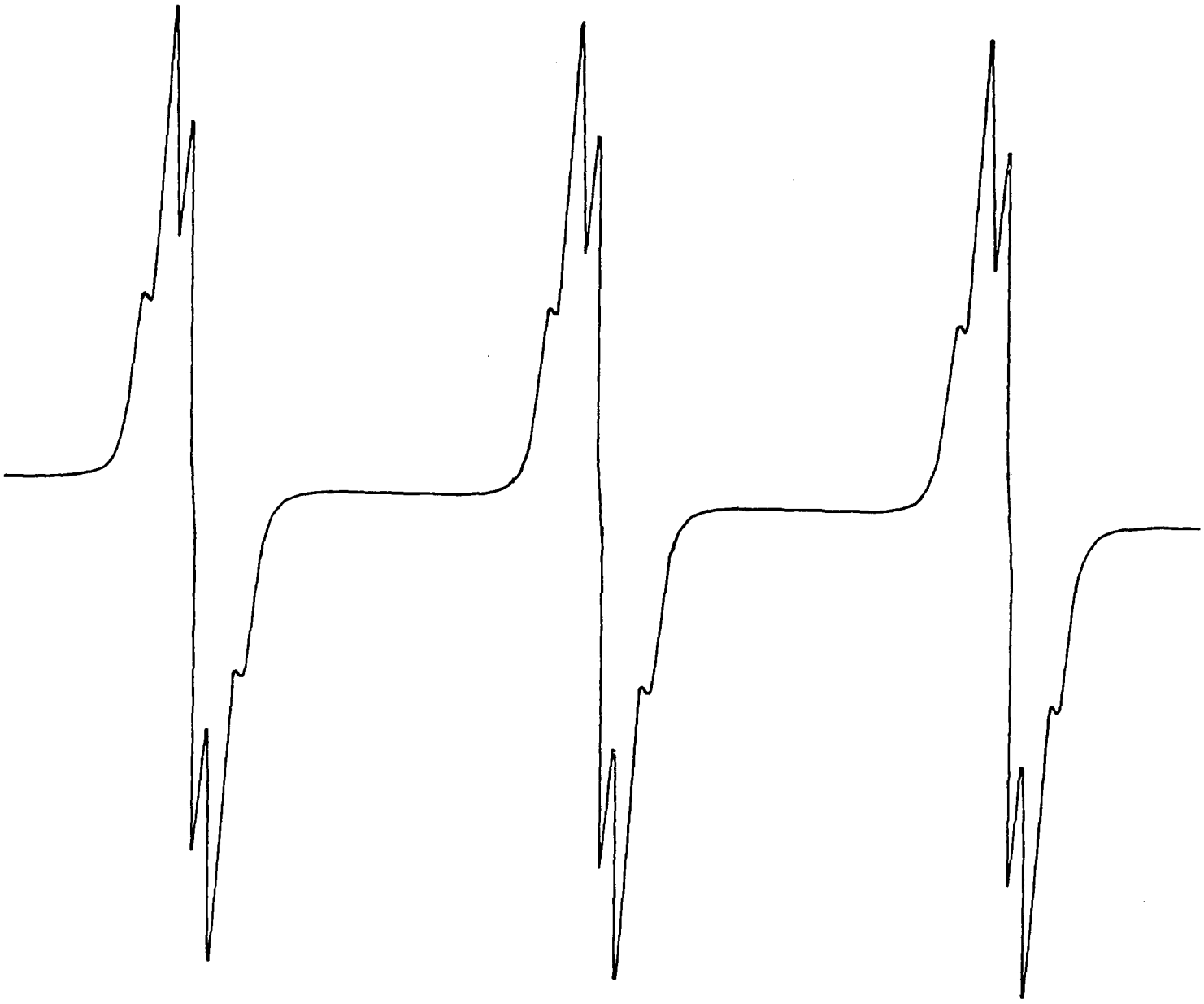
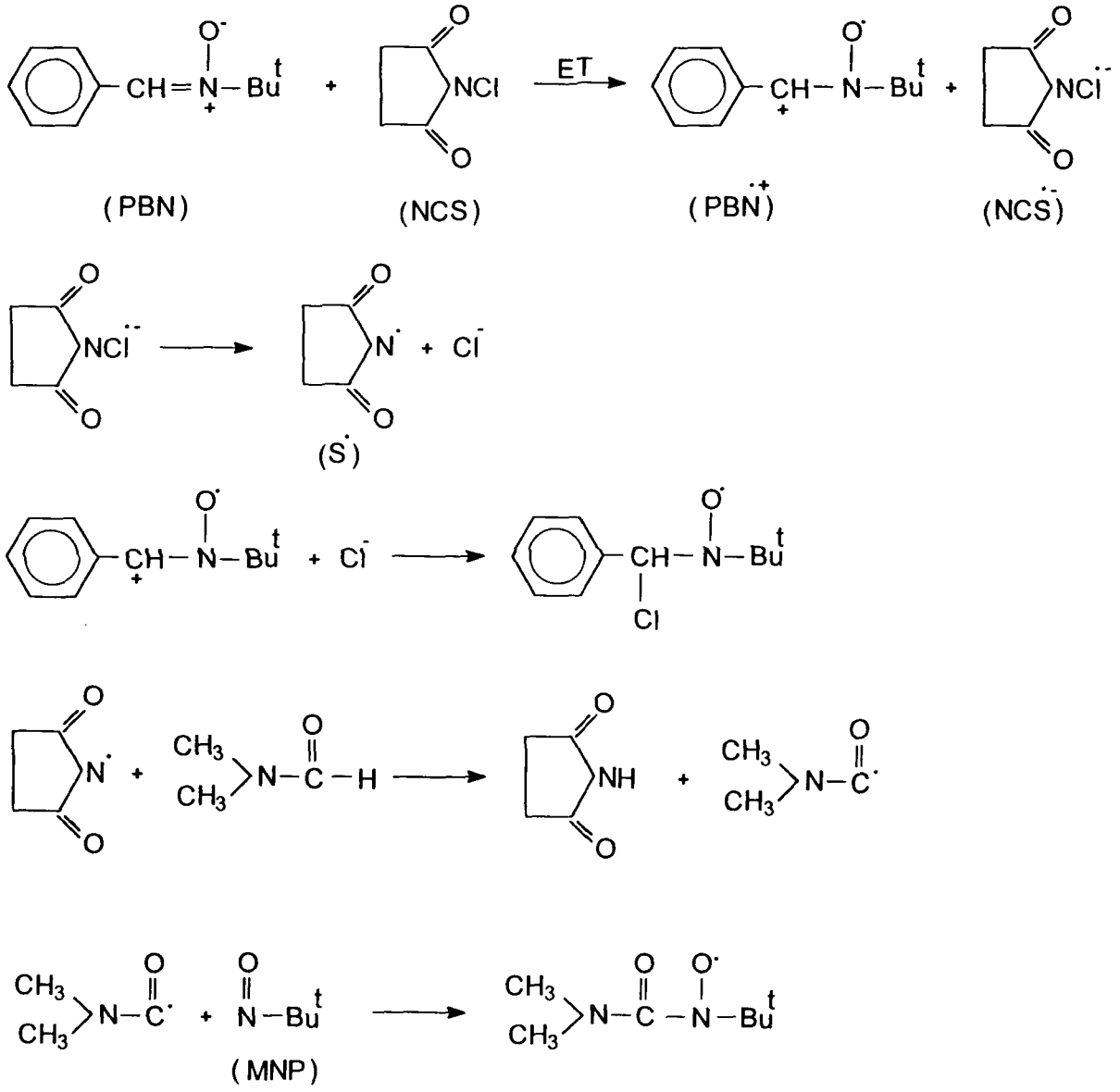


Fig. 4.28 : Simulated spectra of 4.27 using parameters calculated from experimental spectra.

Scheme 4.7



earlier. The absence of succinimidyl adduct is attributed to low stability of this adduct in this solvent. Another possible reason could be H- abstraction by succinimidyl radicals from the solvent giving rise to solvent derived radicals.

Reactions were also carried out with DMPO. The immediate spectra observed at comparable concentration of NCS and DMPO showed a set of signals with hyperfine splittings a_N = 14.40 G, a^{β}_H = 20.30 G and $a_{N'}$ = 2.00 G. The order and magnitude of the hyperfine splittings are similar to those observed earlier and are assigned to succinimidyl adduct of DMPO (S-DMPO·). However, this adduct was not stable and was replaced by signals of DMPOX with hyperfine splittings a_N = 6.80 G and a^{β}_H = 3.26 G. Reactions carried out at other concentration ratios yielded similar results. We suggest the mechanism similar to that propose in Scheme 4.1. As observed earlier that in alcohols the chloride ions are removed from the reaction site through solvation, reactions were carried out in 10 % ethanol in DMF. The immediate spectra observed at comparable concentrations of NCS and PBN showed a medium intensity triplet of doublets with hyperfine splittings a_N = 14.61 G and a^{β}_H = 2.80 G. The order and magnitude of the hyperfine splittings are similar to that observed

earlier and is assigned to ethoxy radical adduct of PBN. However, this adduct disappeared in ca. 40 minutes and was replaced by a spectra consisting of three adducts. A triplet of triplet (3 x 3) with hyperfine splittings a_N = 16.7 G and $a_{N'}$ = 1.82 G and is assigned to succinimidyl adduct of MNP (S-MNP·). This was accompanied by triplets of PBNOX and another adduct assigned to $(CH_3)_2NCO$-MNP·. The hyperfine splittings are similar to that observed earlier. PBNOX was the only signal left at the end of the reaction. In the light of these results we suggest that ethoxy radical adduct undergoes β - cleavage yielding MNP which subsequently traps succinimidyl radicals to give S-MNP· adduct. The succinimidyl radicals apart from ethanol, it also abstracts H- atom from DMF giving $(CH_3)_2NCO$-MNP· adduct. The mechanism involved in the generation of ethoxy radical adduct and PBNOX is explained earlier. However, it is surprising that we did not see succinimidyl adduct of PBN probably due to change in reaction pathways.

These results suggest that cleavage of NCS radical anion leads to succinimidyl radicals and chloride ions with no ring opening reaction of succinimidyl radicals. These results also provides a good example of solvent participation in radical reactions.

N- Chlorosuccinimide and Nitrone in DMSO

DMSO is a widely used solvent and presents with some interesting results at several different levels. It has been routinely used as a source of $\cdot CH_3$ radicals both thermally and photochemically [23]. Attack of oxygen centered radicals on sulphur followed by scission of resulting sulfonium radical has been proposed in various cases for $\cdot CH_3$ radicals generation [24]. During the course of study in this solvent we have come across some new and interesting results and are described here.

Degassed solutions of NCS in 10 % DMSO in benzene was mixed with degassed solutions of PBN. The whole operation was carried out in minimum day light. The immediate spectra observed was of chloro adduct of PBN. The hyperfine values are a_N = 12.60 G, a^{35}_{Cl} = 6.20 G, a^{37}_{Cl} = 5.16 G and a^{β}_{H} = 0.8 G. However, it was replaced by another set of signals after ca. 15 minutes shown in Fig. 4.29. The hyperfine splittings measured from the observed spectra are, a_N = 15.20 G, a^{β}_{H} = 11.40 G and $a_{N'}$ = 1.40 G (from succinimidyl nitrogen). This splitting pattern is a characteristic splitting of some nitrogen centered radical adduct and could be analysed as follows : The primary nitrogen (^{14}N) gives splitting pattern 1 : 1 : 1. Each of these lines further splits up into signals of

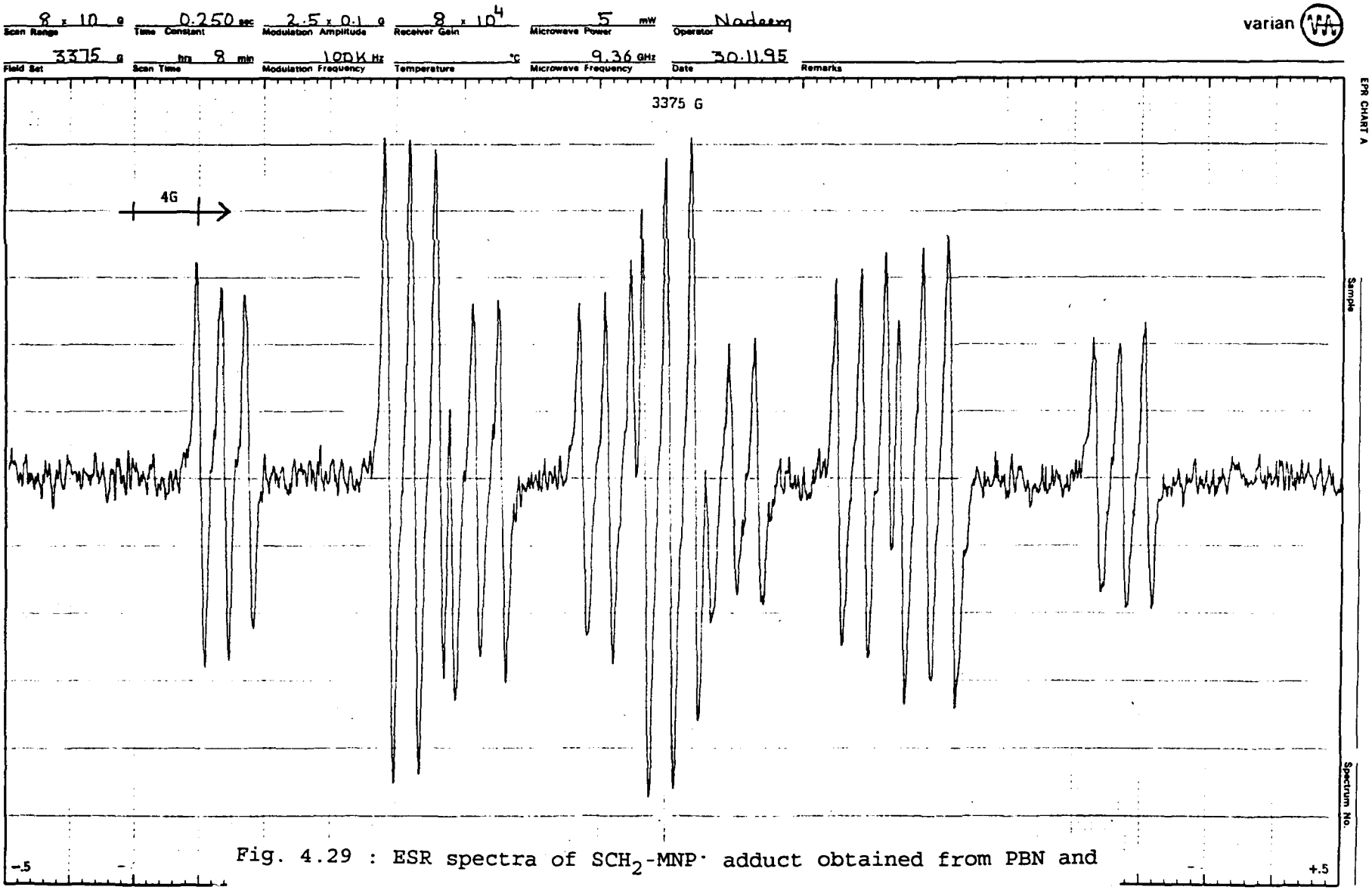


Fig. 4.29 : ESR spectra of SCH_2-MNP· adduct obtained from PBN and NCS in DMSO.

intensity pattern 1 : 2 : 1, signifying the presence of two equivalent secondary hydrogen atoms. Each of these lines further splits up into a triplet of intensity pattern 1 : 1 : 1. This clearly shows the presence of another nitrogen atom (^{14}N) in the adduct. On this basis it is assigned to succinimidylmethyl radical adduct of MNP (SCH_2-MNP$^{\cdot}$). The simulated spectra Fig. 4.30 agrees with the experimental one. The hyperfine parameters are in good agreement with those reported by Perkins et al. [25]. They have reported the similar spectra in photochemical and / or thermal decomposition of tert.- butylsuccinimide peroxycarboxylate using MNP as a spin trap.

The reactions were carried out at varying concentration ratios of substrate to nitrone. The results obtained were essentially the same. However, in reactions carried out at higher concentration ratios of PBN to NCS another triplet with hyperfine splittings a_N = 15.70 G and g = 2.0060 was observed in later stages of the reaction and is assigned to di- tert. butyl nitroxide. The proposed mechanism is shown in Scheme 4.8.

We suggest that the chloro adduct (Cl-PBN$^{\cdot}$) formed in the system is unstable and decays out in ca. 15 minutes. We postulate its β - scissioning, leading to the formation of MNP and the intermediate (R$^{\cdot}$). The formation of di-

