FREE RADICAL PHENOMENA

IN

IRRADIATED ORGANIC CRYSTALS

By

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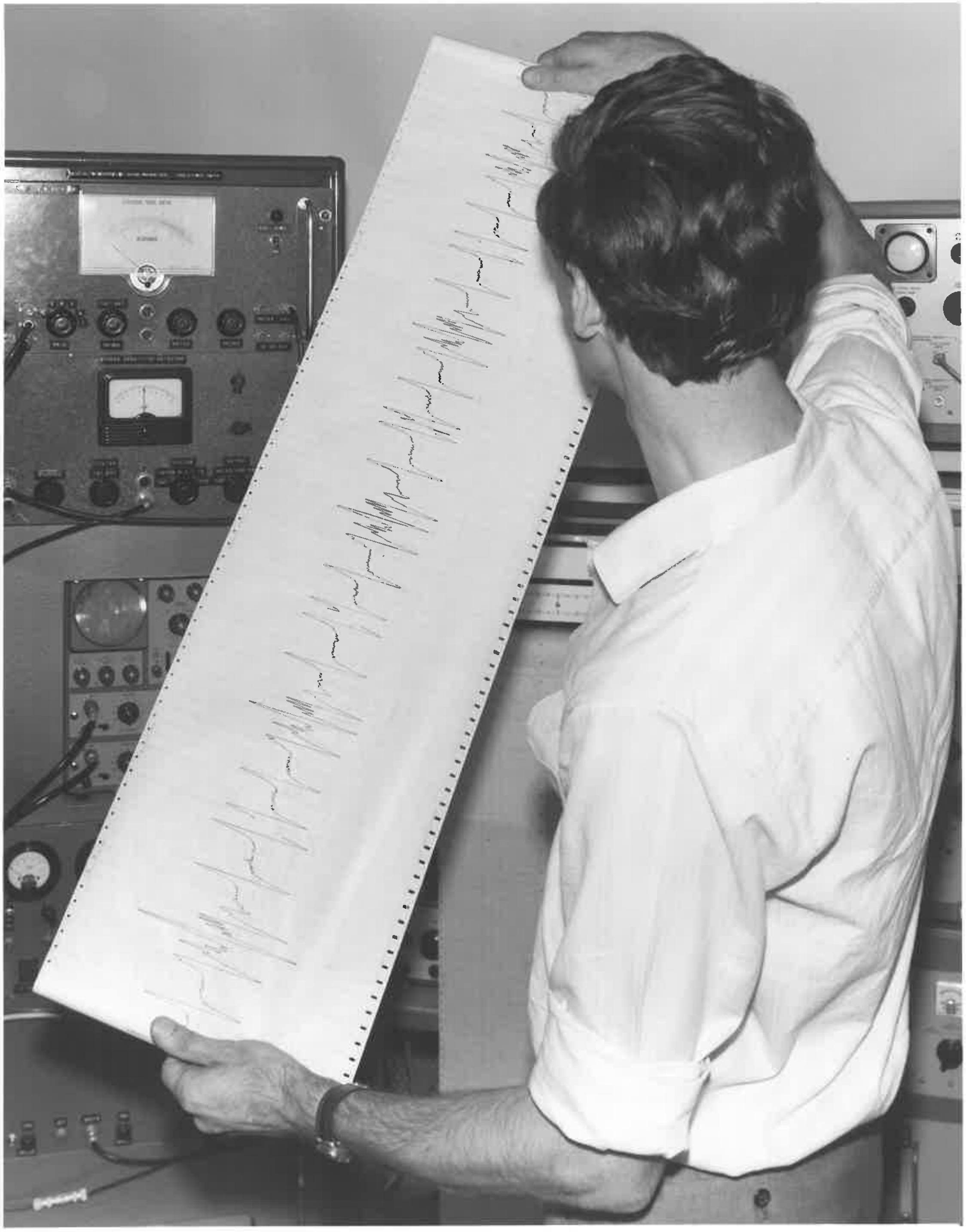

FRONTISPIECE

Shows the author examining a series of E.S.R. spectra obtained from an irradiated succinic acid crystal during its annealing.

SUMMARY

The thesis describes an experimental and theoretical investigation of the behaviour of free radicals in irradiated organic single crystals. Attention is confined to problems concerned in the production and post-irradiation behaviour of free radicals as distinct from previous work which has been concerned mainly with problems of their identification and interpretation of their ESR spectra. The work centres around the problem as to whether mobile hydrogen atom vacancies play a role of any importance in free radical behaviour and especially in their thermal annealing. In this regard the literature has been reviewed and a search made for evidence implicitly related to this question. The necessary and reasonable consequences of the hydrogen atom vacancy being readily mobile have been analysed in some detail to provide a guide to experiments aimed at the verification of this hypothesis. A by-product of this part of the work is the proposal of a new and convenient nomenclature for complex organic radicals.

The thesis describes apparatus designed and constructed in the course of this work, the most important of which is a variable temperature cavity enabling the thermal behaviour of free radicals to be observed at elevated temperatures.

Experimental studies showed the production rates of free radicals and their rates of thermal annealing to be quite reproducible from specimen to specimen to an extent indeed, beyond what one expects for reactions in the solid state. The kinetics of free radical thermal destruction was investigated in selected systems; reaction kinetics were found to be usually second-order; activation energies were measured where possible. Selected cases were examined for the deuterium isotope effect on reaction rates which was found in two instances. Several systems were examined by means of differential infrared spectroscopy for evidence of the phenomenon known as "isotopic mixing". This was found to occur in one case (viz OO' - dideuterosuccinic acid single crystal) to such an extent that it is easily observed in the infrared spectra. Other techniques (namely differential thermal analysis, free radical production by hydrogen atom bombardment and macroscopic diffusion measurements) were employed on account of their relevance to these problems.

The general conclusion of the thesis is that the hydrogen atom vacancy probably does play a major role in post-irradiation behaviour of organic free radical phenomena. The best new evidence brought forward, for at least the occasional relevance of this mechanism, is the abovementioned occurence of large scale isotopic mixing in partially deuterated succinic acid single crystal. However, it seems likely from the evidence that it is not the sole mechanism which provides the radical state mobility necessary to explain the thermal annealing of free radicals at moderate temperatures.

PREFACE

The text of this thesis, except where due reference is made, describes the original and personal work of the author which was carried out between January, 1964, and September, 1968, in the Physics Department of the University of Adelaide. No material contained in this thesis has been submitted for a degree or diploma in this or any other university.