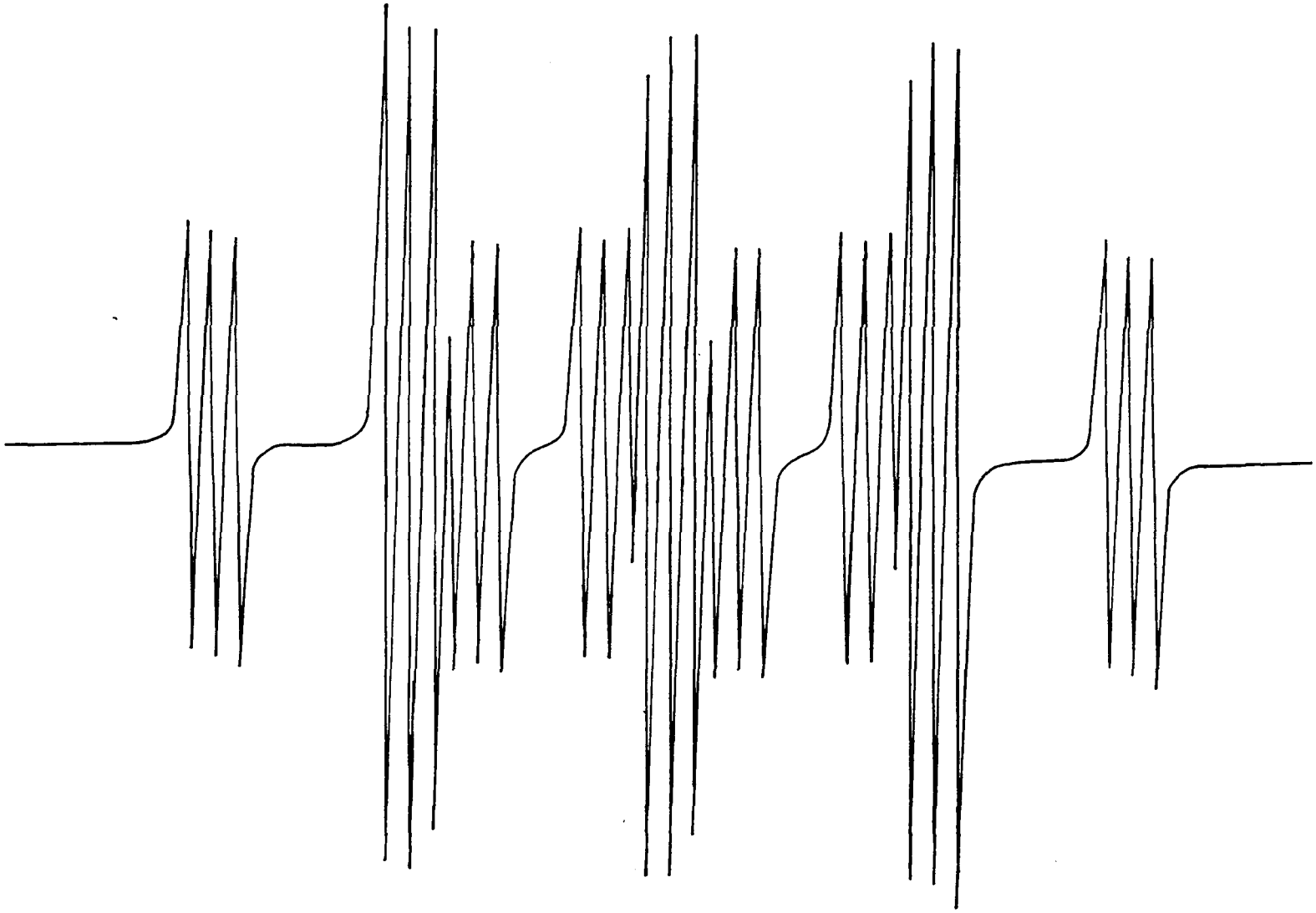
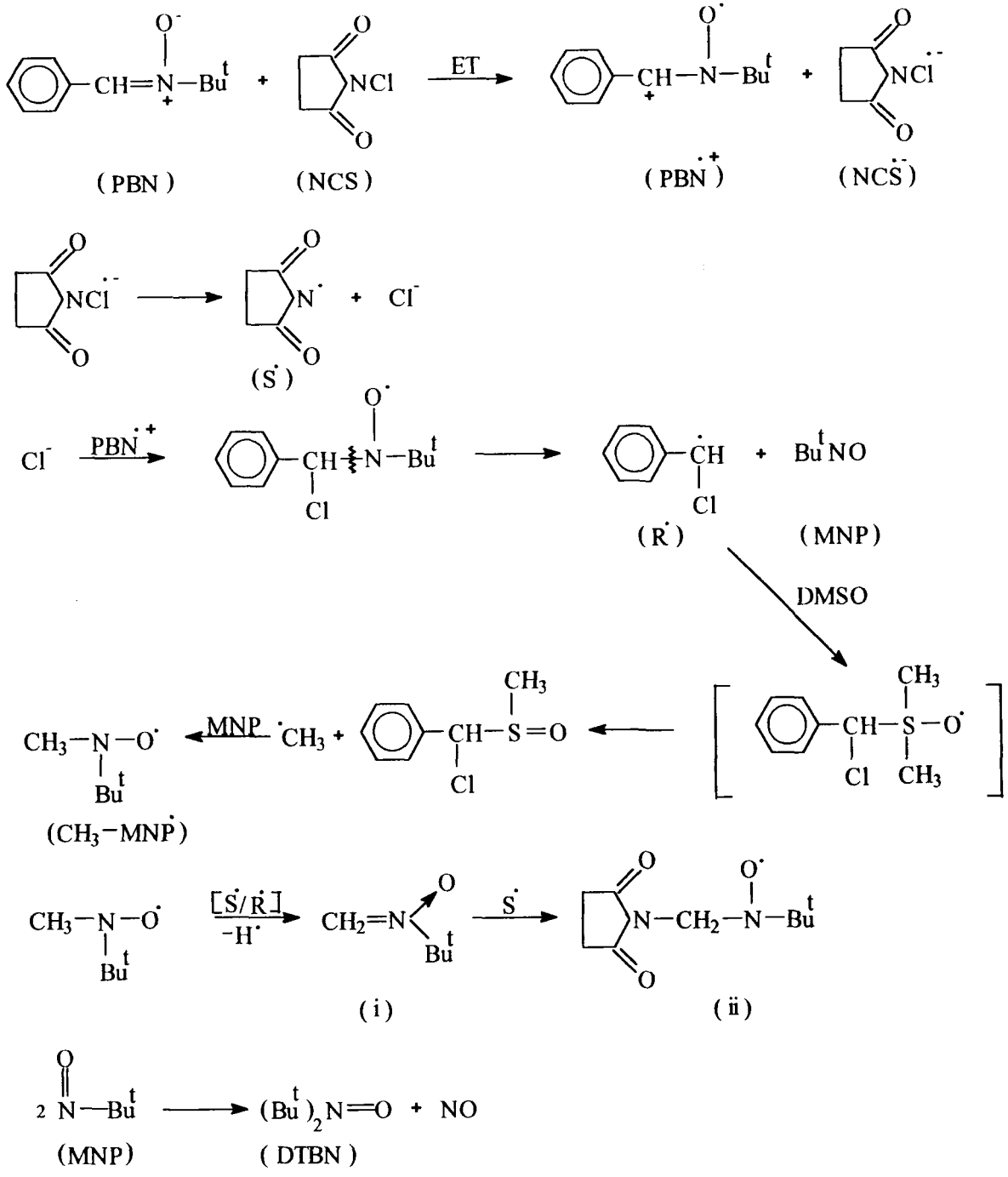


Fig. 4.30 : Computer simulated spectra of 4.29 using parameters determined from experimental spectra L.W = 0.4.

Scheme 4.8


ET
(PBN)
(NCS)
(PBN•+)
(NCS•−)
Cl⁻
PBN•+
(S•)
(R•)
(MNP)
DMSO
MNP
(CH3−MNP•)
[S•/R•]
-H•
(i)
(ii)
2
(MNP)
(DTBN)
NO

tert. butyl nitroxide in later stages of the reaction confirms the formation of MNP in the system. We suggest that R· being reactive, add to DMSO yielding $\cdot CH_3$ which is trapped preferentially by MNP. The R· and / or S· abstract hydrogen from CH_3-MNP· adduct leading to methylene nitrone (i). The methylene nitrone thus formed is itself a highly reactive spin trap and reacts with S· yielding succinimidylmethyl nitroxide (ii).

Under similar reaction conditions in one of the sets, traces of MNP was added and intense signal due to adduct (ii) was observed which again confirms the formation of MNP during the course of the reaction. In another set, traces of N- Methylsuccinimide was added but no effect on the appearance or intensity of the adduct (ii) was observed and therefore it rules out the possibility of the formation of N-Methylsuccinimide from $\cdot CH_3$ and S· followed by H-abstraction and subsequent trapping by MNP leading to the formation of adduct (ii), as another possible pathway.

We have postulated the origin of $\cdot CH_3$ from DMSO. In order to confirm it the reaction was repeated with deuterated DMSO. The immediate spectra observed was a triplet of septet Fig. 4.31 with hyperfine splittings as a_N = 15.25 G, a^{β}_{D} = 1.75 G (2D) and $a_{N'}$ = 1.40 G (from

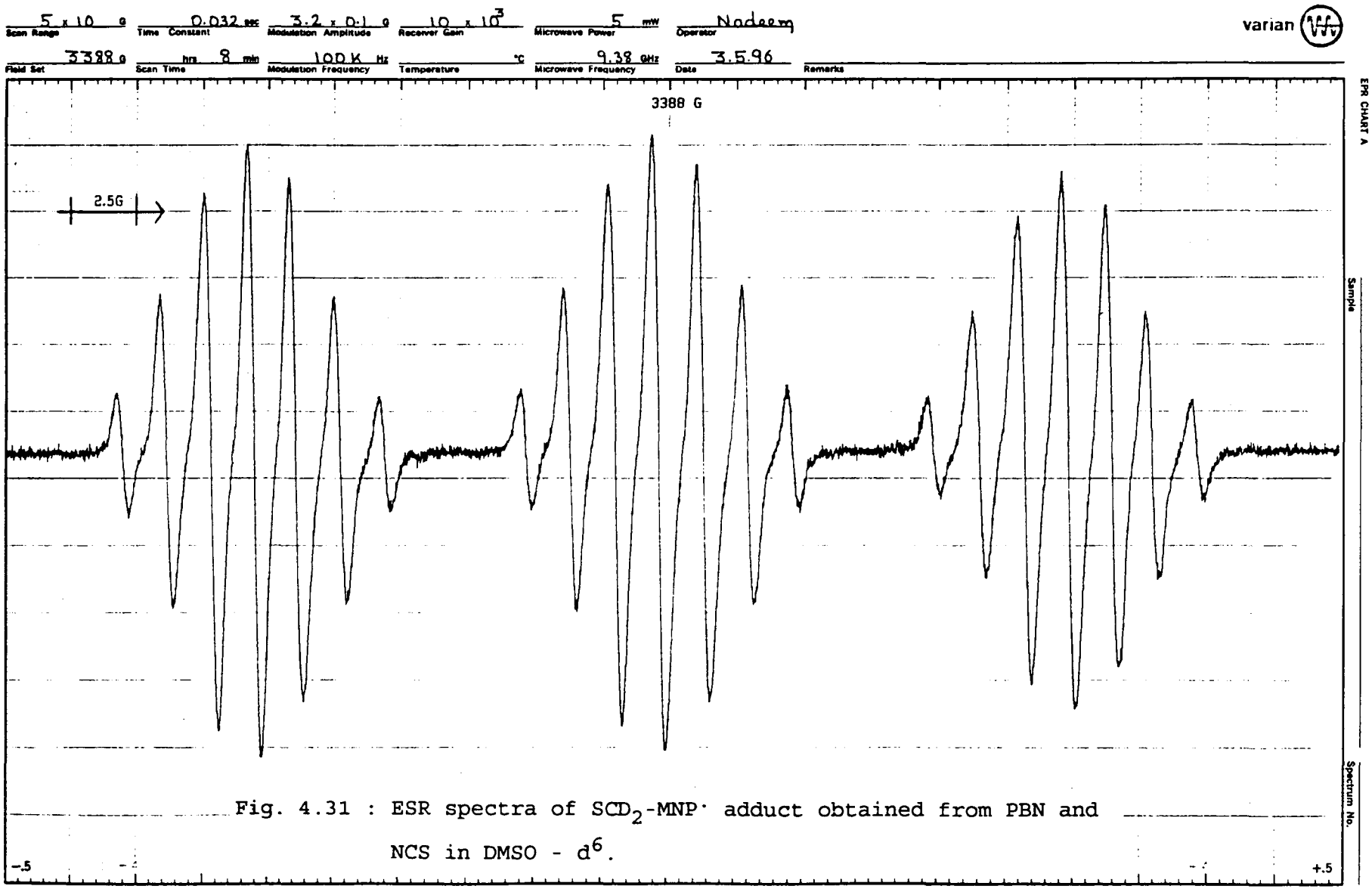


Fig. 4.31 : ESR spectra of SCD_2-MNP$^{\cdot}$ adduct obtained from PBN and NCS in DMSO - d^6.

succinimidyl nitrogen). The simulated spectra Fig. 4.32 matched very well with the experimental spectra. If our postulation that $\cdot CH_3$ originates from DMSO alone is correct, then the hyperfine splitting from the deuterated analogue a_{CD2} should be in accordance with the ratio of magnetic moments of hydrogen and deuterium (μ_H / μ_D = 6.51). The hyperfine values observed in our case is indeed (11.40 / 6.51 = 1.75 G) 1.75 G. The spectral line width of the deuterated analogue is 0.5 G which is more than the difference between the hyperfine splittings from CD_2 and nitrogen atom of the succinimidyl moiety, hence hyperfine splitting from nitrogen atom of the succinimidyl moiety could not be resolved from CD_2. The similar behaviour has been reported [26] and is ascribed due to difference in the rotational barrier between the CH_2 and CD_2 groups of the spin adduct. Thus the spectra in Fig. 4.31 is assigned as decidedly due to the deuterated analogue SCD_2-MNP$\cdot$.

Reactions carried out with DMPO yielded only succinimidyl adduct followed by DMPOX. The hyperfine splittings of the succinimidyl adduct are a_N = 14.41 G, a^{β}_H = 20.36 G, $a_{N'}$ = 2.2 G and that of DMPOX are a_N = 6.80 G and a^{β}_H = 3.30 G. Since DMPO is not known to undergo β - scissioning, the absence of the final adduct (ii) in this

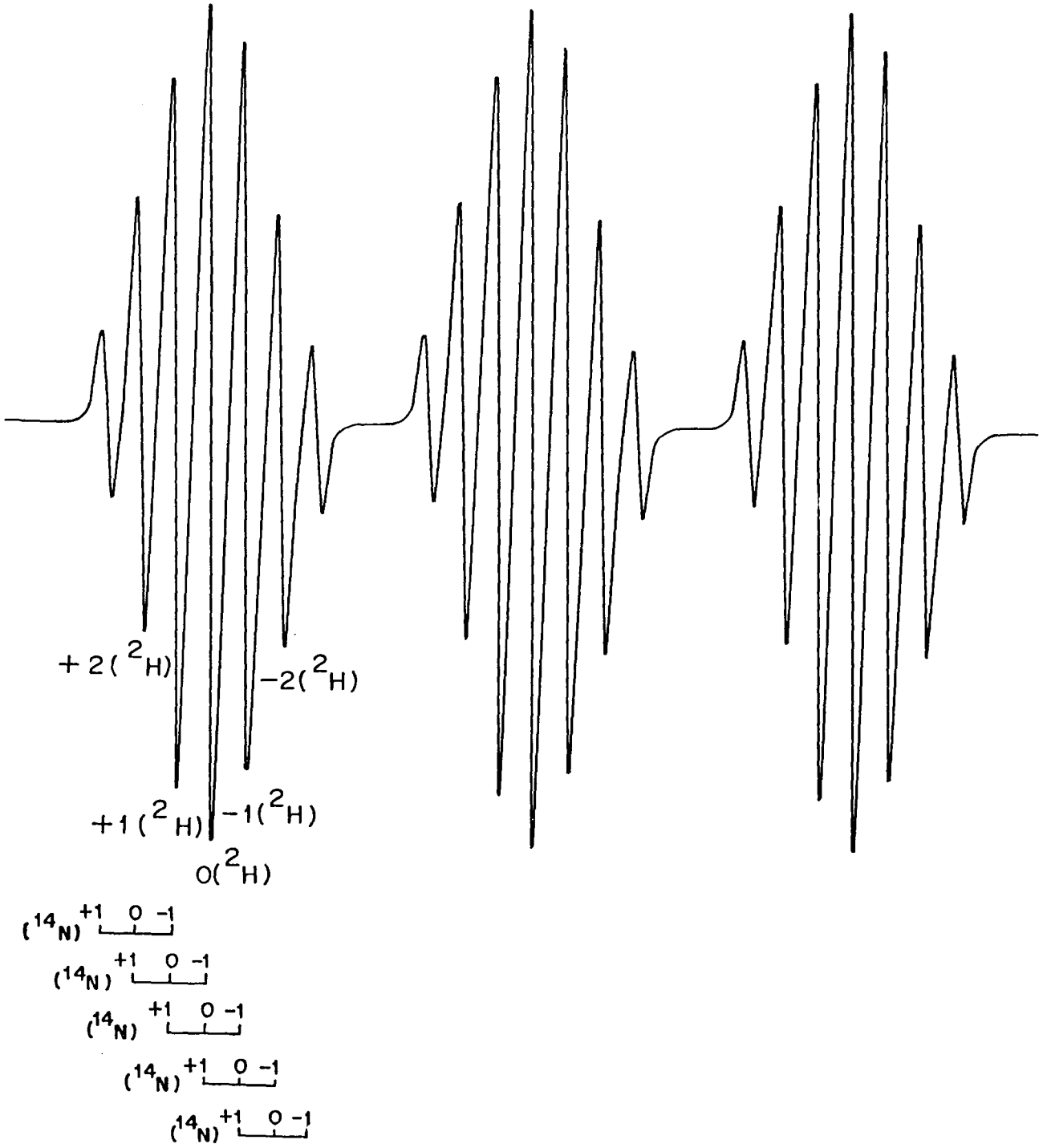


Fig. 4.32 : Simulated spectra of 4.31 using experimentally determined hyperfine parameters L.W = 0.5.

system supports our postulation of generation of methyl radicals from DMSO through the path shown in the Scheme. When similar experiments were done in DMSO alone, we did not see chloro adduct but adduct (ii) was observed after ca. 15 minutes. The chloro adduct seems to be highly unstable in DMSO. Thus the origin of $\cdot CH_3$ radicals from DMSO through a new path is established. To the best of our knowledge, the spectra for the deuterated analogue of tert.-butyl succinimidylmethyl nitroxide is being reported for the first time.

Salient features of the above work are listed below :

1. It has been demonstrated through UV experiments that PBN is relatively a better electron donor than acceptor.
2. Charge transfer complexes believed to be precursors to ET processes has been demonstrated through the appearance of an isosbestic point, a positive indication for the feasibility of electron transfer processes.
3. We confirm that electron captured dissociation of NCS leads to Succinimidyl free radical ($S\cdot$) and Chloride ion (Cl^-).

4. The observance of succinimidyl radical adduct of PBN in benzene at higher concentration of PBN refutes earlier proposals that succinimidyl radicals are trapped by benzene.

5. The observed enhanced stability of the chloro adduct (Cl-PBN·) in benzene as compared to other solvents, lends support to the hypothesis that " spin adducts with good leaving groups will be unstable and could be detected only in solvents of relatively low permitivity or under conditions of continuous generation for example, during photolysis ".

6. We are successful in observing satellite signals from ^{13}C in all the different positions of PBNOX. To the best of our knowledge it is being reported first time. Such examples are rare for conformational studies by ESR.

7. The recently proposed mechanism " inverted spin trapping " is successfully demonstrated at ambient temperatures.

8. Succinimidyl adduct of DMPO is being reported first time.

9. We propose that the system involves only two possible chain carriers, succinimidyl free radical and chloride ions. We did not observe any sign of ring opening of succinimidyl radical, a feature highlighted by some

workers.

10. The role of polar and hydroxylic solvents in solvating the charged species and thus diverting the reaction pathways have been clearly observed. The observance of succinimidyl adduct of PBN in alcohols confirms the cleavage mode of $NCS\cdot^{-}$.
11. A new route for the generation of methyl radicals from DMSO is being suggested.
12. None of our results provide evidence for the two states of succinimidyl radical, σ and π proposed by some researchers.

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CHAPTER V

RESULTS & DISCUSSION

N - BROMOSUCCINIMIDE AND N - IODOSUCCINIMIDE

This chapter describes the results of single electron transfer (SET) reaction study of N- Bromo and N- Iodo succinimides with Nitrones.

N- Bromosuccinimide (NBS)

The bromine is next to chlorine in the group in the periodic table. It is less electronegative but heavier than chlorine, bromine atoms dimerise with greater ease than chlorine atoms therefore, replacement of chlorine in N- Chlorosuccinimide by bromine may have significant effect on the reaction mechanism. With this information in hand the study of SET chemistry was extended to NBS to establish whether the reactivity of NBS is a function of the bromine substitution in the molecule or is dependent on the reaction conditions (solvent, concentration etc.). The other aspects of NBS such as ring opening reaction, H-abstraction etc., were also investigated.

As discussed in previous chapter, the necessary and essential conditions for an electron transfer to take place were taken care of first. The possibility of the formation of charge transfer complexes through UV was investigated. As discussed earlier the appearance of an isosbestic point is a proof good enough to establish the charge transfer complex formation between NBS and PBN.

UV STUDY

In our system there are two components, PBN as an electron donor (as well as spin trap) and NBS as electron acceptor. As a representative plot Fig. 5 wherein the UV spectra of the mixture of NBS and PBN in acetonitrile in different relative proportions are shown. It is evident from the spectra that a clear isosbestic point is observed at 244 nm. This isosbestic point does not shift with the change in the relative concentration of the constituents, indicating the presence of a single equilibrium. Similar isosbestic points were observed in other solvents also. Thus the formation of charge transfer complex between PBN and NBS suggests the feasibility of ET reaction. The results of ESR studies are described below.

ESR STUDY

N- Bromosuccinimide and Nitrone in Benzene

The immediate spectra observed at 1 : 1 concentration of NBS and PBN showed only a triplet of (1 : 1 : 1), with hyperfine splittings a_N = 8.00 G, g = 2.0066. The spectra with these features and parameters have been assigned (preceding chapter) to PBNOX. The reaction was monitored continuously. A continuous increase in the PBNOX intensity was observed and this was the only signal left at the end of the reaction. It could be recorded with well

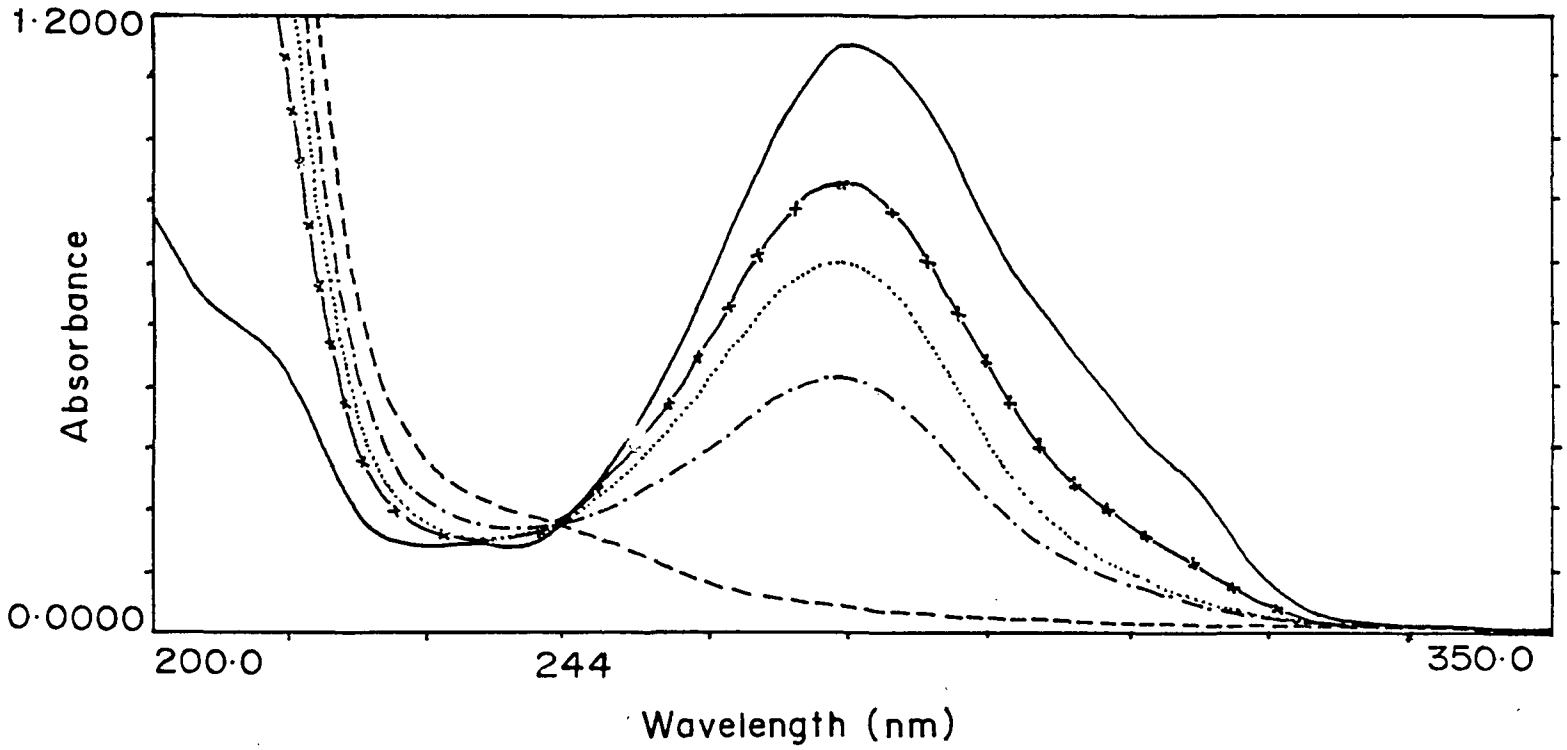
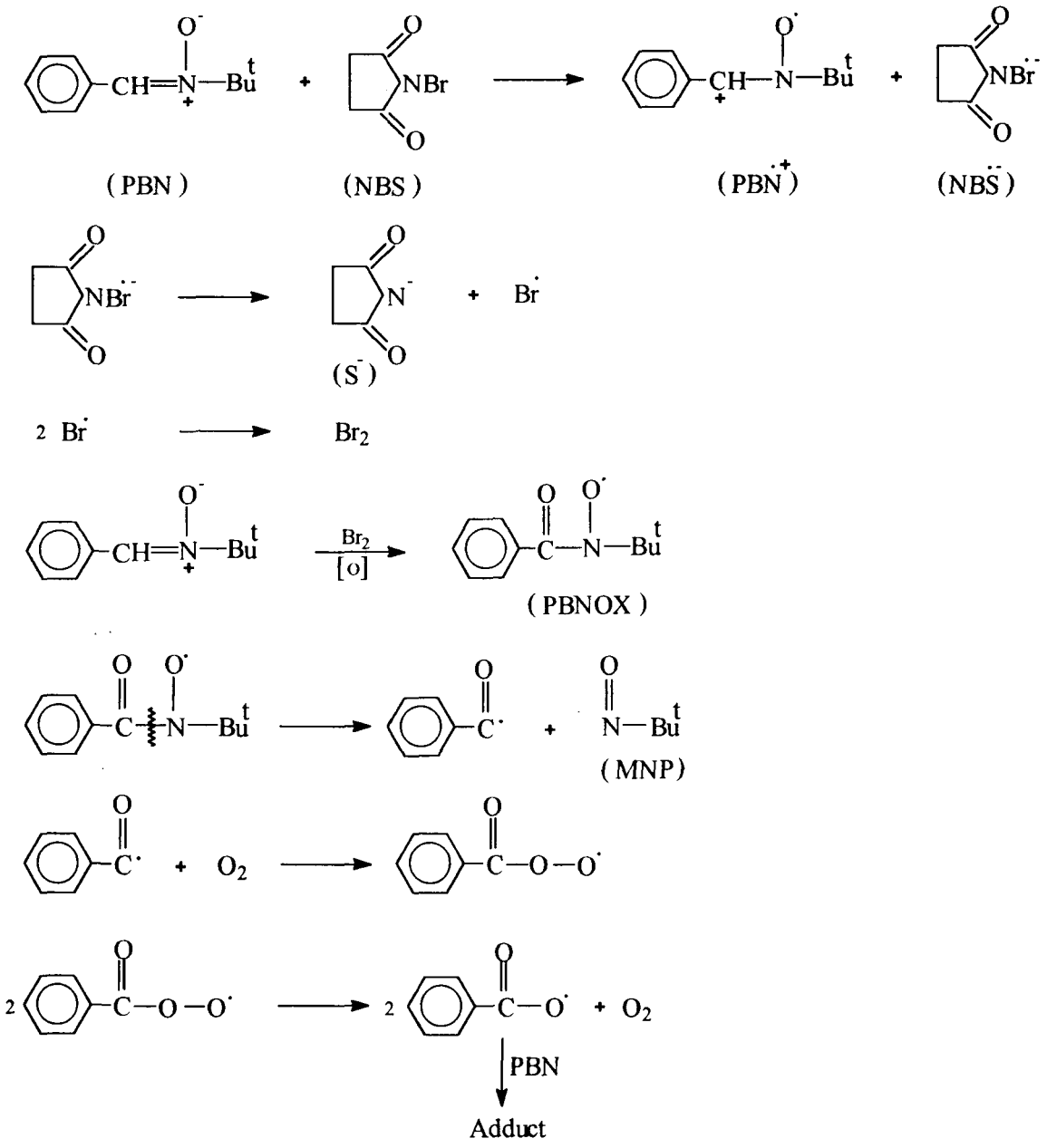


Fig. 5 : UV spectra of PBN and NBS at different relative concentrations. ——— , PBN alone (6.6×10^{-5}) ---, NBS alone (6.62×10^{-5}) ; ·····, NBS & PBN in I:I -x-x-, I:II ; —·—·—, II:I

defined ^{13}C and ^{15}N isotope splittings as a_N = 8.00 G, $a^{\alpha}_{13\text{-}C}$ = 4.78 G, $a^{\beta}_{13\text{-}C}$ = 3.87 G, $a^{\gamma}_{13\text{-}C}$ = 2.75 G and a^{15}_{N} = 11.20 G. Reactions carried out at higher concentration ratio of NBS to PBN (2 : 1), showed two set of signals ; one triplet of doublet (3 x 2) with hyperfine splitting a_N = 13.12 G, a^{β}_{H} = 1.50 G, g = 2.0061 and the other was PBNOX. The 3 x 2 spectra disappeared in ca. 30 minutes and PBNOX was the only signal left. This triplet of doublet with these parameters in the previous chapter has been assigned to benzoyloxyl radical adduct of PBN. The reaction carried out at other concentration ratios of NBS to PBN showed similar results. Solution turned yellow in these runs signifying the formation of molecular bromine (Br_2) [1].

Similar results were obtained in reactions carried out at higher concentration ratios of PBN to NBS. On the basis of these experimental results the proposed mechanism is shown in Scheme 5. We propose that, the reaction is initiated by an electron transfer from PBN to NBS, resulting in the formation of PBN radical cation ($PBN^{\cdot +}$) and NBS radical anion ($NBS^{\cdot -}$) which undergoes cleavage to give succinimidyl anion and bromine atom. This is proposed on the basis of redox properties of the substrates (PBN E^{O} = 1.50 V, NBS E^{O} = 0.30 V) [2] and in

Scheme 5



accordance with electronegativity difference between succinimidyl and bromine moities (3.0 versus 2.8) [3]. In spite of our best efforts under these conditions we did not see any bromo and / or succinimidyl radical adduct of PBN. The absence of bromo adduct could be postulated either due to high rate of dimerisation of bromine atoms leading to the formation of molecular bromine (a powerful oxidant) or could be due to the reported high instability of the bromo adduct [4] of PBN. The absence of succinimidyl adduct of PBN can be explained on the ground that molecular bromine formed immediately oxidises any S-PBN· formed. Br_2 also oxidises PBN to PBNOX, through a mechanism recently proposed by Janzen [5]. We suggest that benzoyloxyl radicals are formed by the inadvertantious oxidation of benzoyl radicals by the traces of oxygen present in the system and subsequent trapping by PBN, as shown in Scheme 5.

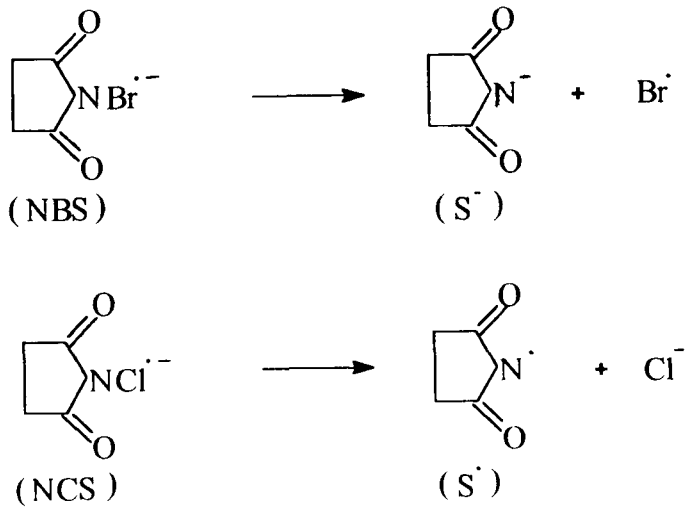
If our postulation of the formation of Br· is correct then the effective removal of Br· from the system by some strong Br· scavenger like bicyclopentadiene should have a qualitative impact on the reaction pathways. Experiments were repeated in the presence of traces of bicyclopentadiene. Weak signals which grew in intensity to a well resolved spectra of splitting pattern 3 x 3 x 2

were observed. This is a characteristic spectra of some nitrogen centered radical adduct of PBN. The hyperfine splittings measured from the observed spectra are ; a_N = 14.39 G, a^{β}_{H} = 6.12 G and $a_{N'}$ = 1.12 G. On the basis of analysis of the hyperfine couplings and the splitting pattern it has been assigned to succinimidyl adduct of nitrone (S-PBN·) [6]. This was accompanied by extremely weak triplets of PBNOX. Succinimidyl adduct disappeared in ca. 20 minutes while only weak signals of PBNOX were left at the end of the reaction.

These results clearly show that once bromine is removed from the system, the oxidation of S-PBN· is inhibited and only then it is observed. Weak signals of PBNOX also signifies the removal of bromine to a large extent from the reaction system. In order to test the postulation that origin of PBNOX is due to Br_2, degassed and dilute solution of Br_2 was added to degassed solution of nitrone (of same concentration used in our experiments) in the ESR cell. The triplets corresponding to PBNOX with hyperfine splitting a_N = 8.00 G, g = 2.0066 was observed immediately along with another weak triplet of doublets with hyperfine splittings, a_N = 13.12 G, a^{β}_{H} = 1.50 G and g = 2.0061 assigned to benzoyloxyl radical adduct of PBN. A continuous increase in the intensity of this signal was

observed. However, this triplet of doublet was replaced (ca. four hours) by another triplet with large nitrogen hyperfine splittings a_N = 15.60 G and g = 2.0058 assigned to di-tert. butyl nitroxide (DTBN). We propose that benzoyloxyl radical adduct of PBN undergoes β - cleavage producing MNP which is known to give DTBN. However, the formation of MNP cannot be assigned to a single reaction mechanism. Its formation via β - cleavage of PBNOX is also possible.

The detection of succinimidyl adduct in the presence of bicyclopentadiene confirms our proposal of cleavage mode of NBS radical anion after ET step. Presence of very weak PBNOX signals in these runs, confirms that Br· is formed in the system. One novel and pertinent fact about succinimidyl systems which came to light is the different cleavage mode of radical anions of NBS and NCS, as shown below ;



N- Bromosuccinimide and Nitrone in n- Hexane

The immediate spectra observed on mixing degassed solutions of NBS and PBN in concentration 1 : 1, was a weak signal of PBNOX with hyperfine splittings, a_N = 7.87 G,g = 2.0066. The signal of PBNOX grew continuously and was the only signal left even after ca. 24 hours. It could be recorded with well defined ^{13}C and ^{15}N isotope splittings as a_N = 7.87 G, $a^{\alpha}_{13\text{-}C}$ = 4.87 G, $a^{\beta}_{13\text{-}C}$ = 3.93 G, $a^{\gamma}_{13\text{-}C}$ = 2.62 G and a^{15}_{N} = 11.00 G. Reactions done at other higher concentration of NBS to PBN showed similar results. The solution again turned light yellow due to the formation of molecular bromine. However, at higher concentration of PBN to NBS, another triplet was observed after ca. 4 hours of the reaction with a_N = 15.18 G, g = 2.0060, due to di-tert. butyl nitroxide (DTBN). In some of the cases another set of triplet of doublet was observed with hyperfine splittings ; a_N = 13.36 G and a^{β}_{H} = 1.50 G and has been assigned to benzoyloxyl adduct of PBN (C_6H_5COO-PBN$^{\cdot}$).

We suggests that in this system the reaction is carried away by molecular bromine formed. The major reaction is the oxidation of PBN by bromine formed in the reaction. The reactions were repeated in the presence of bicyclopentadiene. In spite of our best efforts we did not see succinimidyl adduct of nitrone which is in contrast to

the results observed in benzene. Only intense signals of PBNOX were observed. It appears that in n- hexane, the dimerisation of Br· is faster then the addition across the double bond in bicyclopentadiene. Presence of intense signals of PBNOX and the yellow colour of the solution in these runs supports this postulation. Reactions were carried out in photolytic conditions, within the ESR cavity. The immediate spectra observed was an intense triplet of PBNOX. The reaction was monitored continuously with time. A continuous increase in PBNOX intensity was observed. However, another triplet with hyperfine splitting a_N = 15.18 G corresponding to DTBN appeared after ca. one hour of photolysis. No other adduct was observed. These results are in contrast to photo assisted electron transfer in the case of NCS where electron capture dissociation yielded chloro adduct of PBN. Therefore, our postulation made above that the electron capture dissociation of NBS is different from NCS, gets supported.

N- Bromosuccinimide and Nitrone in Acetonitrile

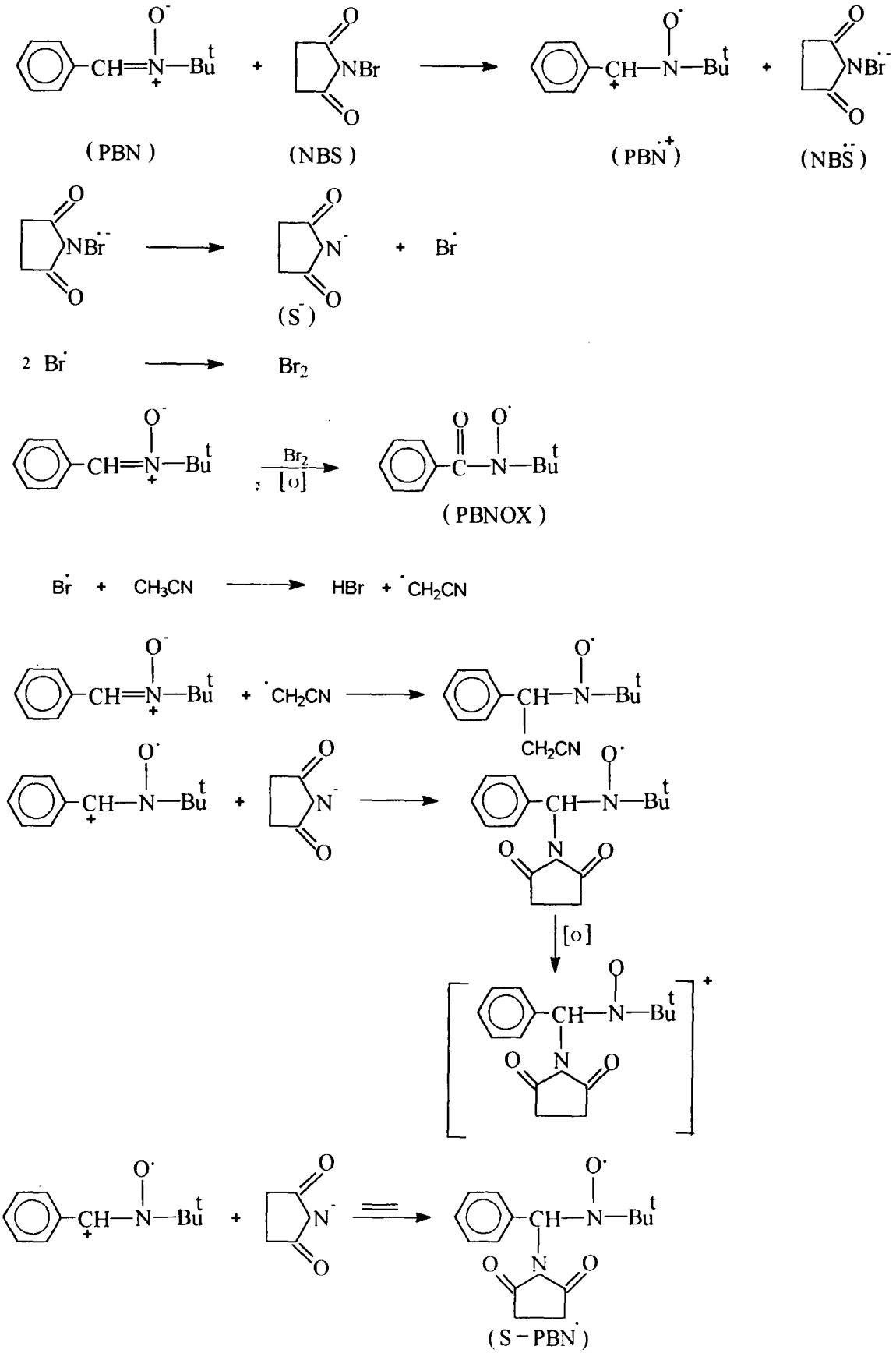
On mixing solutions of NBS and PBN in concentration 1 : 1, the immediate spectra observed was due to PBNOX with hyperfine splittings ; a_N = 8.12 G, g = 2.0066. After ca. 15 minutes along with PBNOX, a triplet of doublet appeared

with hyperfine splittings, a_N = 14.41 G and a^{β}_{H} = 2.20 G, g = 2.0060. A continuous increase in the intensity of PBNOX was observed while the triplet of doublet disappeared after ca. 3 hours of the reaction. PBNOX signal could be recorded with ^{13}C and ^{15}N isotope splittings ; a_N = 8.12 G, $a^{\alpha}_{13\text{-}C}$ = 4.80 G, $a^{\beta}_{13\text{-}C}$ = 4.00 G, $a^{\gamma}_{13\text{-}C}$ = 2.80 G and a^{15}_{N} = 11.50 G. The triplet of doublet is assigned to CH_2CN-PBN· adduct which agrees with the literature [7].