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CHAPTER 1

INTRODUCTION

1.1 Historical Review

The first electron spin resonance (ESR) spectrum from free radicals in an organic compound previously exposed to high energy radiation was reported as early as 1951. (Schnieder, Day and Stein, 1951). Later Gordy, Ard and Shields (1955a, 1955b) examined the ESR spectra of a large number of irradiated organic crystals in powder form. These included amino, carboxylic and hydroxy acids which were chosen because of their biological interest. The results in general appeared to indicate that high energy radiation removed a hydrogen atom from a carbon atom in the molecule and the unpaired electron remaining was primarily localised on this carbon atom. This unpaired electron associated with the larger fragment of the damaged molecule (which is generally called a free radical) was found to interact magnetically with those nuclei in close proximity to it. The hyperfine structure of the ESR spectra that Gordy et al observed resulted from this interaction allowing them to identify the radicals produced in the simpler compounds. Uebersfeld and Erb (1956) made extensive studies on free radicals in γ-irradiated sugars and cellulose, and in particular they studied the anisotopic spectrum from single crystals of glycine. Van Roggen, Van Roggen and Gordy (1956) also observed spectra from X-irradiated single crystals of alanine. McCormick and Gordy (1958) examined several simple compounds with peptide bonds to gain some idea of the breakdown processes in natural products. However, they concluded that only limited information regarding the radical species produced can be obtained from the spectra of irradiated crystalline powders.

Since about 1958 a large number of studies of the ESR from single crystals of organic compounds irradiated at room temperature have been made. Some of the compounds investigated include glycine (Ghosh and Whiffen, 1959, 1960; Windle, 1959; Weiner and Koski, 1963; Morton 1964b; Collins and Whiffen, 1966), alanine (Miyagawa and Gordy, 1960; Horsfield, Morton and Whiffen, 1961c; Miyagawa and Itoh, 1962), valine (Shields, Hamrich and Delaigle, 1967) N-acetylglycine (Miyagawa, Kurita and Gordy, 1960), glycylglycine (Katayama and Gordy, 1961; Lin and McDowell, 1961), malonic acid (McConnell, Heller, Cole and Fessenden, 1960; Horsfield, Morton and Whiffen, 1961b) β-succinic acid (McConnell and Heller, 1960; Pooley and Whiffen, 1961), glutaric acid (Horsfield, Morton and Whiffen, 1961a), adipic acid (Morton and Horsfield, 1961) and dl-aspatic acid (Jaseja and Anderson, 1962). A review of the ESR spectroscopy of orientated radicals in single organic crystals up to 1964 has been made by Morton (1964a). This review also discusses in some detail the now well-established theory of the hyperfine interaction associated with orientated radicals. The ESR of trapped organic radicals in single crystals of known structure has yielded information on the orientation of the radicals in the crystal lattice of their conformation and electronic structure.

A reading of the literature on free radical identification in irradiated organic solids shows that the radicals formed in the crystal lattice usually result from the breaking of a C-H or C-C bond. Other bonds that may be broken are N-H (Morton, 1964b) or C-F (Iwasaki and Toriyama, 1967). A recent report in the literature has claimed that radicals of the form R-COO• do occur (Moulten, Cernansky and Straw, 1967). Sometimes irradiation results in the production of more than one different radical species in a particular crystal structure. For example when malonic acid is irradiated (Horsfield et al, 1961b) the two radicals $HOOC\text{-}\dot{C}H\text{-}COOH$ and $\dot{C}H_2\text{-}COOH$ are formed together. In most of the above studies the crystals were irradiated and observed at room temperature but some crystals including glycine (Collins and Whiffen, 1966) and L-α-alanine (Sinclair and Hanna, 1967) have been irradiated at room temperature and their ESR spectra observed at liquid nitrogen temperature (LNT). These workers found that when such crystals were cooled to LNT the ESR spectra recorded differed from the original spectra. They were able to explain this temperature dependence of the spectra as arising from the cessation of rotation of the amino (NH_3^+) or methyl (CH_3) group in the trapped radical as it was cooled. This change in the spectrum was reversible, that is, the original ESR spectrum was regained when the temperature of the crystal was returned to room temperature.

Recently, it has been reported that ionic species are formed in β-succinic acid (Box, Freund and Lilga, 1965), α-aminobutyric acid (Box and Freund, 1966), glycine (Collins and Whiffen, 1966) and L-α-alanine (Sinclair and Hanna, 1967) when crystals of these compounds are irradiated and observed at LNT. These workers believe that free radical ions are the primary species formed in the irradiation process and that the neutral free radicals observed at room temperature after the crystal was allowed to warm up are the secondary species of this process.

Kinetic studies on free radical disappearance in irradiated semicrystalline polyethylene were published in the literature as early as 1953. The early work has been briefly summarised in the introduction of a recent paper by Cracco, Avia and Dole (1962) who made an extensive study of the radicals in this material. These workers examined free radical annealing at different temperatures and found that the radical concentration at a particular temperature approached a limiting value, whilst on raising the temperature more free radicals disappeared until the concentration again reached a new limiting value. This isothermal free radical reaction was interpreted in terms of the free radicals being formed in regions of high, local concentration, called "spurs", during the primary act of the radiation. The annealing reaction was a bi-molecular process between radicals within each spur. Those free radicals closest to each other were able to react at the lower temperature leaving the radicals further apart unaffected. On raising the temperature some of the radicals further apart can move closer together and react. The mechanism by which the free radicals could move was postulated to be migration by a unique type of vacancy and this was the first time such a mechanism had been proposed. The authors suggested that the "free radical centre", that is, a free bond acting as a chemically active centre, could move along or across the molecular chain. This centre moved by the transference of a hydrogen atom, the atom moving from a neighbouring molecule and forming a bond with the unpaired electron while an unpaired electron is left on its parent molecule. In other words, a type of "hole" is left by the migration of the hydrogen atom; this "hole" representing the radical centre. The formation of spurs is to be expected to occur in materials where the crystallinity varies greatly throughout the material. In some regions one photon may produce many free radicals whereas in other regions this may not occur. Furthermore, some free radicals can be expected to see a different environment from others in the essentially inhomogeneous material. Therefore the reaction rate will vary from region to region and a kinetic law of simple form cannot be expected to be observed. In fact Cracco et al claimed that the reaction obeys first-order kinetics whereas Smith and Jacobs (1962) have claimed that it is second-order. Charlesby, Libby and Ormerod (1961) have also observed that the reaction rate varies with the preparation of the samples, the rate being 50 times faster for stretched polyethylene. After reviewing this work with polymers it was felt that further investigations of these materials with a view to the elucidation of the fundamental process of free radical phenomena in organic solids would be inadvisable. A study of microscopic phenomena of free radical reactions would obviously be very difficult. It appears that a study of free radical reactions in irradiated single crystals would be better as it can be expected that the radicals would be uniformly distributed throughout the crystal; each radical occupying an environment essentially the same as the others. In brief, the single crystal of an organic compound is a uniform and essentially well characterised material. This cannot be said for polymers.

The only other authors who have been concerned with the reaction mechanism of free radicals in organic solids have been Truby, McCallum and Hesse (1962). Octadecyl disulphide ($C_{18}H_{37}-S-S-C_{18}H_{37}$) was irradiated at LNT and two paramagnetic species were observed to form. These two radicals were respectively of the form RS• and an alkyl type radical whose exact nature was not determined. (R represents the paraffin-like chain structure of the molecule). On storing the irradiated powder at a temperature between 0°C and 40°C the RS• concentration was observed to increase while the concentration of radicals of the alkyl-type decreased. The rate of build-up and decrease of each radical was about the same. The reciprocal of the concentration for each radical species as a function of time was found to fit a straight line showing that the reaction kinetics were second-order. The mechanism suggested for this reaction was that molecular diffusion controlled the build-up of the RS• radical. As this organic molecule is a chain molecule (two paraffin-like structures R joined by two linked sulphur atoms) it was postulated that diffusion took place along the direction of the length of the molecule until it was adjacent to an alkyl radical. This radical was then able to react with the disulphide group in this molecule so forming a RS• radical. These authors postulated therefore that the diffusion necessary for free radical reaction is achieved by the diffusive transfer of whole molecules or radicals, as distinct from the mechanism proposed by Dole et al. In the author's opinion the investigation of the relative importance of these two mechanisms is one of the most interesting open questions in the field of free radical reactions in organic compounds.

A search of the literature has revealed that kinetic studies so far reported have been restricted to free radicals in those compounds discussed above. No kinetic studies on free radical disappearance in single crystals have appeared in the literature. Those people who studied the ESR spectroscopy of free radicals in single crystals have apparently not been attracted by the question of kinetic studies on these radicals. However, some of these workers did report that changes occurred in the spectra of some of these irradiated crystals on warming above room temperature. Some of these phenomena will be briefly described. Irradiated glycine crystals have been extensively investigated by various workers for the purpose of identifying the free radicals produced. Ghosh and Whiffen (1959, 1960) attributed the spectrum to $\overset{+}{N}H_3-\dot{C}H-COO^-$ and $\dot{N}H_2$ while Weiner and Koski (1963) disputed this because their results led them to believe that the radicals were $\dot{N}H_4$ and $\dot{C}H_2-COO^-$. However, Morton (1964b) resolved this conjecture on the radical identity by analysing the spectrum from an irradiated crystal enriched with 55% $NH_3^+-C^{13}H_2-COO^-$. Ghosh and Whiffen (1960) also reported an interesting phenomenon occuring in irradiated glycine. The spectrum from freshly irradiated glycine was observed to alter after ageing for several weeks at room temperature. They concluded that one radical, A, disappeared while at the same time a second radical, C, began to appear. The other radical present originally, B, remained essentially the same in concentration. Ehrenberg, Ehrenberg and Zimmer (1957) also reported on this phenomenon. They observed that the area under the absorption curve remained essentially constant which indicated that the total number of magnetic centres remained the same. Neither group of workers made any attempt to provide an explanation for this phenomenon except to say that radical C was not formed by the irradiation process. It is clearly of interest to elucidate the mechanism of this process.

Another interesting phenomenon was reported by Horsfield, Morton and Whiffen (1961b) in freshly irradiated malonic acid crystals. They observed that the intensity of a number of the hyperfine lines in the spectrum could be reduced if the crystal was warmed to 50-60°C for 24 hours. It was found that two radicals were produced originally and one could be removed by annealing, leaving the other radical essentially unaffected. This type of phenomenon was also observed in irradiated single crystals of adipic acid (Morton and Horsfield, 1961). Again no explanation was presented as to why one radical disappears while the second radical remains unaltered and as to how the "dangling bond" on the reacting radical is satisfied.

During the study of ESR spectroscopy of radicals formed in irradiated organic crystals some workers also irradiated the corresponding partially deuterated crystals. These crystals can be prepared by repeated recrystallization from solutions of the original compounds in heavy water. With this procedure the polar protons are replaced by deuterons whereas the protons bound to carbon atoms are not. On irradiating deuterium substituted crystals the radical produced may or may not have the same spectrum as the undeuterated crystal. This will depend on whether or not the unpaired electron interacts with a polar proton. If it does interact strongly then on replacing this polar proton with a deuteron the hyperfine structure of the spectrum will alter since the spins and magnetic moments of these two nuclei are different. Thus, additional information can be gained to establish the identity of a radical in the non-deuterated crystal. This procedure has been used with success but it was realised as early as 1962 that there are frequently complications in this simple picture. Pooley and Whiffen (1962) were the first to observe unexpected phenomena in deuterated crystals. The spectrum of irradiated single crystals of OO'- dideuterosuccinic acid was found to contain additional lines which originated from a free radical, electronically the same as the original radical. In this radical one of the protons on the carbon atom has been replaced by a deuteron. These authors' first thoughts were that the proton was exchanged during the growing of the crystal from heavy water, but this was ruled out when infrared spectra of a crystal were recorded before irradiation. The authors were then convinced that the proton-deuteron (H-D) exchange on the carbon atom only occured during the irradiation. They were also puzzled by the fact that only the hydrogen in one position was replaced, that is, the process was stereospecific. No convincing explanation of these observations was made although the comment was offered that deuteration studies can be misleading when used to help identify free radicals. Several problems immediately arise out of these observations which are a warning against accepting a simple picture of "bond-breaking" as being adequate to deal with the formation of free radicals by the irradiation process. For example, why does the proton-deuteron exchange in the radicals take place during the irradiation process?