In reactions done at concentration NBS to PBN (2 : 1) the immediate spectra observed showed two spin adducts, PBNOX and CH_2CN-PBN·. Initially a continuous increase in the intensity of both the signals was noticed but the latter one decays off after ca. 4 hours leaving PBNOX behind. The experiments repeated at other concentration ratios yielded similar results. Reactions carried out at higher concentrations of PBN to NBS showed only PBNOX signals. Similar results were obtained even under photolytic conditions.

We suggest the mechanism formulated in Scheme 5.1. The only additional feature in this solvent is the formation of the solvent derived free radical·CH_2CN. The most probable reason for the formation of this specie could be due to H-abstraction by Br· from CH_3CN however, other pathways can not be ruled out. The appearance of an intense signal of

Scheme 5.1


(PBN)
(NBS)
(PBN·+)
(NBS·-)
(S-)
2 Br·
Br2
Br2
[o]
(PBNOX)
Br· + CH3CN
HBr + ·CH2CN
CH2CN
[o]
(S-PBN·)

PBNOX suggests that most of the bromine atoms (Br·) formed undergoes dimerisation and only a fraction of Br· participate in H- abstraction reaction. The intense signals of CH_2CN-PBN· at higher concentrations of NBS is due to enhanced H - abstraction from the solvent.

Reactions carried out with traces of bicyclopentadiene showed well resolved spectra with splitting pattern 3 x 3 x 2, Fig. 5.1. The hyperfine splittings calculated are ; a_N = 14.31 G, a^{β}_{H} = 5.25 G and $a_{N'}$ = 1.62 G (from secondary nitrogen). The spectrum with these features have already been assigned to succinimidyl adduct of PBN and is confirmed by simulation Fig. 5.2. It was stable for ca. 30 minutes. No other adduct, not even PBNOX was observed, signifying the complete removal of Br·. Thus it again supports our proposal that ; (i) when bromine is removed from the system, only then succinimidyl adduct is observed (ii) Br_2 oxidises PBN and / or S-PBN· and (iii) in inert solvents dimerisation of Br· is the preferred path.

In the absence of any adduct which could reasonably be assigned to ring opened product, it appears that the system involves only two species : succinimidyl anion and Br·. We feel that succinimidyl anion formed does not participates in any kind of ring opening reaction.

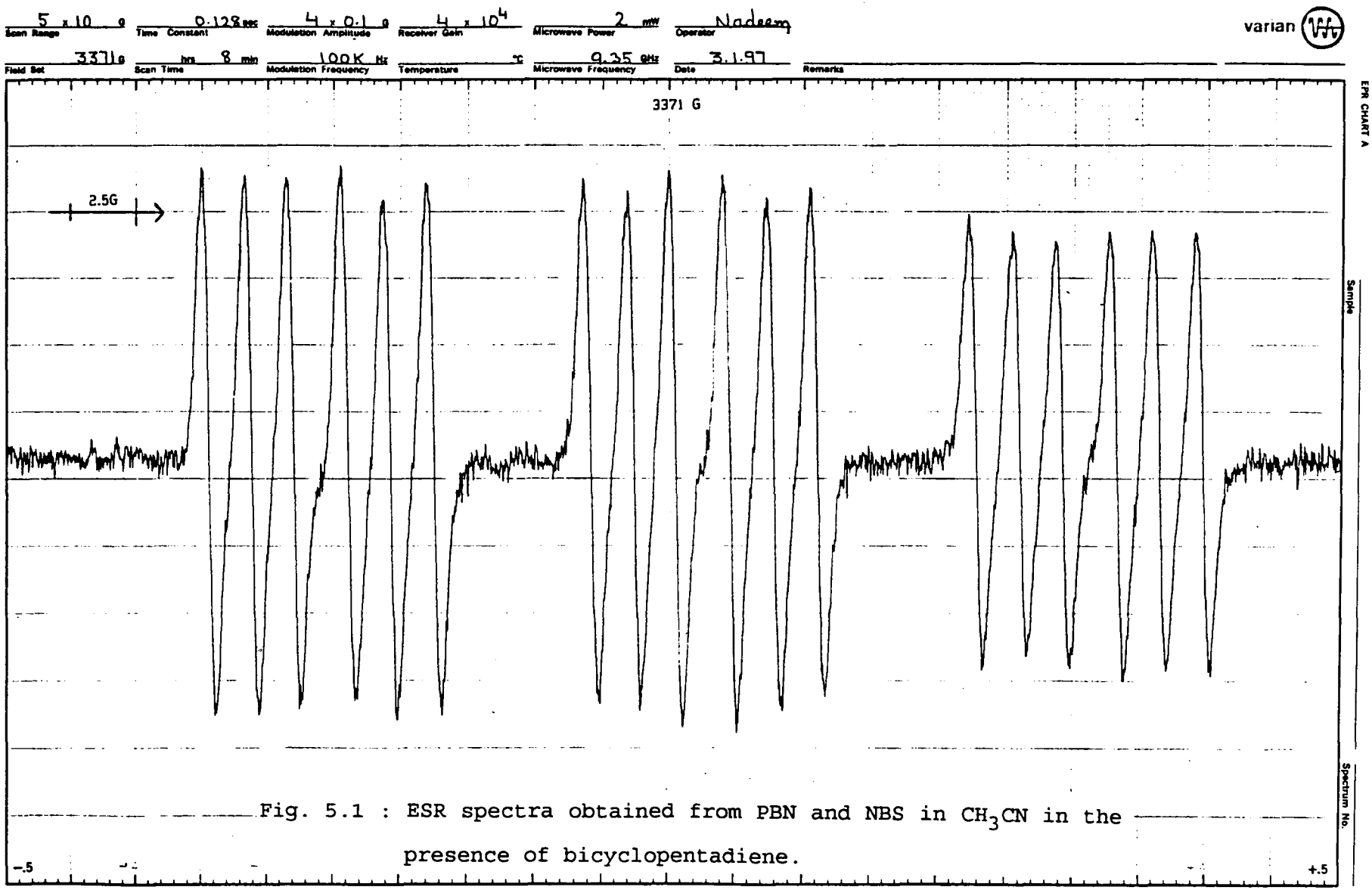


Fig. 5.1 : ESR spectra obtained from PBN and NBS in CH_3CN in the presence of bicyclopentadiene.

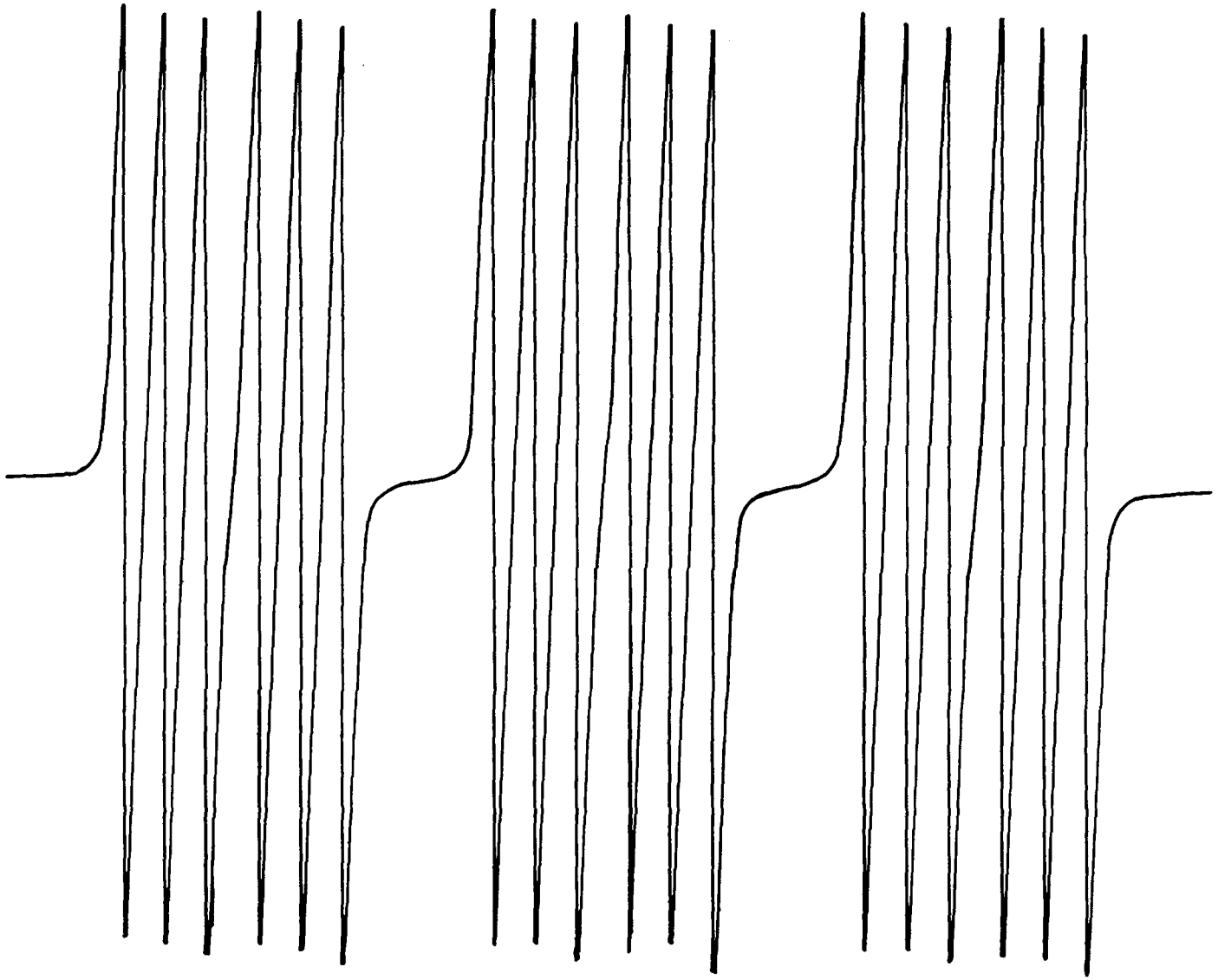


Fig. 5.2 : Simulated spectra of 5.1 using hyperfine parameters calculated from experimental spectra L.W = 0.6.

N- Bromosuccinimide and Nitrone in Dichloromethane

The reaction carried out at concentration (1 : 1), showed initially two set of signals, PBNOX with ; a_N = 8.00 G, g = 2.0065 and a triplet of doublets with hyperfine couplings a_N = 13.20 G, a^{β}_H = 1.52 G, g = 2.0061 assigned to benzoyloxyl radical adduct of PBN. A continuous increase in the intensity of both the signals was observed initially but PBNOX was the only signal left after ca. 2 hours. At concentration (2 : 1) NBS to PBN, the spectra observed initially was due to PBNOX and benzoyloxyl adducts however,later adduct was replaced with another triplet of doublets with hyperfine splittings a_N = 14.60 G and a^{β}_H = 2.27 G, g = 2.0060. These parameters are in good agreement with the literature value for $CHCl_2$-PBN· [8] adduct. Solution turned light yellow. A continuous increase in PBNOX intensity was observed and it was the only signal left at the end of the reaction. Reactions at higher concentrations of NBS yielded similar results except, an increase in the intensity of $CHCl_2$-PBN· adduct. Reactions at higher concentration of PBN to NBS showed PBNOX and benzoyloxyl adduct of PBN. Another triplet with hyperfine splitting a_N = 15.70 G, g = 2.0060 appeared at the later stage of the reaction and is assigned to di-tert. butyl nitroxide (DTBN). A continuous increase in the intensity

of DTBN was observed and was the only signal left at the end of the reaction. It could be recorded with well defined ^{13}C satellite signals with hyperfine splitting a^{13}_{C} = 4.31 G. Results at higher concentration of PBN were essentially same.

The origin of the solvent derived radical adduct can be explained similarly as given for acetonitrile. Under various conditions of concentration variations we did not observe any succinimidyl adduct of PBN due to similar reasons as explained in acetonitrile. Experiments under photolytic conditions also exhibited similar behaviour. Intense PBNOX signal with well defined ^{13}C and ^{15}N splittings were observed with coupling constants ; a_N = 8.12 G, $a^{\alpha}_{13\text{-}C}$ = 4.80 G, $a^{\beta}_{13\text{-}C}$ = 4.00 G, $a^{\gamma}_{13\text{-}C}$ = 2.70 G and a^{15}_{N} = 11.50 G. Reactions in the presence of bicyclopentadiene showed signals of splitting pattern 3 x 3 x 2 with hyperfine splittings a_N = 14.87 G, a^{β}_{H} = 4.13 G and $a_{N'}$ = 1.31 G and is assigned to succinimidyl adduct of PBN. The signal was stable for ca. 30 minutes. No signal corresponding to PBNOX was observed in these runs.

All the observations and conclusions derived from acetonitrile system gets support from this system also. We propose that the system involves simple competeting S^- and $Br^{\cdot}$ chains without any need to invoke any other third

chain carrier. Keeping in view the solvolytic properties of alcohols, reactions were carried out in alcohols.

N- Bromosuccinimide and PBN in Ethanol

The immediate spectra observed at 1 : 1 was a triplet of doublet with hyperfine splittings a_N = 14.60 G, a^{β}_{H} = 2.80 G, accompanied by intense signals of PBNOX with a_N = 8.00 G, g = 2.0066. A continuous decrease in the intensity of the triplet of doublet was observed and disappeared in ca. 20 minutes leaving PBNOX behind. On the basis of the observation so far gained that solvents are participating in the reactions and on the basis of magnitude of hyperfine splittings (which matches with the literature value), the triplet of doublet is assigned to ethoxy adduct of PBN (C_2H_5O-PBN·)[9]. Reactions were carried out at varying concentration ratios of NBS to PBN but the results were essentialy same. No new adduct was observed in all the runs. However, an increase in the intensity of ethoxy adduct was observed in runs carried out at higher concentrations of NBS to PBN while at higher concentrations of PBN to NBS only PBNOX was observed. Oxidation of PBN by Br_2 is still the major pathway. Solvent derived radical adducts are formed by mechanism discussed earlier. We failed to see any other adduct neither under photolytic nor

in presence of bicyclopentadiene. The reactions were marked by signals of ethoxy and intense PBNOX adducts. Failure to carry out the reaction under bromine free conditions seems either due to ineffective removal of Br· by bicyclopen - tadiene, the hydroxylic nature of the solvent can be one of the reason we can think of or very low solvation of Br·.

N- Bromosuccinimide and PBN in Iso- propanol

Iso- propanol is an alcohol with some unique property e.g., when benzophenone is irradiated in this alcohol, the conversion of benzophenone to benzpinacol occurs quantitatively. The proton donating ability of this solvent is remarkable. With this information in mind we thought to do our reactions in this solvent. Reaction carried out in 1 : 1 concentration, showed initially a triplet of doublet with hyperfine values a_N = 14.40 G, a^{β}_H = 2.20 G assigned to solvent derived adduct of PBN [$(CH_3)_2CHO$-PBN·]. The hyperfine parameters agree with literature values [10]. This adduct was replaced (ca. 30 minutes) by PBNOX with hyperfine splittings a_N = 8.10 G, g = 2.0066. This was the only signal left at the end of the reaction. This sequence of reaction is different from all other solvents used so far. We suggest that H- abstraction from the solvent is faster than the dimerisation of bromine atoms. Reactions

carried out at other concentration ratios of NBS and PBN yielded similar results. We failed to see any other adduct under photolytic conditions as well as in the presence of bicyclopentadiene for the same reasons explained earlier.

N- Bromosuccinimide and PBN in n- Butanol

The immediate spectra observed at comparable concentrations of NBS and PBN, was a triplet of doublet with hyperfine splittings a_N = 14.20 G and a^{β}_{H} = 2.40 G, assigned to solvent derived radical adduct of PBN and is in agreement with those reported [10]. This adduct was unstable and was replaced (ca. 20 minutes) by signals of PBNOX with hyperfine splittings a_N = 8.00 G, g = 2.0066. This was the only signal left after ca. 30 minutes of the reaction. Similar results were obtained at other concentration ratios of NBS and PBN. Reactions carried out in the presence of bicyclopentadiene yielded similar results. Solution turned light yellow in these runs.

We were expecting that since the dielectric constant of this alcohol is lower then the ones studied above, we might observe some new signal of some other specie or even succinimidyl adduct of PBN but the complete absence points

out that the rate of dimerisation of bromine atom in all the alcohols is faster then the addition reaction of $Br^{\cdot}$ across the double bonds. Similar results were obtained in iso- butanol and in 2- ethoxy ethanol and are therefore not mentioned here.

N- Bromosuccinimide and PBN in Methanol

Reactions performed in methanol initially showed triplet of doublet with hyperfine values a_N = 14.40 G and a^{β}_{H} = 2.90 G, g = 2.0058 and is assigned to solvent derived adduct of PBN (CH_3O-PBN$^{\cdot}$). The hyperfine values are in good agreement with those reported [10]. This was accompanied by triplets corresponding to PBNOX with hyperfine splittings a_N = 8.00 G and g = 2.0066. PBNOX was the only adduct left after ca. 30 minutes of the reaction. No new adduct was observed at other concentrations of NBS and PBN. Reactions in the presence of bicyclopentadiene yielded similar results as with other alcohols.

In the light of all these experimental results we propose that the bromine atoms formed after ET step undergoes rapid dimerisation to give Br_2 which oxidises PBN to PBNOX. In spite of our best efforts we failed to remove bromine from the system. Yellow colour of the solution even in the presence of bicyclopentadiene, supports our

proposal. In reactions carried out in the presence of DMPO, DMPOX was the major adduct observed in all the systems discussed above.