Several other cases of H-D exchange have been reported recently which will be briefly described. Morton (1964b) discussed the result of Weiner and Koski regarding the identity of the spectrum from irradiated crystals of $NH_3^+{-}CH_2{-}COO^-$ and $NH_3^+{-}CD_2COO^-$. This can possibly be explained by an exchange taking place between deuterons of the radical $NH_3^+{-}\dot{C}D{-}COO^-$ and the hydrogen atoms of the NH_3^+ group in the molecules of the host crystal. It appears that complete exchange has occured on the radical. Itoh and Miyagawa (1964) published a paper on H-D exchange occuring in free radicals produced in irradiated crystals of deuterium - substituted L-α-alanine. It was observed that if an irradiated crystal was warmed at 100°C for two hours, the ESR spectrum showed additional lines. A complete change in the spectrum occurred if the crystal was heated at higher temperatures and was then in good agreement with a spectrum for the radical $CH_3{-}\dot{C}H{-}R$ with all hydrogen atoms on the carbon atoms replaced by deuterons. The intermediate spectra corresponded to a radical with only a fraction of the hydrogen atoms replaced. The authors concluded from infrared studies that the exchange took place only on the radicals and not on the molecules in the host crystal. First-order kinetics were observed for the very early period of the exchange reaction. The authors did not put forward a general mechanism for H-D exchange in the radicals. However, to account for the complete exchange on the radical they proposed that the deuterons of the amino groups of the molecules must migrate through the crystal, to allow the deuterons onto the carbon atoms. The review on proton-deuteron exchange has pointed out that the exchange appears to proceed at a slow-rate in L-α-alanine as compared to the exchange in glycine or succinic acid. In the last two compounds this exchange must be very rapid as it appears to be complete after irradiation.

A paper recently published by Snipes and Horan (1967) is of considerable interest for this review. The authors looked at the phenomenon of dosage saturation when organic crystals were exposed to ionising radiations. It has been known (Rotblat and Simmons, 1963) that the number of free radicals produced does not continue to rise linearly with dose but a saturation level is eventually reached. In this paper it was argued that either no radicals were produced when saturation is reached or radicals were being continually produced and destroyed at the same rate. To test the mechanism of saturation the previously mentioned phenomenon of proton-deuteron exchange in L-α-alanine was used. Crystals of deuterated L-α-alanine were irradiated with large doses of X-rays and then heated at 60°C for 100 hours. This resulted in selected hydrogen atoms bound to the carbon atoms of the free radicals being exchanged for deuterons. Thus selectively deuterated radicals were present. This crystal was then reirradiated well past the saturation level and the ESR spectrum revealed that no evidence of the selectively deuterated radicals remained at the end of the irradiation. Therefore it was concluded that the labelled radicals were destroyed during the irradiation process.

An interesting phenomenon on which several papers have recently appeared is that of free radical pairs. Experimental observations have shown that radicals can be produced in "pairs", that is to say that two radicals are trapped on adjacent sites. The magnetic dipole interaction of the two unpaired electrons which are delocalised and exchanged, results in a very large anisotropic splitting in the ESR spectrum with the effect that radical pairs can be readily distinguished. Radical pairs have been observed only at LNT in several compounds including dimethylglyoxime (Kurita, 1964a) oxalic acid (Moulten, Cernansky and Straw, 1967) and monofluoroacetamide (Iwaski and Toriyama, 1967). No detailed mechanisms were suggested as to how radical pairs come to be produced as a sizeable fraction of the radical population of the crystal.

1.2 Rationale of these Investigations

The work published so far on damaged organic solids indicates that the major aim has been the investigation of ESR spectroscopy of the free radicals produced in these compounds, that is, the identification of the radicals, determinationoof their orientation in the crystal lattice and their electronic structure. The questions surrounding free radical destruction by annealing has been given little consideration, with only two compounds, namely polythene and n-octadecyl disulphide having been studied in any detail. Some workers in their spectroscopic studies of free radicals in irradiated crystals reported in passing that the radicals disappeared when these crystals were annealed. The joint annealing of two different radical species in a crystal was not considered. An experimental survey is most likely to reveal that free radicals reported in other irradiated crystals can also be destroyed by annealing. The review has shown that no accepted mechanism so far exists to explain free radical phenomena and in particular free radical recombination. In other words the question "How are the free bonds satisfied?" has not been satisfactorily explained. It may indeed be possible to postulate a mechanism that explains H-D exchange as well as free radical destruction. The existence of free radical pairs at LNT needs to be considered in detail.

One's first thought in respect of free radical disappearance is that two radicals recombine to form chemically saturated species. This is expected to be a simple case of reaction kinetics because if two species react to form a new species a reaction of definite kinetic order exists. The second-order reaction kinetics of radicals in n-octadecyl disulphide appear to support this postulate. One also needs to consider that the radicals are randomly distributed through the crystal lattice, initially. Now if they are to react a migration mechanism must be involved if the radicals are to arrive on adjacent sites to destroy each other. One can begin examining the migration phenomenon by postulating mechanisms. Two principle mechanisms have been proposed by other workers. In the first case it is said that the radical as a whole migrates through the lattice until it arrives at a site adjacent to another radical to react. This really implies self diffusion within the crystal because a radical usually is only the host molecule minus a hydrogen atom. Truby et al have used this mechanism to explain free radical build up and disappearance in n-octadecyl disulphide. Migration of the gross free radical appears to be feasible as several papers have recently been published on self diffusion of C^{14}-anthracene in single crystals of anthracene (Sherwood and Thomson, 1960). This self diffusion was studied by evaporating C^{14} labelled anthracene on to one face of a crystal of anthracene grown from the melt. This crystal was heated between 170°C and 190°C for some hours and then sectioned to determine the activity through the crystal. Lee et al (1965) studied self diffusion in anthracene in two particular directions perpendicular to each other and an anisotropic effect in the diffusion was observed. A vacancy mechanism combined with a loosening of the structure near the melting pt.

was proposed as being most likely responsible for self diffusion. Self diffusion has also been studied in cyclohexane by observing the line widths of the nuclear magnetic resonance lines (Andrew and Eades, 1953; Andrew, 1961). The alternative mechanism that can allow free radical migration is the migration not of the whole free radical but of the free radical state which is effectively transfered to an adjacent site when a hydrogen atom is abstracted from the molecule on this site, converting it to the same free radical while the hydrogen atom attaches itself to the radical, viz. $RH + RH + R^{\cdot} \rightarrow RH + R^{\cdot} + RH$. A similar mechanism has been favoured by some workers looking at free radical disappearance in irradiated polymers. Initially, this appeared to the author to be the most promising hypothesis; it certainly would seem to exist in polythene where gross migration of molecules and very large radicals seems to be out of the question. If one accepts this mechanism several predictions can be made. If free radical destruction is observed in deuterated crystals where a deuterium atom has replaced the hydrogen atom in the jumping mechanism then the reaction rate can be expected to be reduced by a factor of 5 to 8. This is known as the kinetic isotope effect. Infrared spectroscopy can be used to examine the extent of isotopic mixing in irradiated and annealed crystals which results from the movement of the hydrogen atom vacancy. Free radical reactions are best studied with single crystals of high melting points (viz. hydrogen bonded molecules) in which self diffusion is very unlikely. Crystals from the amino and carboxylic acid groups were therefore regarded as most suitable for this work. It was planned to investigate principally reaction kinetics, the deuterium isotope effect, and proton-deuteron exchange. These investigations had to be preceded by a large amount of preliminary work on the reproducibility of free radical annealing which in itself gave results of some interest. As well as the experimental studies an important part of the thesis is devoted to an examination of theoretical aspects of the behaviour of free radicals in solids.

CHAPTER 2

THE RADICAL STATE MIGRATION HYPOTHESIS

2.1 Introduction

The last Chapter has reviewed the work on free radical phenomena which take place either during or after formation of the radicals by high energy radiation, pointing out that some of these phenomena are completely unexplained. The usual, rather naive model of free radical formation is that of simple bond-breaking. However, on further examination this simple picture is found inadequate to explain some of the observed phenomena in particular free radical thermal destruction and isotopic mixing.

In an attempt to understand more about free radical phenomena and to act as a guide to an experimental study of these phenomena, a model based on a hypothesis as proposed by Ericson and Cutten (1968) will be introduced. This leads to a number of predictions about free radical reactions including several new phenomena not yet observed. These predictions formed the basis on which the experimental work to be described in this thesis was undertaken.

2.2 The Hypothesis and its Predictions

The hypothesis can be given precise statement as follows:-
an organic crystal that is exposed to high energy radiation remains essentially the same in structure except for the formation of radiation produced impurities and defects and the occasional removal here and there of hydrogen atoms from the host molecules and the impurities. The "holes" or vacancies left by the removal of the hydrogen atoms are in principle and often in fact, mobile and may be transfered to other hydrogen atom positions on their own or other molecules by the transfer to them of hydrogen atoms from those sites. The transfer of the vacancy between normal molecules of the crystal, the so-called host molecules, is what leads to diffusion of the radical state

while the transfer of the vacancy within the molecule can be recognised as an isomeric transformation. Indeed, the essence of the hypothesis is the treating of the irradiated crystal as a whole as a system in which free radical isomeric transformations occur. A crystal containing a single vacancy on a site A which is transfered to a site B can be regarded as undergoing an isomeric conversion. When two such radicals reach adjacent sites they are able to react and so the model has the essential property of explaining the free radical migration that must be involved in the annealing process. The predictions which may reasonably be made are discussed in some detail.

1. <u>Free radicals in organic crystals are classifiable into two categories to be called I- and H- radicals respectively.</u>

All of the free radicals so far reported in the literature can be converted into saturated molecules by the insertion of a hydrogen atom in the "dangling bond". If the molecules so produced are the same as the normal molecules of the crystal the radicals are called host-type radicals (H-type radicals or H-radicals). They may be regarded as being formed by the removal of a hydrogen atom from one of the molecules of the host crystal. Their structure is similar to the host molecules with only slight differences in bond lengths and angles. If however, the addition of the H atom produces a molecule differing from those of the host crystal it is designated as an impurity-type radical (I-type radical or I-radical). Although a particular I-radical is to be regarded essentially as an impurity which is lacking a hydrogen atom it may well be produced under irradiation by the removal of a group other than hydrogen from the host molecules. As an example of the application of this classification consider the two different radicals that have been identified in malonic acid (Horsfield, Morton and Whiffen, 1961b). With the $HOOC-\dot{C}H-COOH$ radical the addition of a hydrogen atom produces the malonic acid molecule and so it is recognised as an H-radical. The $\dot{C}H_2-COOH$ radical is called an I-radical because the addition of a hydrogen atom produces the acetic acid molecule.

2. <u>Each free radical species has present with it in thermal equilibrium its corresponding free radical isomers which are in principle detectable and identifiable as such in favourable cases.</u>

The phenomenon of isomerism among free radicals is of course well known in the gas phase. To consider an example the radicals $\dot{C}H_2-CH_2-CH_3$ and $CH_3-\dot{C}H-CH_3$ are isomers essentially derivable from propane by the introduction of a vacancy among the attached hydrogen atoms. Because the hydrogen atoms exhibit a greater bond strength (Cottrell, 1958) in their binding on the centre carbon atom the vacancy can be regarded as being preferentially bound to the outer carbon atoms to the extent of the energy difference of these bond strengths which in this case amounts to an enthalpy of 6 kcal. per mole. Now, in general, a larger proportion of isomeric species will be present where the bond energy differences are small that is, the "hole" only requires small energy for it to be excited, thermally, into one of the available sites on the molecule. The equilibrium partition of the "hole" between sites is expressed by the following relation

$$^{n_1}/_{n_2} = {}^{z_1}/_{z_2} \exp(-{}^{\Delta E}/_{kT})$$

where the Z's refer to the partition functions of the radicals concerned and are essentially a sum over their vibrational states and ΔE is the difference in the ground vibrational state energies of the radical isomers. At a sufficiently low temperature (which may be the temperature at which the compound is irradiated) only one radical isomer is expected to be detected. As the temperature is raised both radical isomers can exist because the thermal equilibrium is altered allowing more of the "holes" to move to the other site. Provided the equilibrium is not prevented by steric and rate considerations the ESR spectra will be reversibly temperature dependant in the sense that the spectrum is simple at low temperatures and develops new resonance absorption lines as the temperature is raised with a reduction in strength of the original lines which however cannot proceed as far as their complete disappearance. This phenomenon has not so far been reported.

3. <u>The number of distinct species of free radicals resulting from the irradiation of an organic crystal will be small and rarely greater than two.</u>

The essential basis of this statement is evident from the above discussion in that to a first approximation each damaged molecule appears only as its isomeric form of lowest energy whatever was the initial act of the irradiation which removed a fragment of it to give it free radical status. For example if the radicals $\dot{C}H_2-CH_2-CH_3$ and $CH_3-\dot{C}H-CH_3$ are produced by removing different hydrogen atoms only the latter should be detected. A stronger argument for the above statement can however be given. The irradiated crystal consists of host molecules and impurities, the hydrogen atoms of all of which offer potential sites for the "holes". These sites differ in respect of the energy associated with their occupation by a vacancy. Assuming that the "holes" are mobile they will prefer to occupy those hydrogen atom sites to which hydrogen is bound least strongly and if the "holes" are mobile, they will be found exclusively on these sites, leading to a single radical species being present unless the prefered sites are completely occupied by vacancies when the excess will be forced to reside elsewhere. In the absence of metastable binding of "holes" one therefore can expect only one or possibly two radical species to be present. The prefered sites for the "holes" may be situated on a particular molecular impurity or on the host molecule of the crystal. An impurity which cannot offer sites which the "hole" prefers energetically to those on the host molecules will not bind "holes". In a particular crystal system therefore certain molecular fragments will not be present unless they are preserved in metastable equilibrium. Thus one can now see that although there is a large number of ways in which bonds can be broken even without invoking molecular rearrangements, only one or at the most two radical species will, in fact, be detected.