N- Bromosuccinimide and Nitrone in Carbontetrachloride

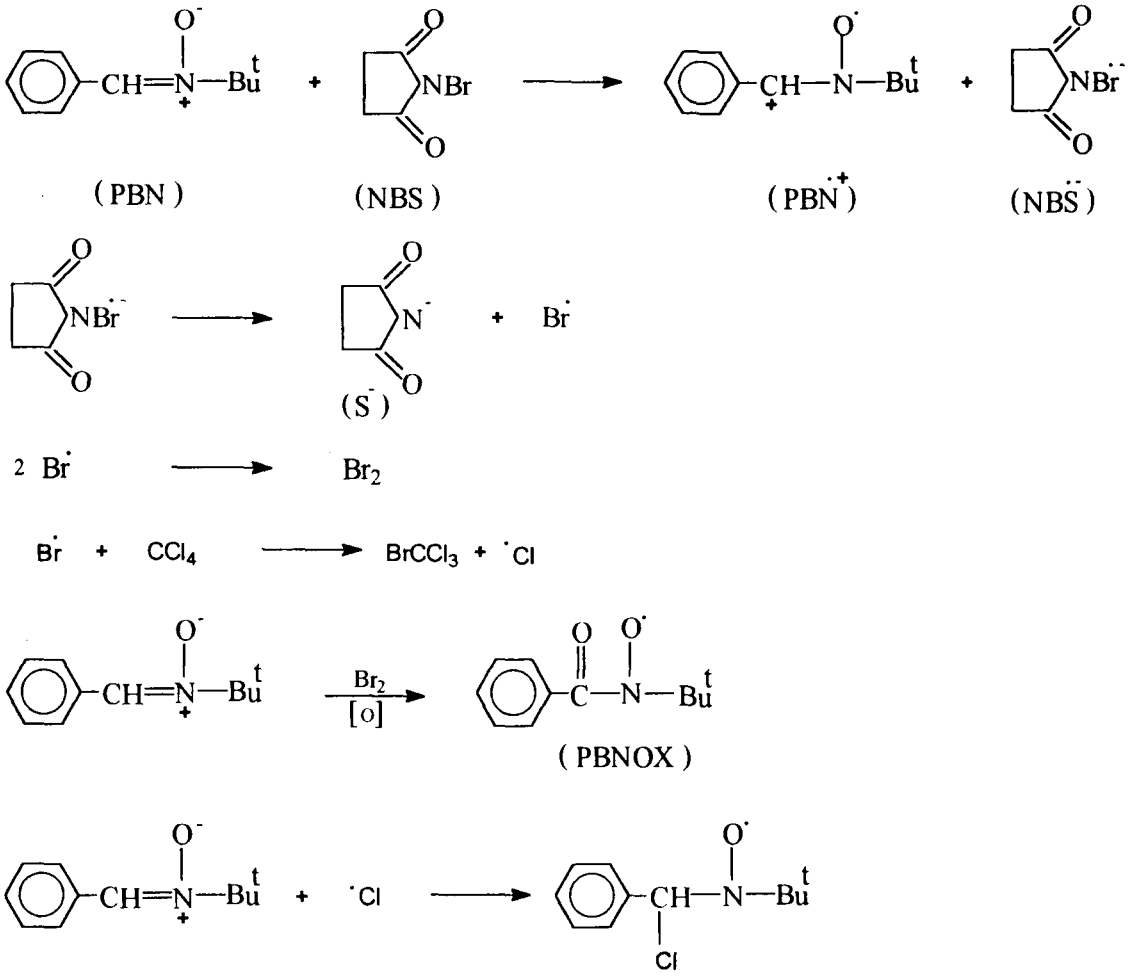
The bromination of allylic compounds by NBS was first attempted by Ziegler in carbontetrachloride as solvent. Therefore, an attempt was made to elucidate the NBS chemistry in this solvent.

Reactions performed in carbontetrachloride showed peculiar solvent behaviour. To our surprise, the immediate spectra observed (concentration 1 : 1) was a well characterised spectra of chloro adduct of PBN and PBNOX with hyperfine splitting a_N = 7.93 G, g = 2.0067. The hyperfine splittings of the chloro adduct were similar to those observed in preceding chapter. The chloro adduct was stable upto ca. 30 minutes while PBNOX was the only signal left at the end of the reaction. In the blank reaction between PBN and CCl_4, no adduct was observed. Reactions carried at varying concentrations of NBS and PBN showed similar results. No new adduct was observed in all the runs. With DMPO, DMPOX was the only specie observed. The hyperfine splittings are similar to those observed in previous chapter.

Reactions in the presence of bicyclopentadiene showed weak signals of PBNOX along with another weak triplet of doublets with hyperfine splittings a_N = 13.20 G and a^{β}_{H} = 1.41 G. No sign of chloro adduct was found. A continuous decrease in the intensity of the PBNOX signal was observed and it disappeared after some time while there was a continuous increase in the intensity of triplet of doublet and it was quite stable. The hyperfine splittings and other parameters matches very well with the reported values for benzoyloxyl radical adduct of PBN [11]. No other adduct was observed. Similar results were obtained when the reaction was carried out at other concentration ratios.

As shown in the Scheme 5.2, electron (donated by PBN) capture dissociation of NBS anion leads to the formation of succinimidyl anion (S^-) and bromine atoms ($Br^{\cdot}$). We propose that in this system the bromine atoms undergo two reaction pathways : (i) Usual dimerisation to give molecular bromine which in turn oxidises PBN to PBNOX and (ii) reaction with CCl_4 itself replacing one of the chlorine atom yielding $BrCCl_3$ and $Cl^{\cdot}$. We suggest that the chlorine atoms ($Cl^{\cdot}$) thus formed are trapped by PBN giving rise to chloro adduct. Continuous generation of chlorine atoms by this pathway, gives rise to a significant concentration of the chloro adduct. The reason for the

Scheme 5.2



absence of succinimidyl adduct is explained earlier. The formation of PBNOX in this system could be due to more than one pathways.

When reactions were carried out in the presence of bicyclopentadiene (an effective Br· scavenger), neither chloro adduct nor succinimidyl adduct (observed in many cases) were observed. This confirms our proposed reaction step that Br· replaces Cl· from CCl_4. The Br· formed is removed by bicyclopentadiene inhibiting the further reaction pathways leading to Cl-PBN· adduct. The absence of succinimidyl adduct could be due to its high instabi - lity.

These results clearly establish the limitation of carbontetrachloride as solvent in radical reactions. Again we did not find any sign of ring opened product in this solvent also and the reaction is marked by only succinimidyl anion and bromine atoms. Our results support the postulation of Ziegler that Br· is the dominant chain carrier.

N- Bromosuccinimide and Nitrone in 1,4-Dioxan

On mixing degassed solutions of NBS and Nitrone in 1 : 1 concentration, the immediate ESR spectra observed was

a triplet of PBNOX with hyperfine values a_N = 8.00 G, g = 2.0066, which grew continuously. After some time a triplet of doublet also appeared with hyperfine splittings ; a_N = 13.25 G and a^{β}_H = 2.70 G which disappeared after ca. 15 minutes leaving PBNOX behind. At this stage we are not in a position to assign this adduct. Results of the reactions in different concentrations of NBS and PBN were essentially similar. DMPOX was the only adduct observed in reactions carried out with DMPO.

The reactions were repeated in the presence of bicyclopentadiene. The immediate spectra observed showed a triplet of doublet with hyperfine values a_N = 13.12 G and a^{β}_H = 1.50 G assigned to benzoyloxyl radical adduct of PBN and another set of signals which developed into a well resolved spectra with splitting pattern 3 x 3 x 2. The hyperfine couplings measured from the observed spectra are a_N = 14.37 G, a^{β}_H = 5.62 G and $a_{N'}$ = 1.12 G, a well characterised spectra of succinimidyl adduct of PBN (S-PBN·). Reactions repeated at varying concentrations of NBS and PBN did not show any new adduct. These results suggest that the reaction pathway is similar to that discussed earlier.

N- Bromosuccinimide and Nitrone in Dimethylformamide (DMF)

With the wide use of DMF as a selective and specific solvent in organic synthesis [12] the understanding of the radical processes is of interest because of potential side reactions which might be initiated by radicals produced from amides [13]. Little work appears to have been done on free radical chemistry of amides. With this motive as well as to study the NBS chemistry, reactions were carried out in this solvent.

The ESR spectra obtained on mixing solutions of NBS and PBN in DMF is shown in Fig. 5.3. It consists of two spin adducts ; (i) PBNOX along with its ^{13}C and ^{15}N satellite splittings as ; a_N = 8.10 G, $a^{\alpha}_{13\text{-}C}$ = 4.80 G, $a^{\beta}_{13\text{-}C}$ = 3.80 G, $a^{\gamma}_{13\text{-}C}$ = 2.70 G, a^{15}_{N} = 11.20 G and (ii) signals with splitting pattern 3 x 3 x 2, clearly suggesting a nitrogen centered radical adduct of PBN. The hyperfine splittings calculated from the spectra are ; a_N = 8.60 G, a^{β}_{H} = 7.30 G and $a_{N'}$ = 0.70 G. The hyperfine splittings suggests the $\cdot CON(CH_3)_2$ radical adduct of PBN and are in good agreement with the literature data [14]. The spectra simulated using these hyperfine values is shown in Fig. 5.4, confirming our spectral assignment. However, the latter signal decayed in ca. 45 minutes and another spectra developed after ca. one hour shown in Fig. 5.5. The

Field Set : 3370 ± 20 G

Time Constant : 0.250

Scan Time : 8 minutes

Modulation Amplitude : 0.1

Receiver Gain : 10^5

Microwave Power : 5 mw

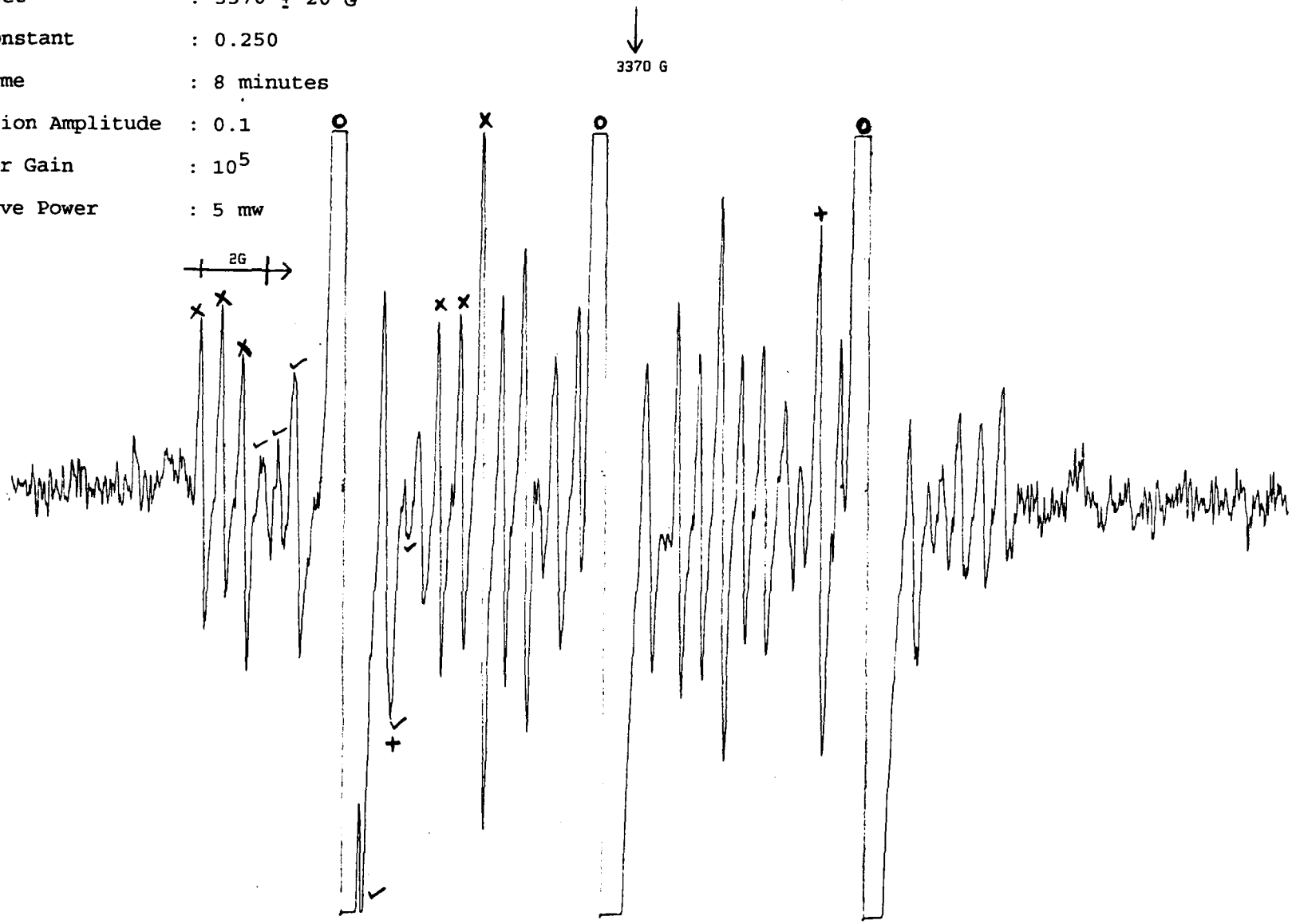


Fig. 5.3 : ESR spectra obtained from PBN and NBS in DMF.

X , $(CH_3)_2NCO$-PBN· adduct ; O , PBNOX.

✓ , ^{13}C ; + , ^{15}N.

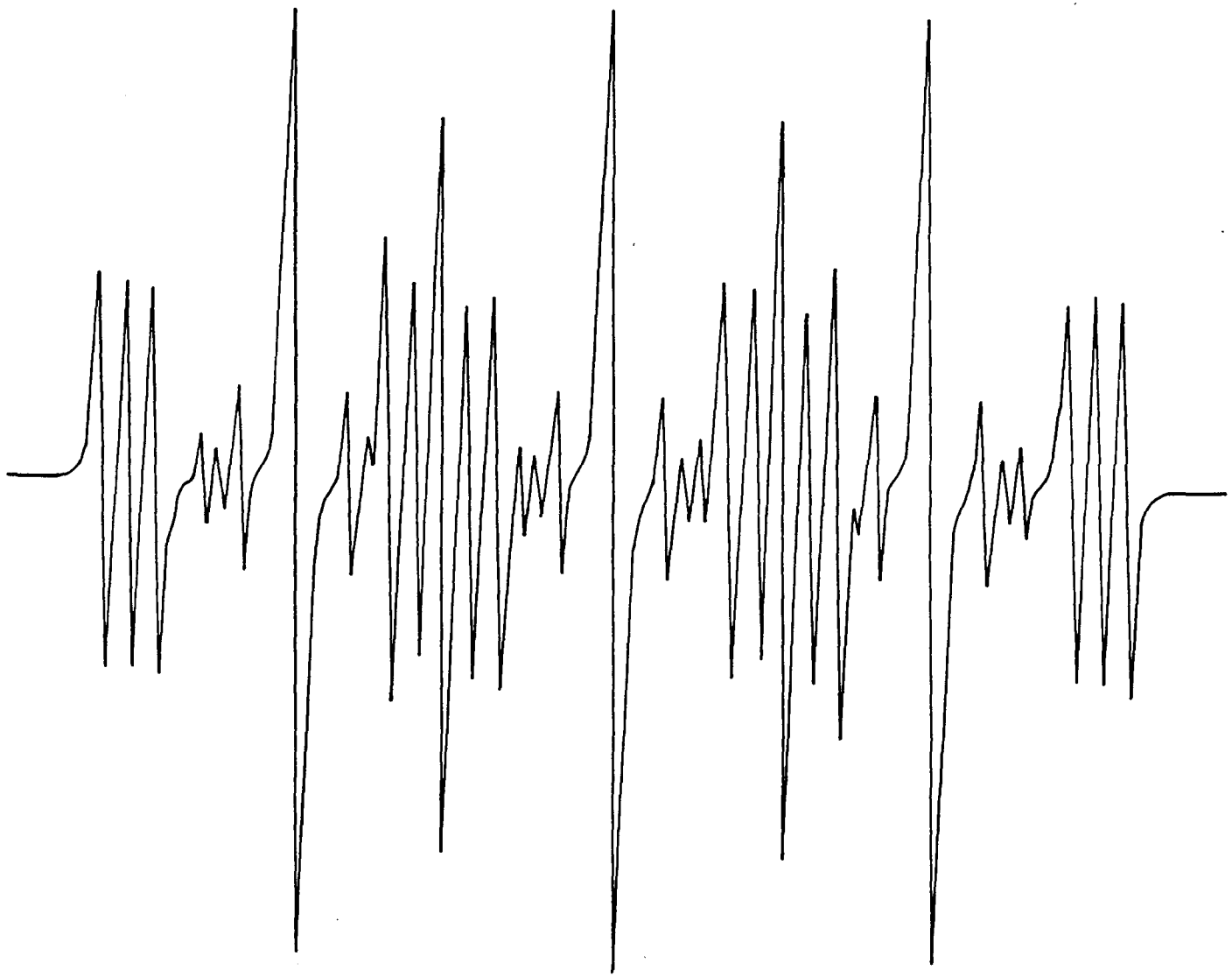


Fig. 5.4 : Simulated spectra of 5.3 using experimentally determined hyperfine parameters. $(CH_3)_2NCO\text{-}PBN^{\cdot}$ L.W = 0.3 ; PBNOX L.W = 0.2, ΔG = 0.

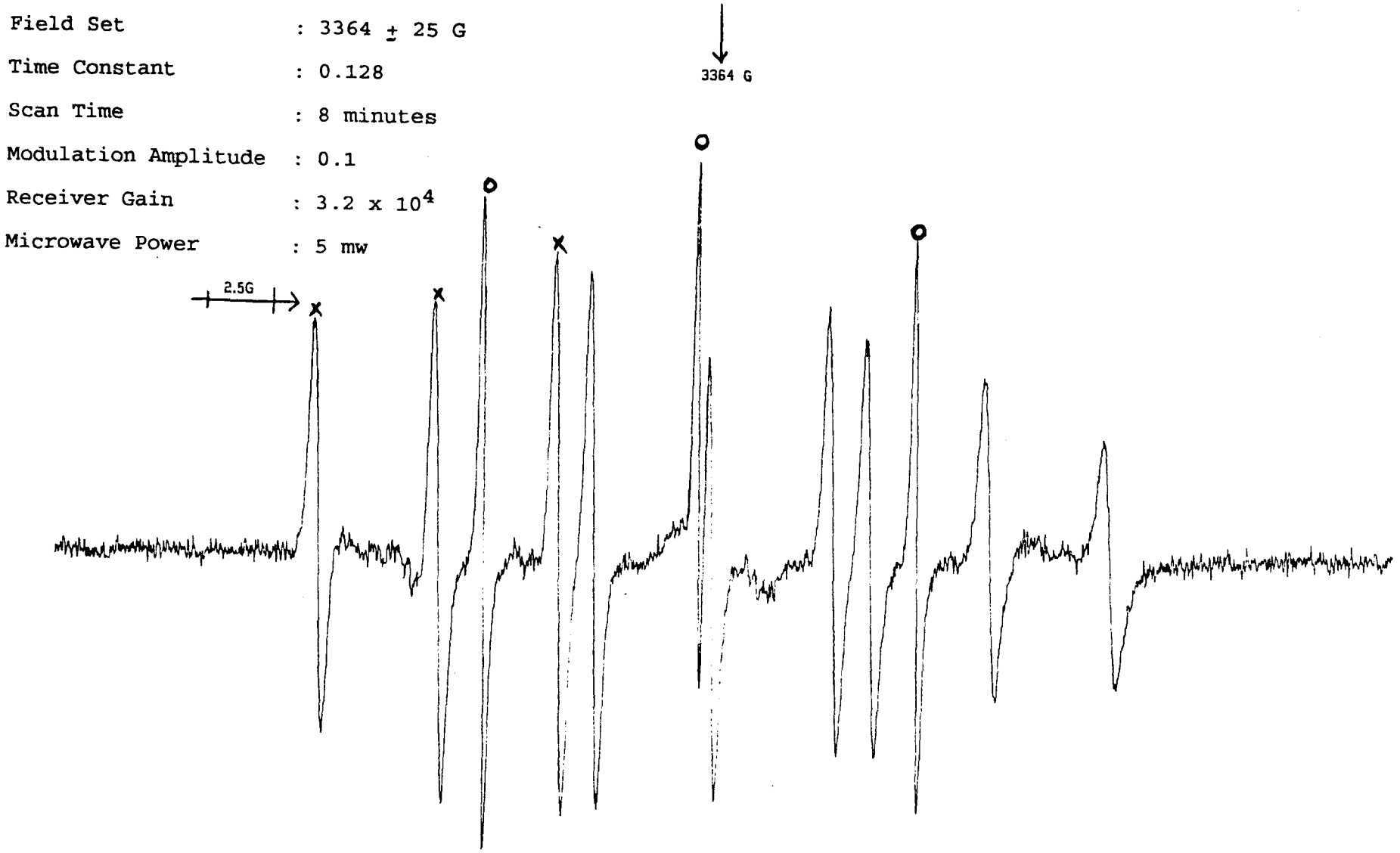


Fig. 5.5 : ESR spectra obtained from PBN and NBS in DMF.

X , $(CH_3)_2N$-MNP· adduct ; O , PBNOX.

splitting pattern is 3 x 3 which indicates the interaction between two non equivalent nitrogen atoms. The hyperfine splittings are a_N = 10.25 G and $a_{N'}$ = 4.50 G. The hyperfine splittings and the splitting pattern suggest a nitrogen centered radical adduct of MNP and we assign it to $(CH_3)_2N$-MNP· adduct. The spectra simulated Fig. 5.6 matches with the experimental spectra. However PBNOX was the only signal left after ca. two hours of the reaction.

Reactions carried out at higher concentrations of NBS to PBN (2 : 1) showed only PBNOX and $(CH_3)_2NCO$-PBN· adduct. Reactions carried out at higher concentrations of PBN to NBS (2 : 1) showed three adducts (i) PBNOX, (ii) $(CH_3)_2NCO$-PBN· adduct and (iii) a triplet of doublet with hyperfine splittings as ; a_N = 13.40 G and a^{β}_H = 3.60 G. The hyperfine splittings of triplet of doublet suggest the trapping of carbon centered radical by PBN. On the basis of the reported literature values it is assigned to $\cdot CH_2NCH_3CHO$ radical adduct of PBN. PBNOX was the only signal left at the end of the reaction. Reactions carried out with DMPO in place of PBN yielded only septets of DMPOX with hyperfine splittings a_N = 7.30 G and a^{β}_H= 4.10 G. This was the only signal observed in all the runs.

In one of the sets traces of MNP was added in the system. The immediate spectra observed at 1 : 1 concen -

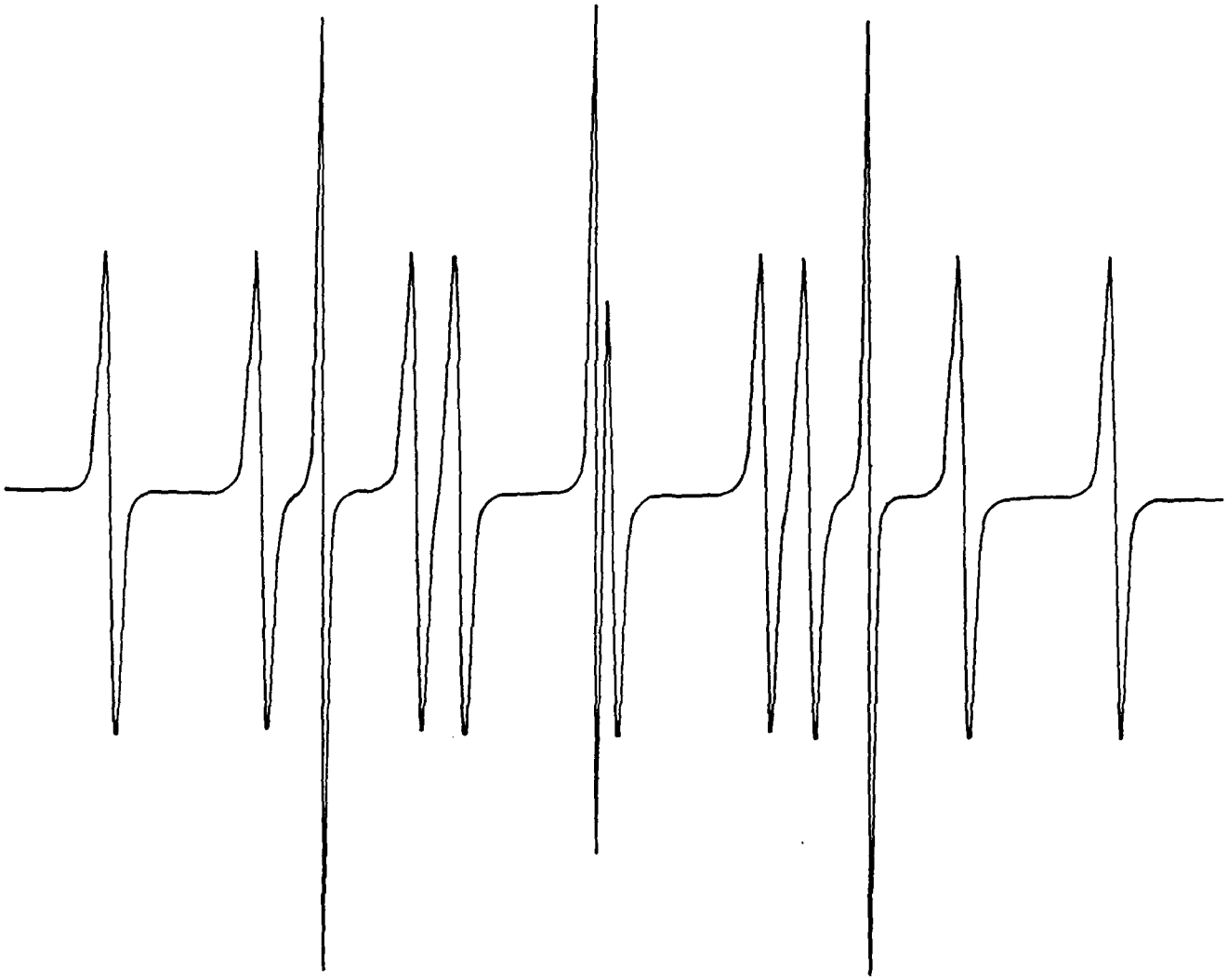


Fig. 5.6 : Simulated spectra of 5.5 using experimentally determined hyperfine parameters. $(CH_3)_2N$-MNP·
L.W = 0.4 ; PBNOX L.W = 0.2, ΔG = - 0.5.

tration of NBS and PBN showed $(CH_3)_2NCO$-PBN· adduct along with PBNOX. However this adduct decayed in ca. 15 minutes and another set of weak signals which grew in intensity to a well resolved spectra shown in Fig. 5.7 was observed. When the middle component was scanned at small field variation and low scan speed, the hyperfine splittings measured are a_N = 11.70 G, $a_{N'}$ = 0.48 G and a^{γ}_H = 0.67 G (3H). Hyperfine coupling parameters and splitting pattern analysis suggests it to be $(CH_3)_2NCO$-MNP· adduct. The spectra simulated Fig. 5.8 matches well with the experimental one and the hyperfine parameters matches with literature values [15]. This adduct decayed out in ca. 40 minutes and was replaced by another set of signals shown in Fig. 5.9. The hyperfine splittings calculated are a_N = 14.70 G, $a_{N'}$ = 0.40 G and a^{γ}_H = 0.50 G (2H). The order and the magnitude of the hyperfine splitting suggest the presence of secondary nitrogen atom at β - position. We tentatively assign this spectra to $BrCH_2CH_3NCO$-MNP· adduct. The spectra simulated Fig. 5.10, using these hyperfine values is in good agreement with the experimental spectra. This adduct disappeared in ca. one hour of the reaction.

On the basis of these results we suggest the mechanism formulated in Scheme 5.3. The absence of succinimidyl adduct is attributed to the reasons discussed earlier. The

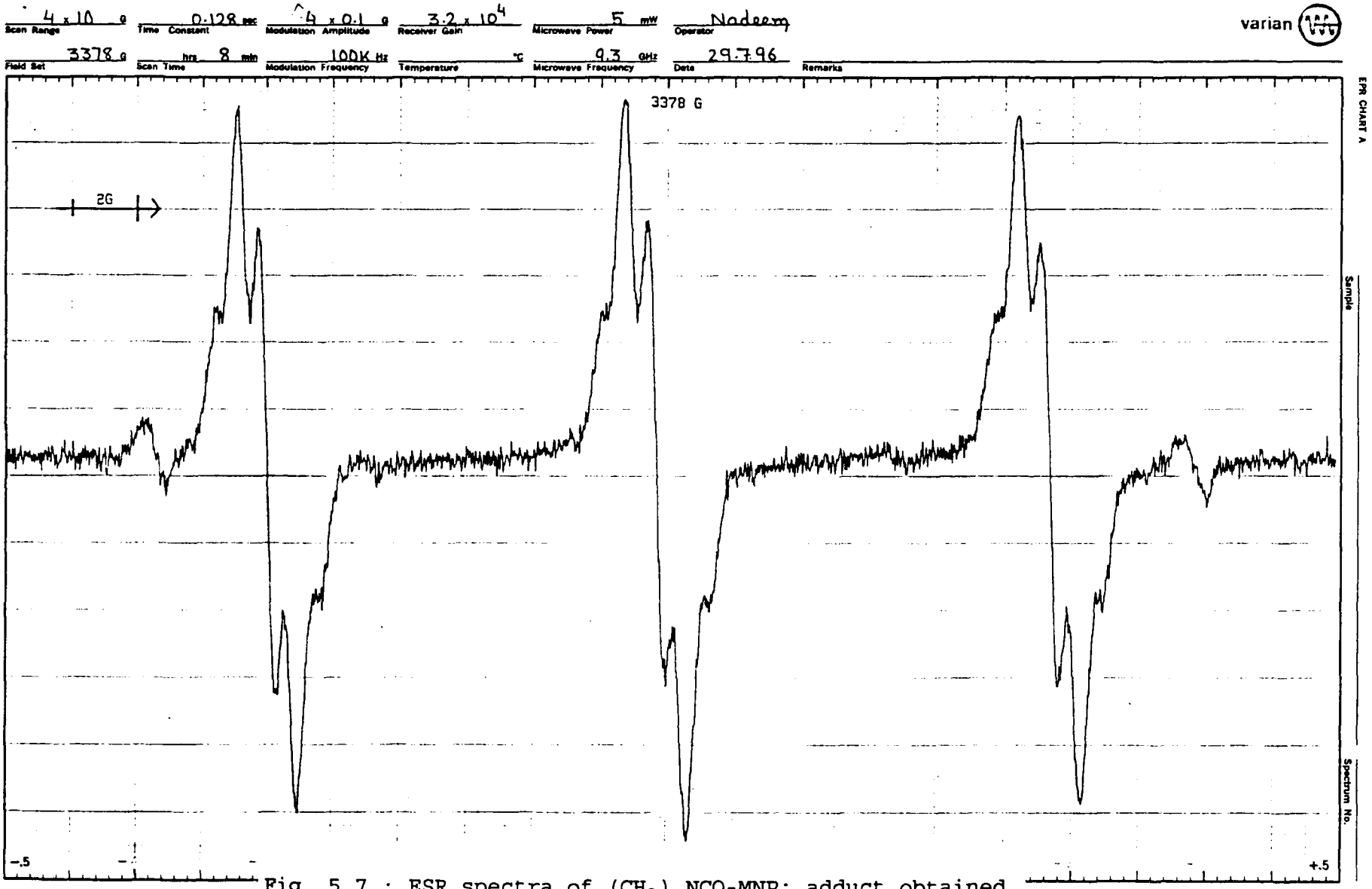


Fig. 5.7 : ESR spectra of $(CH_3)_2NCO$-MNP$^{\cdot}$ adduct obtained from PBN and NBS in DMF.

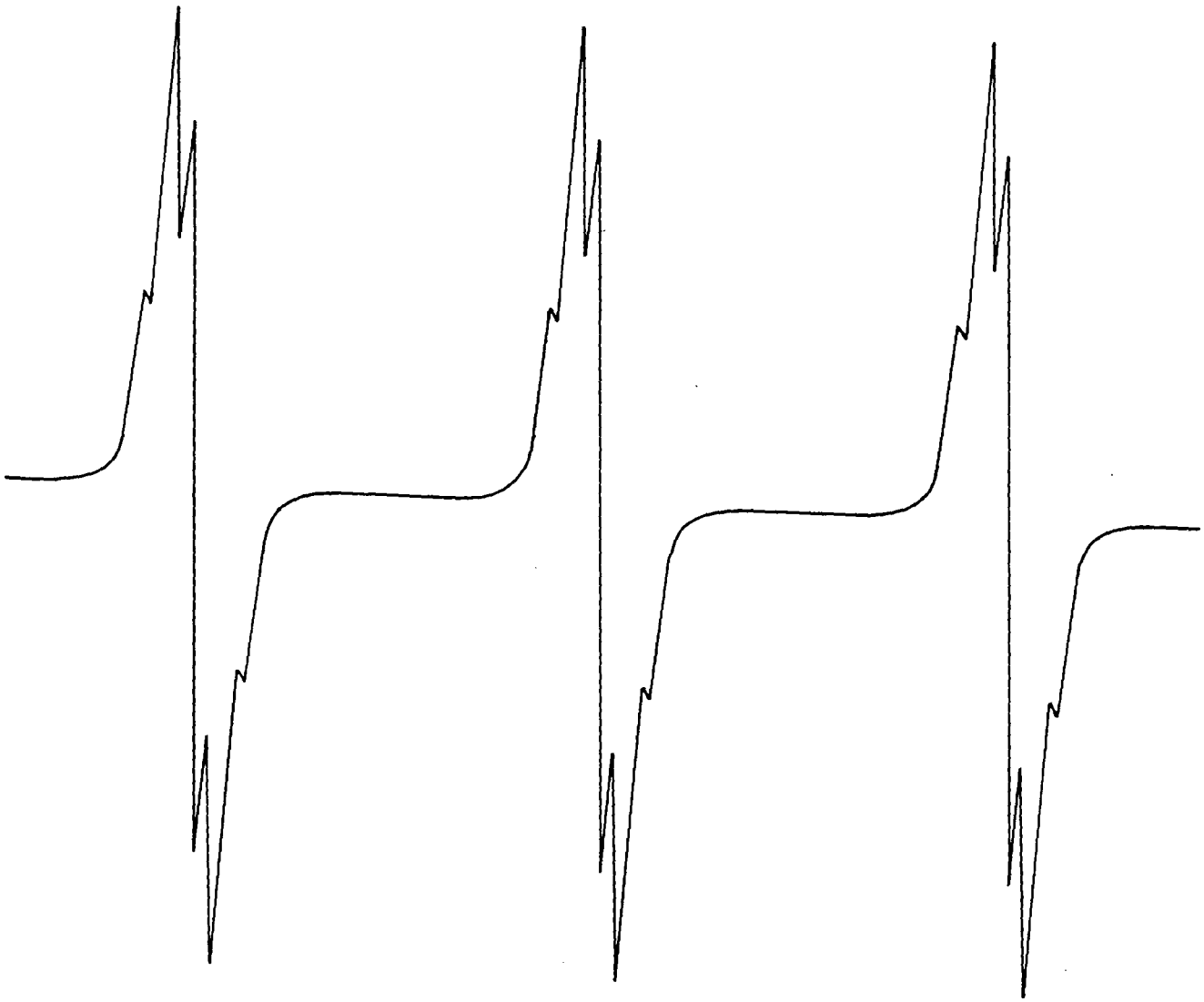


Fig. 5.8 : Simulated spectra of 5.7 using experimentally determined hyperfine parameters L.W = 0.5.

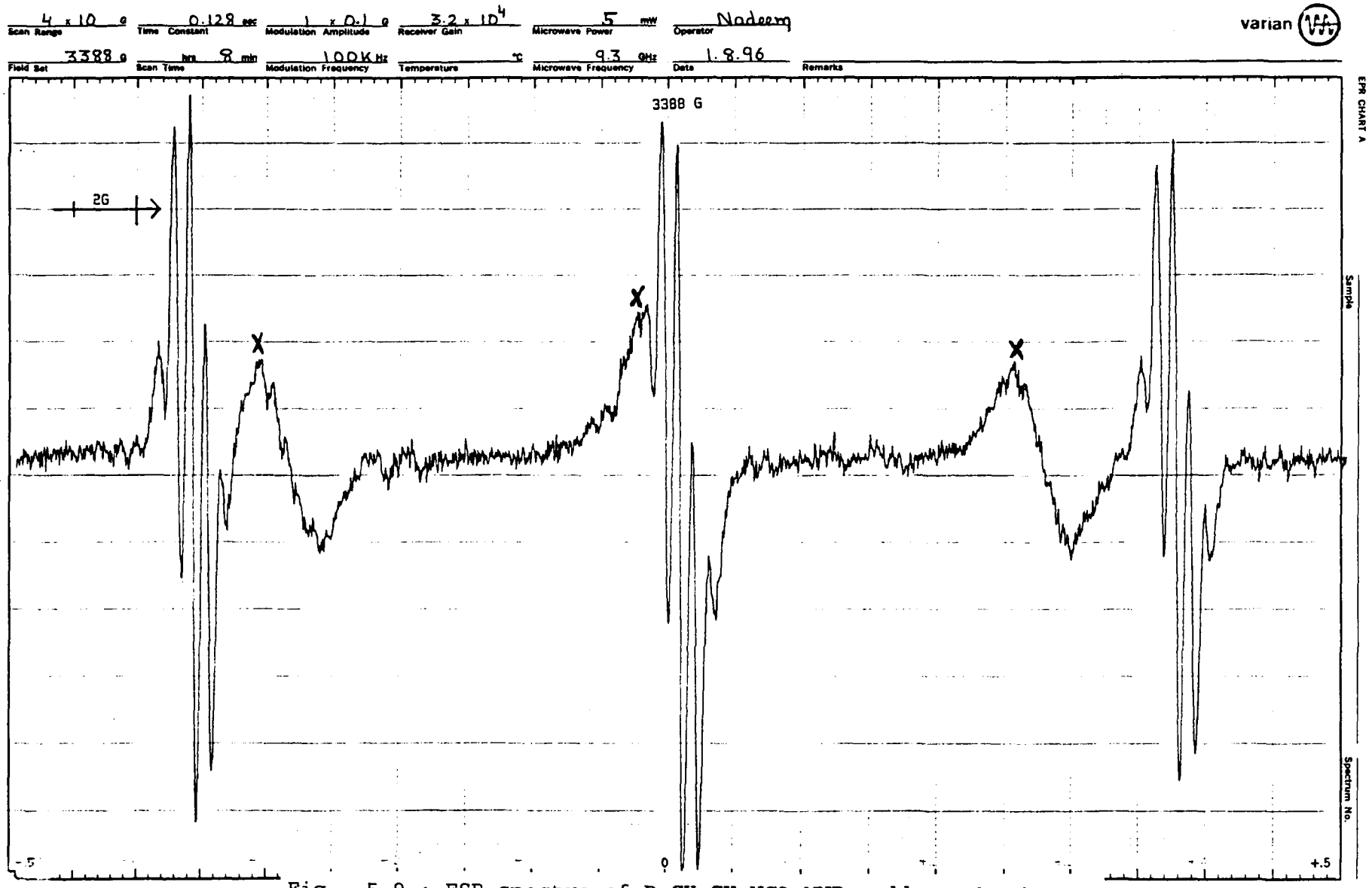


Fig. 5.9 : ESR spectra of $BrCH_2CH_3NCO\text{-}MNP\cdot$ adduct obtained from PBN and NBS in DMF. X , decaying spectra of $(CH_3)_2NCO\text{-}MNP\cdot$.