4. Phenomena of metastable equilibrium play an important role in the post-irradiation behaviour and annealing of free radicals.

The simplest metastable equilibrium which can be imagined is that involved in the unimolecular conversion of one radical into another. An alternative form of metastable binding which should be observable is that of a "hole" metastably bound to a site on an impurity molecule which is surrounded by host molecules able to offer energetically preferable sites.

It is interesting to classify free radical conversion reactions in terms of the categories of radicals involved, viz. the distinction that must be made between the I- and H-type radicals. If the conversion from one H-type radical to a second of the same type is observed to occur then one expects that what one is observing is the excitation of the "hole" from a place on the host molecule where it is metastably bound to another site of tighter binding. It is expected that the reaction will be irreversible. Such a conversion reaction was recently reported by Bernhard and Snipes (1967) in dihydrothymine where, they suggested, a hydrogen atom was either abstracted from within the radical or from a neighbouring host molecule. Similar remarks apply to the interconversion of two I-type radicals of identical molecular architecture. For obvious reasons one does not expect thermal conversion between I-type radicals of different molecular architecture or, at least not by a process merely involving the movement of "holes". A type of radical conversion that might be reasonably expected to be fairly common is the conversion of an I-type radical into an H-type radical. In terms of the hypothesis this will be recognised as the process whereby a "hole" bound on an impurity is transfered to a neighbouring H molecule by the process of hydrogen atom abstraction. It seems very unlikely that a radical conversion involving the change of an H-radical into an I-radical will be observed for the reason that a typical H-radical is very unlikely to have an impurity molecule situated nearby because of the usually relatively low concentration of impurities present in the crystal. It is interesting to speculate that in some cases the conversion of an I-radical to an H-radical may exhibit the following behaviour. Consider the case where the impurity offers a site to the "hole" of such tight binding that it is preferred by the "hole" to any other hydrogen atom sites in the crystal. Even in this case one expects in principle that raising the temperature sufficiently will drive the "hole" off the impurity onto the sites of less tight binding on the much larger number of host molecules in the crystal. The situation may be compared with the process familiar in ionic solids whereby vacancies bound adjacent to immobile impurities may yet be "boiled off" them and dispersed in the crystal. In this latter case the vacancies may be recondensed onto the impurities if the crystal is held for a sufficiently long time at a temperature adequate to ensure their mobility but not enough to disrupt their binding in the sites adjacent to the impurities which they prefer energetically. If the "holes" exhibit a similar reversible binding to impurities one may expect that the relative numbers of free and bound "holes" will be given by a law of essentially the following form :

$$^{n_f}/_{n_b} = {}^{n_H}/_{n_I} . {}^{Z_H}/_{Z_I} \exp(-\frac{\Delta E}{kT})$$

where $^{n_I}/_{n_H}$ is the molar concentration of the impurity, Z_H and Z_I are the partition functions of the H- and I-type radicals involved and ΔE is the relative binding energy of the "hole". If the reasonable assumption is made that $Z_H \sim Z_I$ and taking $^{n_H}/_{n_I} \approx 10^4$ and $^{n_f}/_{n_b}$ as unity at 300°K then $\Delta E \triangleq 0.2eV$. Behaviour such as this should be evident in the ESR spectrum when the specimen is temperature cycled. Raising the temperature causes complete conversion of the I-type radical to the H-type and the conversion is reversed when the temperature is lowered. It should be emphasised that the conversion of an H-type radical to an I-type radical here proceeds on the lowering of the temperature. One does not expect heating ever to cause the conversion of an H-type radical to an I-type. Essentially it is entropy considerations which preclude this from taking place. It may be mentioned that this process of "boiling" a radical state off an impurity by heating and subsequent recondensation by recooling onto the original or other impurity has so far not been reported.

Finally, one can say that all types of conversion reactions mentioned above are expected to proceed with first-order kinetics and with the total number of spins remaining constant.

5. Thermal destruction of free radicals in organic crystals usually proceeds by the process of radical state migration, the diffusion paths terminating where the "holes" reach adjacent molecules or come to the same molecule. This

reaction will usually proceed by second-order kinetics.

This statement results from the application of the hypothesis to the problem of the mobility which must be involved with free radical destruction. The actual destruction of the free radicals essentially involves the pairing of two unpaired spins which can hardly take place other than by a bimolecular reaction. The saturated chemical species is presumed to form in one of two ways. In the first case the two radicals (R$^{\cdot}$) may form a covalent bond R-R involving the unpaired electrons from the two adjacent radicals. Alternatively if both "holes" have arrived on the same molecule then the two unpaired electrons on this molecule are able to pair up forming a saturated chemical species containing a double bond.

6. The activation energy experimentally measured for free radical annealing may represent either the energy barrier against mobility of the "hole" or the activation energy associated with the reaction of the free radicals in proximity with each other.

When the "holes" arrive on adjacent molecules the resulting closely spaced free radicals can conceivably react rapidly with small or even zero activation energy. In this case processes connected with the mobility will be rate limiting and determine the reaction rate. If the activation energy of the reaction represents an energy barrier for recombination it can be expected that the radical state is mobile at a temperature below that at which the free radicals recombine. Thus if a crystal was heated at this lower temperature it would be expected that the radical state visits a large number of lattice sites. In other words the total migration path of the radical state is long at this temperature and macroscopic diffusion may be observable.

7. The activation energy associated with the migration of the "hole" from molecule to molecule can sometimes be identical with the energy difference

between two isomers of the H-radical of the crystal.

The H-radical will have present with it its isomers in equilibrium. These are to be regarded as having the "hole" promoted to a site on the molecule which is of higher energy. If the transfer of a "hole" to a neighbouring molecule proceeds much more rapidly from this site then the rate limiting step for migration can be the formation of the isomers of higher energy. The transfer of the "hole" from molecule to molecule will proceed with a rate dependant on the population of the excited state for which an expression has already been given.

8. Free radical reactions in organic crystals and in particular free radical destruction will often exhibit the kinetic isotope effect when studied in partially or wholly deuterated crystals.

Any reaction involving the transfer of a hydrogen atom will be decreased in velocity if the relevant hydrogen is replaced with deuterium. At the temperatures at which free radical reactions are studied (300 - 400°K) the reaction rate will be reduced by a factor of 5 to 7 (Wiberg, 1964). Chapter 5.2 will summarize the theory involved with the isotope effect in reactions. This phenomenon is also expected to be seen in conversion reactions. Only one brief report to date (Kurita and Kushiwagi, 1966) has been made on the isotope effect in free radical reactions in single crystals.

9. I-radicals cannot be mobile as such by the mechanism of hydrogen atom jumping.

If the "hole" leaves the impurity the radical state is converted at once to an H-type. On this basis it might seem that the observation of thermal annealing of an I-type radical below the melting or destruction temperature of the solid should offer strong evidence that the mobility in the reaction is achieved by the gross migration of the radicals. However, it is only necessary to have a steady release of the I-radical "holes" into the (mobile) H-radical state to allow the annealing to proceed. The activation energy for the reaction is then recognisable as that for the liberation of the "hole" from the impurity and the H-radical involved in the mobility can remain unobservable as the mobile "holes" meet and combine with others, bound or free.

One could also argue that the I-radicals could migrate by the movement of a molecular group (such as NH_2, COOH or OH) from neighbouring molecules. In other words, the I-type radical state has been transferred to a new site. If this group was the same as that removed by the primary act of the irradiation to form the I-radical initially, the saturated molecule formed on the site where the I-radical state was, would be converted to an H-type molecule. Thus the movement of such molecular groups from molecule to molecule would allow the I-radicals to migrate. Detailed consideration of this mechanism has not been persued in this work since the aim, as one will recall from the beginning of this chapter, was to obtain experimental evidence to test the hypothesis of migration of the radical state by hydrogen atom jumping.

If both I- and H-radicals are present and the I-radical does not convert to an H-radical then one does not expect the I-radical to be annealed out before the H-radical. If the I-radicals can be removed first, by thermal annealing, the situation can be discussed in much the same way as outlined above where only I-radicals are present in the irradiated crystal.

10. <u>The presence of a "hole" on a molecule can promote isotopic mixing of hydrogen atoms between various sites on the molecule through chains of isomeric transformations</u>.

This can be best discussed using a reasonable though hypothetical example.

Consider the molecule CH_3-CD_3, a partially deuterated ethone. The species $\dot{C}H_2-CD_3$ and $CH_3-\dot{C}D_2$ are the radicals which can be formed from the molecule. Now a sequence of isomeric transitions lead to the species

$$\dot{C}HD-CHD_2$$

$$\dot{C}D_2-CH_2D$$

$$CH_2D-\dot{C}HD$$

$$CD_2H-\dot{C}H_2$$

The "hole" acts as a vacancy and promotes isotopic mixing only among the H atom sites which it visits. Thus the phenomenon of isotopic mixing already observed in the radicals produced in succinic acid and L-α-alanine finds a ready interpretation in terms of the hypothesis.

11. The presence of mobile "holes" can promote isotopic mixing involving essentially all molecules in the crystal that is, the isotopic mixing need not be confined to the free radicals.

In principle the "hole" can promote isotopic mixing on each molecule it visits and if the "hole" is transfered from molecule to molecule, as for example in the course of thermal annealing to destruction, the "holes" will visit essentially every molecule in the crystal, causing isotopic mixing on each.

12. "Holes" in an organic crystal interact mutually with a force transmitted via the molecular and lattice distortion they cause. If the nett interaction force is attractive then the "holes" may be bound on neighbouring molecules to form free radical pairs.

The removal of a hydrogen atom to form a free radical alters the shape of the molecule mainly by the change of some of the bond angles. For a molecule in a molecular crystal this results in a strain being transmitted to the lattice in the neighbourhood of the free radical. On the nearby molecules the sites available to "holes" are now no longer equivalent to those at greater distances and they offer positions where another "hole" may be bound either more or less strongly than usual. In this way a sort of pairing energy of the "hole" arises. If the binding energy is positive and sufficiently large with respect to kT then stably bound free radical pairs can in principle exist. Thus one can picture a free radical pair as consisting of two adjacent molecules each of which has lost a hydrogen atom and which have mutually accomodated to the molecular distortion entailed. Whether free radicals on adjacent molecular sites will survive as a free radical pair or destroy each other quickly will depend on the details of the crystal and molecular structure and the distortion involved.

13. <u>In the terms of the radical state migration hypothesis free radical pairs are formed by the migration to adjacent sites of "holes" individually produced at separated sites</u>.

As one can recall from Chapter 1 all free radical pairs have been seen only in crystals irradiated at LNT. It would seem to be out of the question that they are formed by the gross migration and pairing of the free radicals. It has been suggested (Kurita, 1964b) that the pairs are produced <u>in situ</u> as such by the action of the irradiation. In the problem of the genesis of free radical pairs this interpretation must be regarded as in competition with that offered by the radical state migration hypothesis.

2.3 <u>Free Radical Nomenclature</u>.

The essential idea of this chapter has been that free radicals in an organic crystal introduce a "hole" or "vacancy" which allows the operation of various migration mechanisms. It is natural to coin a name to describe this "hole". It is proposed that it be called the kenon (Gk. κενος, empty), as suggested by Ericson and Cutten (1967). The diffusion through the crystal lattice of the radical state by hydrogen atom jumping can be regarded as "kenon diffusion". The hypothesis in section 2.2 can be called the "kenon hypothesis".