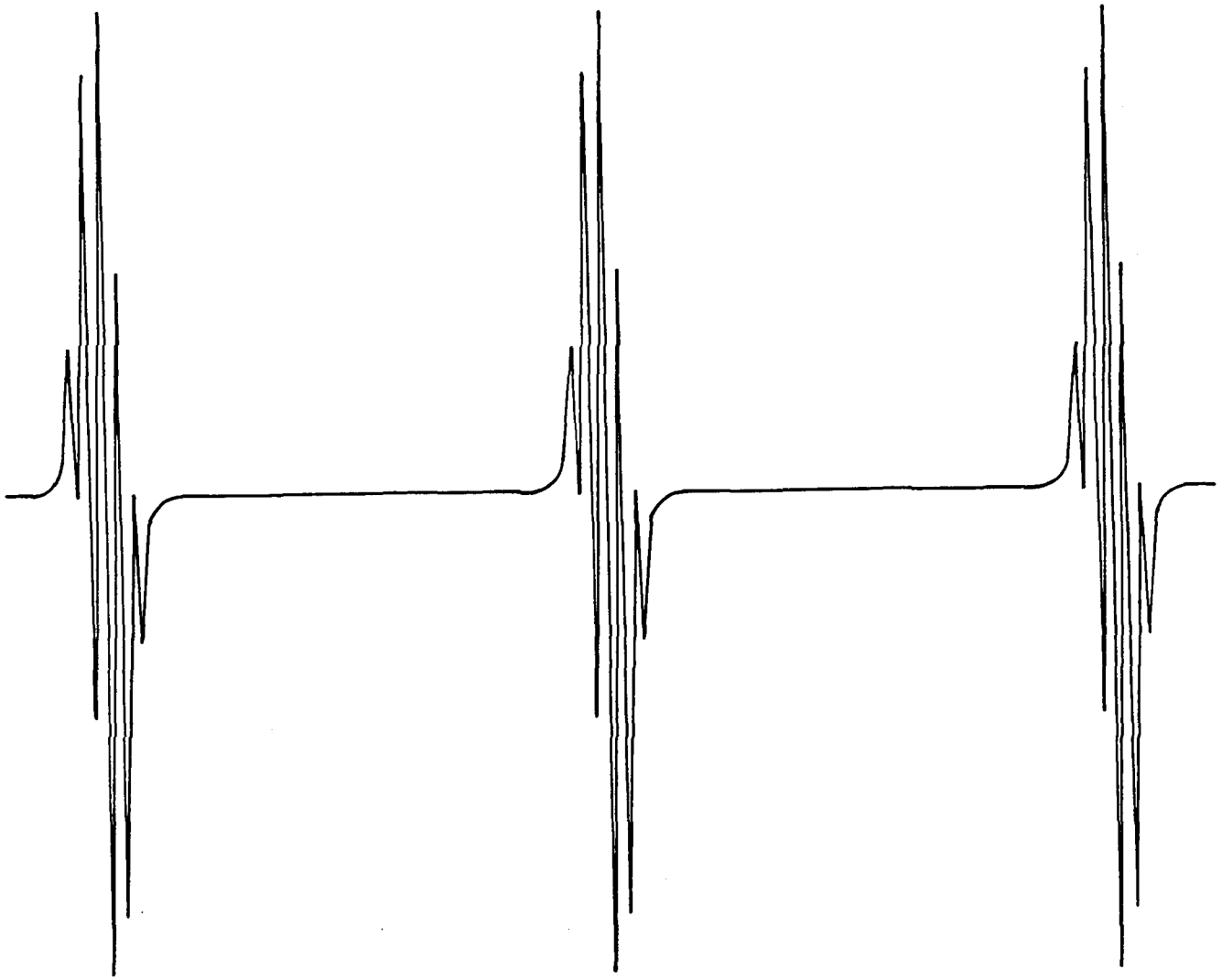
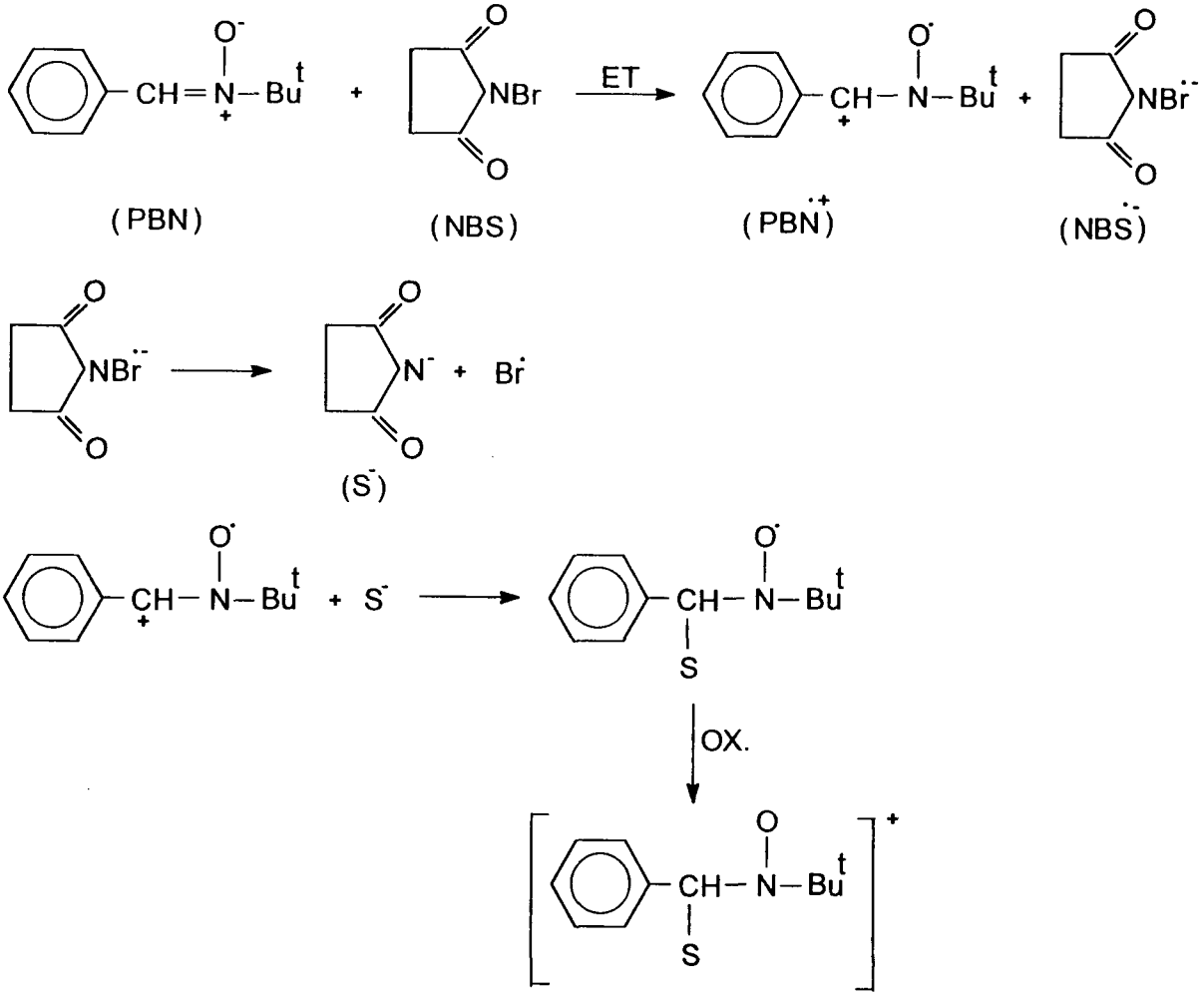
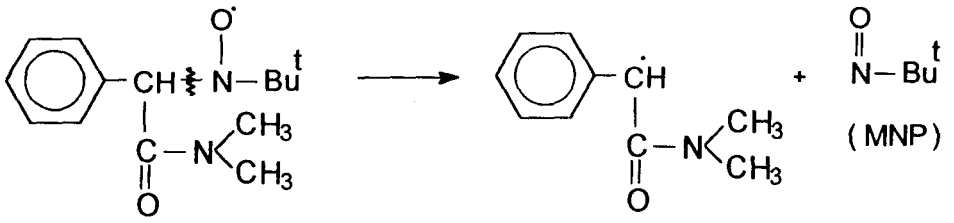


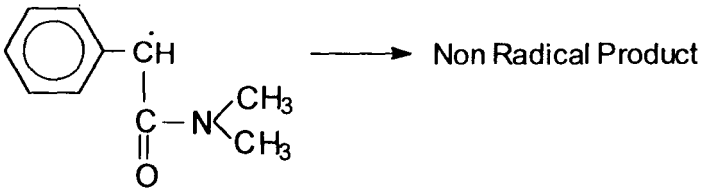
Fig. 5.10 : Simulated spectra of 5.9 using experimentally determined hyperfine parameters L.W = 0.28.

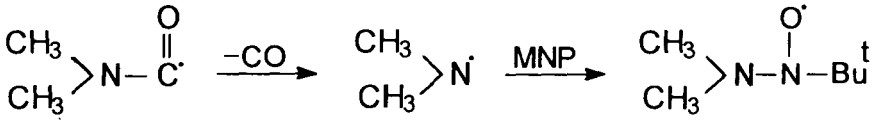
Scheme 5.3

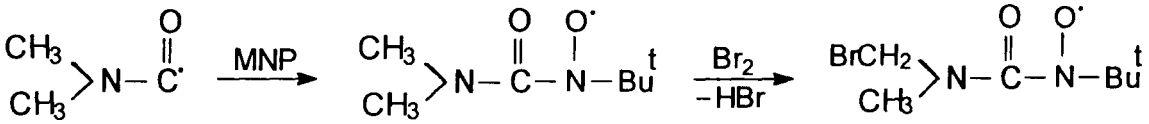


contd..


(MNP)


Non Radical Product


-CO
MNP


MNP
Br2
-HBr

Br· undergoes H- abstraction from the formyl group of DMF yielding $\cdot CON(CH_3)_2$ which is subsequently trapped by PBN. We suggest that this adduct undergoes β - cleavage yielding MNP as shown in the mechanism. It appears that $\cdot CON(CH_3)_2$ radicals undergoes decarboxylation giving $\cdot N(CH_3)_2$ radicals which are trapped by MNP giving spectra Fig. 5.5.

The failure to detect any solvent derived adduct when PBN was replaced by DMPO is attributed to its rapid oxidation by Br_2. When traces of MNP was added in the system, we suggest that the initial adduct $(CH_3)_2NCO\text{-}MNP\cdot$ undergoes reaction with Br_2 yielding $BrCH_2CH_3NCO\text{-}MNP\cdot$ adduct as shown in the last step of the proposed Scheme. The results obtained with traces of MNP in the system supports our results of PBN. These results shows the various possible modes of DMF participation in radical reactions. Again we did not observe any ring opened adduct of NBS in all the runs.

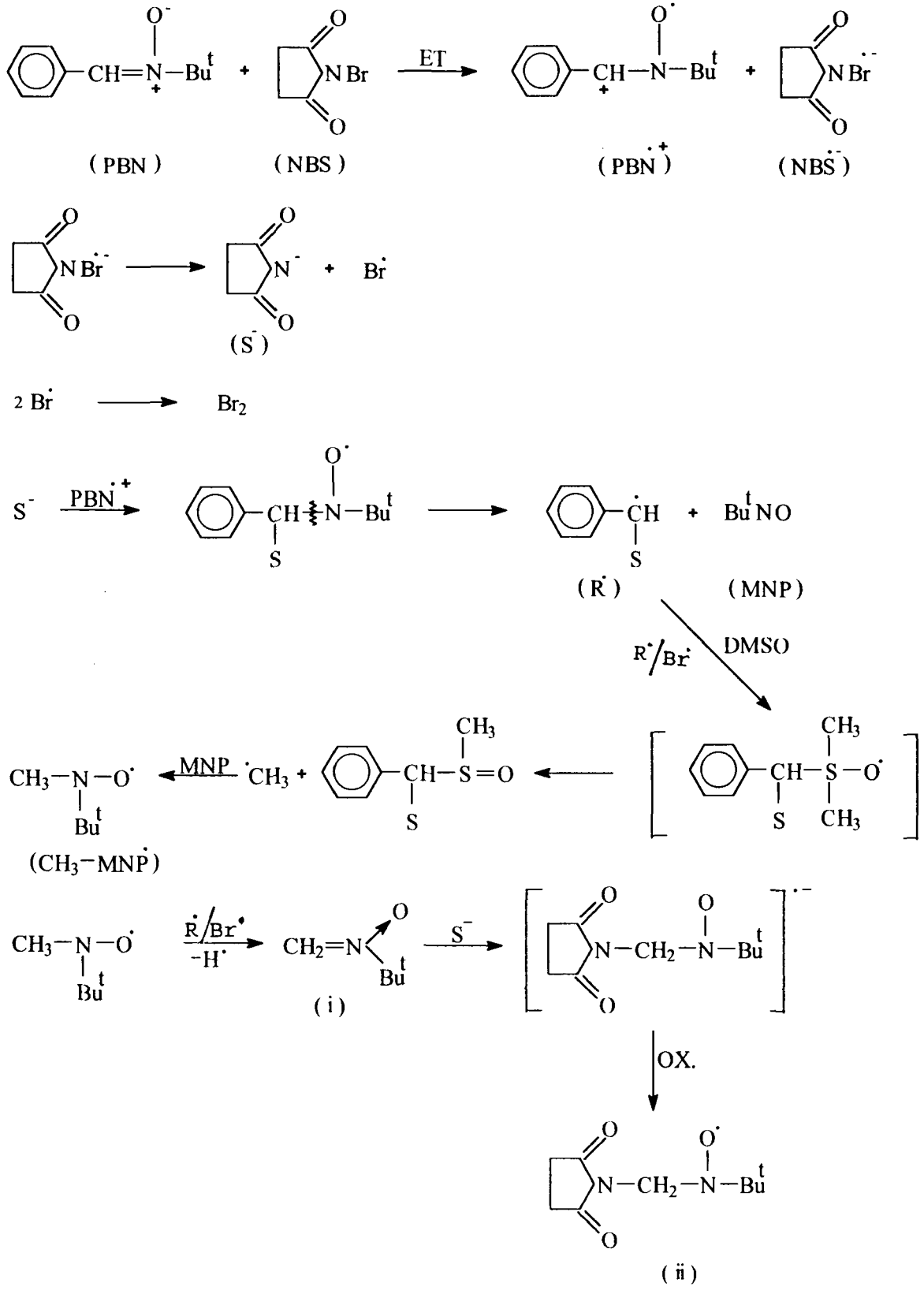
N- Bromosuccinimide and Nitrone in DMSO

In the preceding chapter we found that DMSO participated in a novel manner and some new and interesting results were observed. Therefore, the work was extended to NBS. Degassed solutions of NBS and PBN in 10 % DMSO in benzene were mixed in minimum day light. The immediate spectra

observed was due to PBNOX with hyperfine splittings a_N = 8.00 G and g = 2.0066. Over a period of time another spectra which grew in intensity to a well resolved spectra (similar to that shown in the previous chapter Fig. 4.29) was observed. The hyperfine splittings measured from the observed spectra are a_N = 15.20 G, a^{β}_H = 11.40 G and $a_{N'}$ = 1.40 G (from secondary nitrogen). The hyperfine splittings are of the same order as observed in case of NCS and is assigned to succinimidylmethyl radical adduct of MNP. However, this adduct decayed in ca. 25 minutes while PBNOX was the only signal left at the end of the reaction. The reactions performed at other concentrations yielded similar results. The reaction was repeated with deuterated DMSO. The immediate spectra observed was a weak set of triplet of septet which developed in ca. 20 minutes to a well defined spectra (similar to that observed with NCS, Fig. 4.31) assigned to SCD_2-MNP$^{\cdot}$. The hyperfine splitt - ings are similar to those observed in case of NCS. On the basis of all these experimental observations we suggest the mechanism shown in Scheme 5.4.

We suggest that after the primary act of electron transfer, expected succinimidyl adduct of PBN undergoes rapid β - cleavage as shown in the Scheme, leading to the formation of MNP and the intermediate specie (R$^{\cdot}$). We

Scheme 5.4


ET
(PBN)
(NBS)
(PBN·+)
(NBS·-)
(S-)
2 Br·
Br2
PBN·+
(R·)
(MNP)
R·/Br·
DMSO
MNP
(CH3-MNP·)
-H·
(i)
S-
OX.
(ii)

suggest that R· and / or Br· both being reactive, may add to DMSO yielding $\cdot CH_3$ which is trapped exclusively by MNP. This preferential trapping has been explained in the case of NCS. We suggest that both R· and / or Br· are possible candidates for H- abstraction from CH_3-MNP· adduct leading to methylene nitrone (i). We suggest that succinimidyl - methyl nitroxide (ii) is formed by the addition of succinimidyl anion to methylene nitrone followed by subsequent oxidation by molecular bromine. Under similar reaction conditions in one of the sets, traces of MNP was added and intense signal due to adduct (ii) was observed, which confirms the formation of MNP during the course of the reaction. In another set, traces of N- Methylsucci - nimide was added, but it showed no effect on the appearance or intensity of the adduct (ii). The reaction was carried out with cyclic spin trap, DMPO. The reaction showed signals of splitting pattern 3 x 3 x 2 with hyperfine splittings a_N = 14.10 G, a^{β}_H = 20.00 G and $a_{N'}$ = 2.20 G. The order and magnitude of the hyperfine splittings is same as that observed in previous chapter and it is unambiguously assigned to succinimidyl adduct of DMPO. This adduct was overlapped by intense septet signals. The signals of S-DMPO· disappeared in ca. 10 minutes while a continuous increase in septet signal was observed and was the only signal left after ca. 10 minutes of the reaction.

The hyperfine values calculated are a_N = 6.80 G and a^{β}_H = 3.40 G. These hyperfine values are similar to those observed in parallel reactions done in previous chapter and therefore it is assigned to DMPOX. These results clearly demonstrate that with DMPO, the possibility for some sort of cleavage as occured with PBN (leading to the formation of MNP) does not exist. Therefore, the sequence of reactions leading to adduct (ii) does not occur. These results further support our proposed mechanism for the observance of succinimidylmethyl nitroxide.

N- Iodosuccinimide (NIS)

After studying the system N- Chloro and N- Bromo substituted succinimides, the next logical choice was to study the N- Iodosuccinimide chemistry. Iodine being next down the group in the periodic table may present with some interesting results. It is less electronegative and heavier then bromine so it was expected that whatever ambiguity is in the differences between the mechanistic interpretation of SET with NCS and NBS, may become clearer for example, we observed that with NBS the transferred electron stays preferentially with succinimide moiety while Br· formed dimerises to Br_2. The other incentive to work with this compound was that very little work has been done with this compound.

N- Iodosuccinimide and Nitrone in Benzene

At comparable concentrations of NIS and PBN the immediate spectra observed was a triplet of doublet along with another triplet. The hyperfine values for triplet of doublet are a_N = 13.15 G and a^{β}_{H} = 1.50 G and for the triplet is a_N = 8.00 G and g = 2.0066. The spectra with these magnitude of hyperfine splittings observed with NBS has been assigned to benzoyloxyl radical adduct of PBN and PBNOX respectively. A continuous increase in PBNOX signal

intensity was observed and was the only signal left at the end of the reaction. Solution turned light violet in colour immediately on mixing the substrates. This indicate the formation of molecular iodine at a rate faster then the formation of molecular bromine in case of NBS. Reactions performed at varying concentration ratios of NIS and PBN yielded similar results. However, in reactions carried out at higher concentrations of PBN, an additional triplet of DTBN was observed in later stages of the reaction.

The mechanism seems to be identical as proposed in case of NBS. The primary act of electron transfer results in the formation of PBN cation ($PBN^{\cdot +}$) and NIS radical anion ($NIS^{\cdot -}$). We suggest that $NIS^{\cdot -}$ dissociates giving S^- (succinimidyl anion) and $I^{\cdot}$ (iodine atoms). We suggest that $I^{\cdot}$ being highly reactive immediately dimerises to give molecular iodine, the cause of violet colour of the solution. The succinimidyl anion formed should have been trapped by PBN radical cation, but it is not observed in all the runs. As suggested with NBS here too, molecular iodine formed may oxidise any S-PBN$^{\cdot}$ adduct formed and this could be one of the reason for the non observance of S-PBN$^{\cdot}$ adduct. Molecular iodine also oxidises PBN to PBNOX as Br_2 does through a mechanism discussed in case of NBS. As proposed earlier PBNOX undergoes β - cleavage giving

benzoyl radical and MNP. Benzoyl radical reacts with traces of oxygen might present in the system yielding benzoyloxyl radical which is trapped by PBN thus giving rise to benzoyloxyl radical adduct. The observance of di-tert. butyl nitroxide with hyperfine splitting a_N = 15.50 G, in later stages of the reaction supports this reaction pathway. In NBS and PBN system, the bromine was effectively removed by using a radical scavenger bicyclopentadiene and we could observe spectrum due to succinimidyl adduct of PBN. Here too we thought that bicyclopentadiene could also remove iodine from the system and we might observe similar results. However, when reactions were carried out in the presence of bicyclopentadiene we observed PBNOX as the major specie and no spectra due to succinimidyl adduct of PBN. This indicate that bicyclopentadiene is less effective in removing I· from the system and dimerisation is the only course left. The formation of violet colour in these runs too, supports our postulation. Reactions done with other scavengers yielded similar results.

In order to achieve a better understanding of the reaction, the cyclic spin trap DMPO was employed. However, these experiments also yielded only signals corresponding to DMPOX with hyperfine splittings a_N = 6.60 G and a^{β}_H =

3.40 G. The spectra of this adduct is similar to that shown in Fig. 4.11 of previous chapter. Thus these results clearly show that the major reaction is the oxidation by molecular iodine formed in the system.

N- Iodosuccinimide and Nitrone in n- Hexane

Reactions carried out in n- Hexane, an inert solvent with very low dielectric constants, were extremely fast. The immediate spectra observed at 1 : 1 concentration of NIS and PBN showed intense signals of PBNOX with hyperfine splitting a_N = 7.88 G, g = 2.0066. A continuous increase in its intensity was observed and was the only signal observed throughout the reaction. The isotope splittings observed from the PBNOX signal are $a^{\alpha}_{13\text{-}C}$ = 4.88 G, $a^{\beta}_{13\text{-}C}$ = 4.06 G, $a^{\gamma}_{13\text{-}C}$ = 2.60 G and a^{15}_{N} = 11.00 G. Reactions carried out at other concentration ratios also exhibited similar behaviour. In spite of our extensive efforts even with other radical scavengers we could not succeed in removing iodine from the reaction system. Reactions performed with DMPO were also marked by only DMPOX signals with hyperfine splittings a_N = 6.70 G and a^{β}_{H} = 3.25 G. Reactions carried out under photolytic conditions showed initially two set of signals. Benzoyloxyl radical adduct of PBN with hyperfine values a_N = 13.34 G and a^{β}_{H} = 1.50 G

and PBNOX with hyperfine splittings a_N = 7.88 G. Benzoyl - oxyl radical adduct disappeared in ca. 10 minutes of continuous photolysis while a considerable increase in PBNOX signal intensity was observed. After ca. 30 minutes of photolysis it was accompanied by well known signals of di- tert. butyl nitroxide with a_N = 15.20 G. This was the only adduct left at the end of the reaction. The mechanism proposed on the basis of these results is similar to that described in case of benzene. We suggest that the reaction is carried away by oxidation by molecular iodine formed in the system.

N- Iodosuccinimide and Nitrone in Acetonitrile

The immediate spectra observed at comparable concen - trations of NIS and PBN was ; (i) an intense triplet of PBNOX with hyperfine splittings a_N = 8.12 G and (ii) a short lived (ca. 10 minutes) triplet of doublets with hyperfine splittings a_N = 14.40 G and a^{β}_{H} = 2.18 G. This triplet of doublet in the preceding chapter has been assigned to CH_2CN-PBN· adduct. PBNOX was the only signal left at the end of the reaction. Reactions carried out at other concentration ratios yielded similar results. Solution turned violet in all these runs signifying the formation of iodine. We suggest that most of the iodine

atoms produced in the system undergoes dimerisation and only a very small fraction might participate in H-abstraction giving rise to short lived solvent derived adducts. Repeated attempts to remove iodine from the system using bicyclopentadiene failed in this solvent also. DMPOX was the only signal observed in reactions with DMPO as spin trap. Photolysis experiments also showed only PBNOX and CH_2CN-PBN· adducts.

We did not find any adduct which could reasonably be assigned to ring opened adduct and hence we suggest that succinimidyl anion produced in the system does not participates in ring opening reaction as proposed by other workers.

N- Iodosuccinimide and Nitrone in Dichloromethane

On mixing degassed solutions of NIS and PBN in concentration 1 : 1, the initial spectra observed was due to benzoyloxyl radical adduct and PBNOX. The hyperfine values of benzoyloxyl adduct and PBNOX calculated from the observed spectra are a_N = 13.26 G, a^{β}_H = 1.50 G and a_N = 8.09 G respectively. The former signal decayed leaving PBNOX behind. The solution turned light violet. Reactions carried out at other concentration ratios also yielded similar results. With DMPO, DMPOX was the only signal

observed in all the runs. Reactions performed under photolytic conditions also exhibited similar behaviour.

N- Iodosuccinimide and PBN in alcohols

Alcohols being solvents with high capability of solvating charged species and thus might change the course of the reaction mechanism for example, in NCS system the results observed were different. Therefore, an attempt was made to elucidate NIS chemistry in these solvents.

N- Iodosuccinimide and Nitrone in Ethanol

The immediate spectra observed in reaction carried out at comparable concentrations, was a triplet of doublet with hyperfine splittings a_N = 14.62 G and a^{β}_{H} = 2.80 G and triplets of PBNOX with a_N = 8.00 G, g = 2.0066. The triplet of doublet is also observed in parallel reactions carried out in case of NBS and is assigned to solvent derived radical adduct of PBN (C_2H_5O-PBN$^{\cdot}$). This adduct decayed in ca. 30 minutes while a continuous increase in PBNOX signal was observed and it was the only signal left at the end of the reaction. Similar results were obtained in other concentration ratios of NIS and PBN. The solution turned light violet signifying the formation of molecular iodine. These results suggests a similar mechanism as

proposed in case of NBS. The reactions carried out under photolytic conditions or in presence of bicyclopentadiene or with DMPO yielded similar results. Reactions carried out in other analogues of alcohols showed similar trend. Since the hyperfine splittings of the solvent derived adducts and PBNOX are similar to those observed in case of NBS, they are not mentioned here.

N- Iodosuccinimide and Nitrone in Carbontetrachloride

Reactions carried out in CCl_4 showed different behaviour as compared to NBS. The immediate spectra observed at comparable concentrations of NIS and PBN, was a triplet of doublet with hyperfine splitting a_N = 13.25 G and a^{β}_{H} = 1.40 G and is assigned to benzoyloxyl radical adduct of PBN. This was accompanied by PBNOX signals with a_N = 7.93 G. The former signal decayed in ca. 20 minutes while PBNOX was the only signal left at the end of the reaction. The PBNOX signal could be recorded with well defined ^{13}C and ^{15}N isotope splittings. The hyperfine values calculated are a_N = 7.93 G, $a^{\alpha}_{13\text{-}C}$ = 4.75 G, $a^{\beta}_{13\text{-}C}$ = 3.90 G, $a^{\gamma}_{13\text{-}C}$ = 2.70 G and a^{15}_{N} = 11.20 G. Reactions performed at other concentration ratios yielded similar results. Reactions carried out with DMPO and even in presence of bicyclopentadiene showed similar adducts as

discussed earlier. One remarkable difference in present system is the absence of chloro adduct as observed in case of NBS. We propose that due to very high rate of dimerisation of iodine atoms it does not participates in any reaction with CCl_4. The absence of succinimidyl adduct is attributed to its rapid oxidation by molecular iodine.

The reactions carried out in 1,4- Dioxan and DMF showed PBNOX as the major specie in all the runs. DMPOX was the only adduct observed in reactions done with DMPO. This observation is in contrast to the one we found with NCS and NBS.

N-Iodosuccinimide and Nitrone in DMSO

As mentioned in case of NCS and NBS, we have observed some new and interesting results. Therefore, similar work was done with NIS. Surprisingly, only PBNOX signal was observed. It appears that in some of the crucial steps where Br· participates for example, reaction with DMSO where $\cdot CH_3$ are formed, we feel that in this case I· is no longer available to react with DMSO (I· dimerises very fast to form I_2) and hence we did not observe adducts as observed in case of NBS. Since an important intermediate is not formed, reaction does not proceed to give succini -

midylmethyl nitroxide. These results also points out that addition of Br· to DMSO is a major pathway for the formation of methyl radical.

All the results obtained with N- Iodosuccinimide suggests that the basic reaction mechanism is similar to N-Bromosuccinimide. The dimerisation of iodine atoms is so fast that all our efforts failed to see any sign of iodo adduct with PBN even the various other radical scavengers employed could not prevent the dimerisation of iodine atoms. So our postulation that after electron is transferred to N- Bromosuccinimide, dissociation leads to succinimidyl anion and Br· gets further support from NIS study. No adduct with hyperfine splittings characteristic of ring opened product of succinimidyl moiety was observed in all the systems mentioned above.

On the basis of these results we conclude the following points :

1. Charge Transfer complexes have also been observed with NBS thus establishing the feasibility of electron transfer reactions between NBS and PBN.
2. The results suggest that electron captured dissociation of NBS and NIS leads to succinimidyl anions and corresponding halogen atoms in contrast to that observed with NCS.

3. The observance of succinimidyl adduct of PBN in the presence of bicyclopentadiene confirms the radical nature of bromine produced in the system.
4. The observance of chloro adduct of PBN in case of NBS in CCl_4 is reported first time. The results are in agreement with Ziegler's postulation.
5. The generation of methyl radicals from DMSO have also been observed with NBS.
6. It has been clearly observed that the rate of dimeri - sation of $I^{\cdot}$ is certainly higher than $Br^{\cdot}$ atoms.
7. The formation of PBNOX is through the oxidation of PBN by halogens.
8. Again we did not come across any sign of two states (σ and π) even with succinimidyl anion produced in the system.
9. The results suggests that succinimidyl anion and corresponding halogen atoms are the major chain carriers with no sign of ring opening of the succini - midyl anion.

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CONCLUSION

The attempts to explain the Ziegler reaction and the search for σ and π radicals opened a new field in radical chemistry : the chemistry of succinimidyl radicals. Though number of researchers have studied the system, a definite reaction mechanism could not be established. In this work a systematic study was carried out by using ESR spectroscopy. The major achievements of this work are summarised below :

1. As mentioned in the objective, examples involving SET reactions are limited. This work provides another good example of SET phenomenon.
2. We are successful in studying electron transfer (ET) reaction between N- halosuccinimides and nitrones,
   (i) under mildest conditions i.e, creating such favorable conditions where just one electron is transferred without any assistance (photoassisted ET) and reaction begins,
   (ii) At ambient temperatures.
3. Spin trapping has been successfully applied in SET reactions from nitrones to N- halosuccinimides.
4. Nitrones (PBN and DMPO) as a spin trap are well known, but their role as an effective electron donor

has been very well demonstrated.

5. PBN is a relatively better electron donor than acceptor is established through UV experiments.
6. Charge Transfer complexes are believed to be precursors to electron transfer processes. This has been demonstrated through the appearance of isosbestic points, a positive indication for the feasibility of ET processes.
7. The recently proposed pathway "inverted spin trapping" is demonstrated through the appearance of chloro adduct of PBN.
8. The relatively high stability of the chloro adduct of PBN in benzene, lends support to the hypothesis that " spin adducts with good leaving groups will be unstable and could be detected only in solvents of relatively low permitivity or under conditions of continuous generation for example, during photolysis ".
9. The observance of succinimidyl adduct of PBN at higher concentrations of PBN to NCS in benzene refutes earlier proposals that in benzene the succinimidyl radicals are trapped by it.
10. We are successful in observing satellite signals from ^{13}C isotope from all the different positions in PBNOX. To the best of our knowledge it is reported first time. Such examples are good for conformational studies by

ESR spectroscopy.

11. The observance of succinimidyl adduct of DMPO with NCS under the conditions employed is being reported first time.
12. Solvent participation particularly from CH_3CN and CH_2Cl_2 has been found by the detection of solvent derived radical adducts of PBN.
13. The role of polar and hydroxylic solvents in solvating the charged species and thus diverting the reaction pathways have been clearly observed. This inference is based on the observance of succinimidyl adduct in all the alcohols (except CH_3OH which proved to be less effective in solvation).
14. A new route for the generation of methyl radicals from DMSO is established.
15. The observance of chloro adduct of PBN in case of NBS in CCl_4 suggests that $Br^{\cdot}$ replaces $Cl^{\cdot}$ from CCl_4.
16. The observance of succinimidyl adduct of PBN (only with NBS) in the presence of bicyclopentadiene (a radical scavenger) confirms the radical nature of bromine produced from NBS.
17. It has been observed that rate of dimerisation of $Br^{\cdot}$ atoms are relatively slower than $I^{\cdot}$ atoms.
18. On the basis of our results we conclude that in the case of NCS, the electron captured dissociation leads

to succinimidyl radical and chloride ion, whereas in case of NBS and NIS it leads to succinimidyl anion and corresponding halogen atoms.

19. In the absence of any adduct with characteristics of ring opened product of succinimidyl moiety, we propose that the studied system involves only two chain carriers succinimidyl and the corresponding halogen moieties.
20. The evidence of charge transfer complexation suggests that the electron transfer proceeds through an " outer - sphere " mechanism.
21. None of our results provide evidence for the two states of succinimidyl radicals (σ and π).

On the basis of our understanding we developed from this system, we attempt to answer some of the questions raised in the objective.

(i) In our opinion, the energetic is " The factor " which determines whether a particular reaction proceeds via a SET or a Polar pathway. In some cases the transfer of just one electron may be enough to raise energetically the species to a level from where they can cross over the potential energy barrier to form the product, while in some cases (polar reactions) minimum of two electron transfer (could be in quick succession) are needed to meet the

energetic requirements.

(ii) It is well known that for a reaction to take place, the reactants must acquire a specific orientation. In some cases the transfer of just one electron is enough to achieve the desired orientation for the given reaction, while in other cases the transfer of two electrons are needed.

(iii) It is accepted beyond any contention that ;

(a) electrons prefer to pair up so as to acquire a state of lower energy

(b) they move singly to generate cations or anions.

It seems bit difficult to accept that under some cases (SET) only one electron can move while in other cases electrons prefer to move only in pairs (polar pathways). It is a fact that an electron exists individually, it occupies orbitals singly. If it can exist individually, why it can not move individually ? Why it requires a partner ?. We therefore, feel tempted to put forward a view that polar reactions are basically two ultra fast single electron transfer reactions in quick succession. The idea is no doubt a simplistic one, but it is purely suggestive in nature.

SCOPE OF THE PRESENT WORK

Since this is a first attempt of this kind at room temperature under mildest conditions, the positive results appears to be quite promising. Therefore, it is certainly worth pursuing with other substituted and structurally similar molecules e.g., N- Halophthalimides, N- Halogluta-rimides etc..

appendix

```
20 DIM SP(3000),MK(3000),LN(100),NU(20),CC(20),SN(20)
25 MT=1
30 PRINT"ESR SIMULATION PROGRAM"
40 PRINT
50 PRINT"BY DR.HARISH CHANDRA"
60 PRINT"CHEMISTRY DEPARTMENT"
70 PRINT"N.E.H.U,SHILLONG"
80 PRINT
90 PRINT"NUMBER OF SPECTRA(TS), X INCREMENT(XC), PHASE(PH)"
100 INPUT TS,XC,PH
110 PRINT
150 FOR I1=1 TO TS :GOTO 200
170 FOR J=1 TO 3000
180 MK(J)=0
190 NEXT J
200 PRINT"NUMBER OF COUPLING CONSTANTS (NC)"
210 INPUT NC
220 PRINT
230 PRINT"LINE WIDTH, MAXIMUM Y, DELTA G, FRACTION LORENTZIAN"
240 PRINT"FRACTION LORENTZIAN IS COMMONLY 0.3-0.5"
250 INPUT LW,YM,DG,LR
260 PRINT
270 LR=.275664*LR/(.275664*LR+.967883*(1-LR))
280 DG=DG/XC
290 LW=LW/XC
300 PRINT"NUMBER OF NUCLEI(NU), COUPLING CONSTANT(CC), SPIN(SN)"
310 FOR J=1 TO NC
320 PRINT J;
330 INPUT NU(J),CC(J),SN(J)
340 CC(J)=CC(J)/XC
360 NEXT J
370 PRINT:PRINT:PRINT
380 'Calculate STICK diagram.
400 N=1
405 MK(1)=1
410 FOR I2=1 TO NC
420 FOR I3=1 TO NU(I2)
440 I4=N
450 IF MK(I4)=0 THEN I4=I4-1:GOTO 450
460 FOR I5=1 TO 2*SN(I2)
470 T1=I4+INT(I5*CC(I2))
480 MK(T1)=MK(T1)+MK(I4)
485 MT=MT+1
490 IF MA<MK(T1) THEN MA=MK(T1)
500 NEXT I5
510 IF T1>N THEN N=T1
515 I4=I4-1
520 IF I4>1 GOTO 450
530 NEXT I3
```

```
540 NEXT I2
541 IF I1=1 THEN FI=N+2*INT(8*LW): GOTO 550
542 T6=INT((FI-N-2*INT(8*LW))/2+DG)
543 IF T6=0 GOTO 550
544 FOR J=N TO 1 STEP -1
545 MK(J+T6)=MK(J)
546 MK(J)=0
547 NEXT J
548 N=N+T6
550 IF TL<N+INT(16*LW) THEN TL=N+INT(16*LW)
560 SR=-INT(8*LW)
570 ST=SR+99
580 IF ST>0 THEN ST=0
590 T4=1
600 FOR I6=SR TO ST
610 T1=-PH*YM/MA*(1-LR)
620 T2=LR*16*YM/MA*-PH
630 T3=I6*2/LW
640 LN(T4)=T3*T1*EXP(-.5*(T3^2-1))
650 LN(T4)=LN(T4)+T3*T2/((3+T3^2)^2)
680 T4=T4+1
690 NEXT I6
700 FOR I7=1 TO N
710 IF MK(I7)=0 GOTO 770
720 T4=1
730 FOR I8=SR+INT(8*LW) TO ST+INT(8*LW)
740 SP(I7+I8)=SP(I7+I8)+LN(T4)*MK(I7)
750 SP(I7+2*INT(8*LW)-I8)=SP(I7+2*INT(8*LW)-I8)+LN(T4)*-MK(I7)
755 T4=T4+1
760 NEXT I8
770 NEXT I7
780 IF ST<>0 THEN SR=SR+100:GOTO 570
783 AR(I1)=LR*2*3.14159/(3^.5)*(YM*(LW^2))
784 AR(I1)=AR(I1)+(1-LR)*(2*3.14159*EXP(1))^.5*(.5*LW)^2*YM
785 AR(I1)=AR(I1)*MT/MA
787 MT=1:MA=0
790 NEXT I1
800 FOR J=1 TO TL
810 IF MN>SP(J) THEN MN=SP(J):GOTO 830
820 IF MX<SP(J) THEN MX=SP(J)
830 NEXT J
880 FOR J=1 TO TS
890 TA=TA+AR(J)
900 NEXT J
910 PRINT:PRINT:PRINT
920 PRINT"AREAS OF COMPONENT SPECTRA"
930 PRINT
940 FOR J=1 TO TS
950 PRINT"AREA OF COMPONENT ";J;" IS ";AR(J)/TA*100
```

```
960 NEXT J
970 PRINT:PRINT:PRINT
980 PRINT "CONTINUE(Y/W)?"
990 INPUT X$
1000 IF ((X$="W")) THEN GOTO 80
1005 SCREEN 2,,0,0:KEY OFF
1010 CLS:MAX=0:MIN=1000
1011 FOR I= 1 TO TL
1012 IF SP(I) < MIN THEN MIN =SP(I)
1013 IF SP(I) > MAX THEN MAX =SP(I)
1014 NEXT I
1015 YI=200/(MAX-MIN)
1016 XI=600/TL:X=1
1017 PSET (SP(1),100)
1020 FOR J=1 TO TL-1
1040 IF ABS(SP(J+1)) > MX THEN SP (J+1) = 0
1050 LINE -(X,100-SP(J+1)*YI)
1052 X=X+XI
1060 NEXT J
1062 WHILE INKEY$="":WEND
1070 KEY ON:SCREEN 0,0,0:END
```

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   S. Bhattacharjee, Md. N. Khan, Harish Chandra and Martyn C.R. Symons.
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