Indeed one can proceed further along these lines and construct a systematic nomenclature for free radicals, whether made by irradiation of organic crystals or otherwise. A survey of the types of radicals produced so far reveals that a familiar organic compound can be made from any of these radicals when a hydrogen atom is linked via the "dangling bond". These considerations lead one to propose the following rules for naming complex free radicals. The unsatisfied valence can be regarded as containing a hypothetical monovalent "substituent". This substituent is to be called the kenon and the radical species be considered as a keno-derivative of a parent compound. Thus for example $NH_3^{+}\dot{C}H\text{-}COO^{-}$ formed by irradiating amino acetic acid (Morton, 1964b) will be called kenoaminoacetic acid and $HOOC\text{-}\dot{C}H\text{-}CH_2\text{-}COOH$ will be called kenosuccinic acid by anology with chlorosuccinic acid (Feiser and Feiser, 1962). γ-irradiation of crystals of aminosuccinic acid (Jaseja and Anderson, 1962) produce kenosuccinic acid by replacing the amino group of the acid with a "hole" or kenon. Furthermore, the ordinary rules for specifying the position of the substituent kenon still hold. Thus HO-  becomes *p*-kenophenol; $\dot{C}H_2\text{-}CH_2\text{-}COOH$ becomes β-kenopropionic acid as distinct from the α-keno-compound $CH_3\text{-}\dot{C}H\text{-}COOH$ (Horsfield et al, 1961c); $\dot{S}CH_2(CHNH_2)COOH$ (Akasaka, 1965) will be called β-kenothiol-α-amino-propionic acid. Radicals of the form CH_3 can be regarded as either kenomethane or methyl kenide. Since a free radical can be given a kenide name only if the corresponding bound radical has already been named, such a term is of little use unless one wishes to emphasise the free radical character by attaching the redundant term, kenide.

For the remainder of this thesis the above nomenclature for free radicals and associated phenomena will be used when appropriate in the discussion on the experimental results. This saves using the cumbersome chemical formula to designate the free radical as has been done in the past.

CHAPTER 3

EXPERIMENTAL APPARATUS

3.1 Introduction

A description of the apparatus made for the purposes of this project is given in this chapter. The ESR spectrometer (described in Appendix A) was already in a useable form when this project began in 1964 and the following apparatus that will be described was made to suit it. An improvement in the sensitivity of the spectrometer was made so it was able to detect a minimum of 10^{14} free radicals. The concentration of free radicals in a crystal while it was being annealed could be followed over one order of magnitude of relative concentration.

3.2 Microwave Resonant Cavities

3.2.1 General Purpose Cavity

The all-purpose cavity used on the ESR spectrometer for room temperature studies is shown in fig. 3.1. Its construction was very similar to the one described by Cavenett (1964); the cavity being of a rectangular type resonanting in the TE_{102} mode and was split $\frac{3}{4}$ of the way up from the bottom. The photograph shows how the PTFE rod was supported in the cavity. This was a push fit into the centre of the cavity so that it would not move when the cavity was in position on the spectrometer. A similar support on the opposite narrow side of the cavity held the standard. Provision was also made to insert a thermocouple junction close to the PTFE rod.

Several of these cavities were constructed and silver-plated, each able to withstand heating to 200°C or more for long periods of time.

3.2.2 Double Cavity

To enable comparison spectra from two irradiated crystals of the same compound to be recorded simultaneously, a rectangular cavity resonanting in

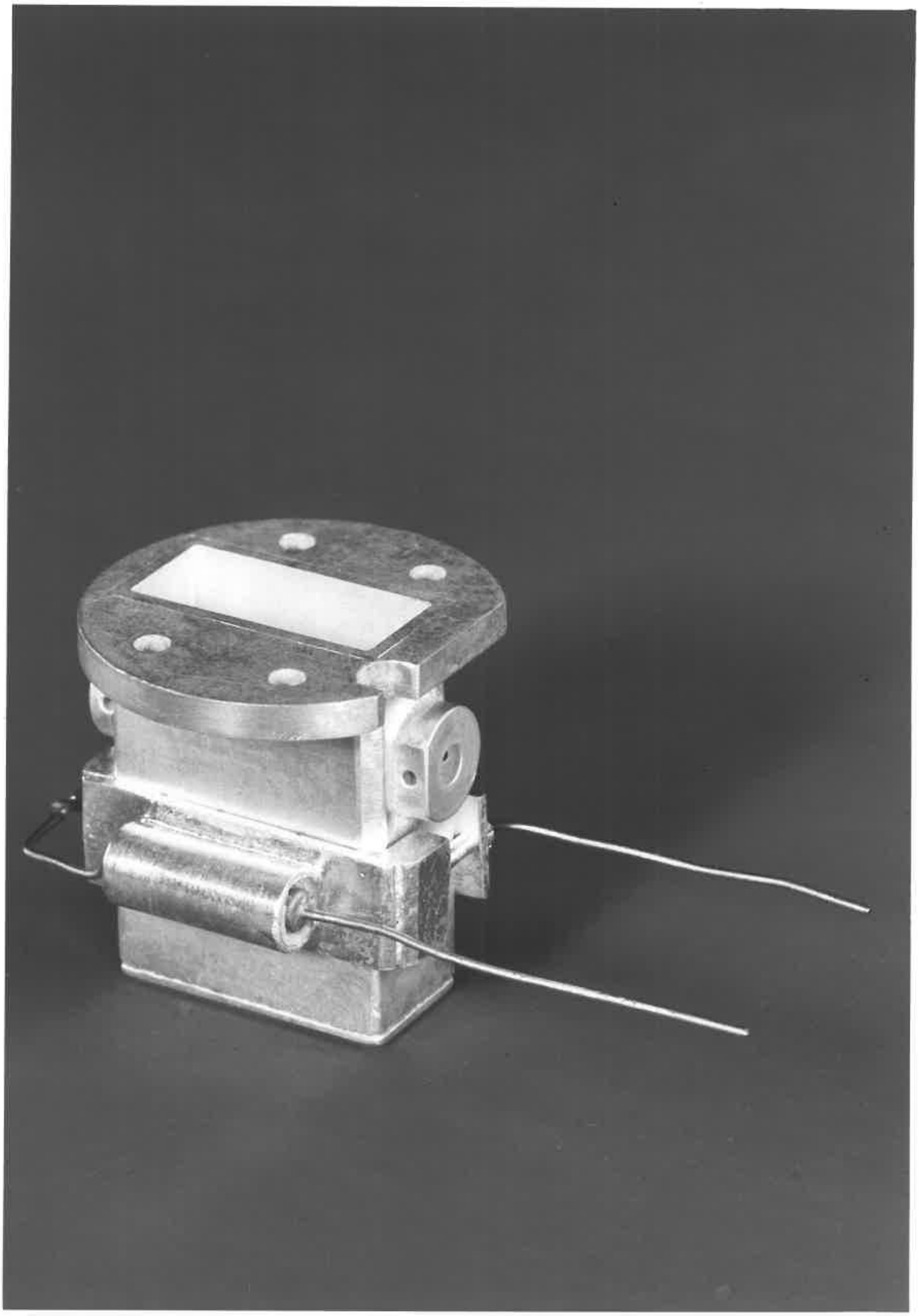


Fig. 3.1 The General Purpose Cavity

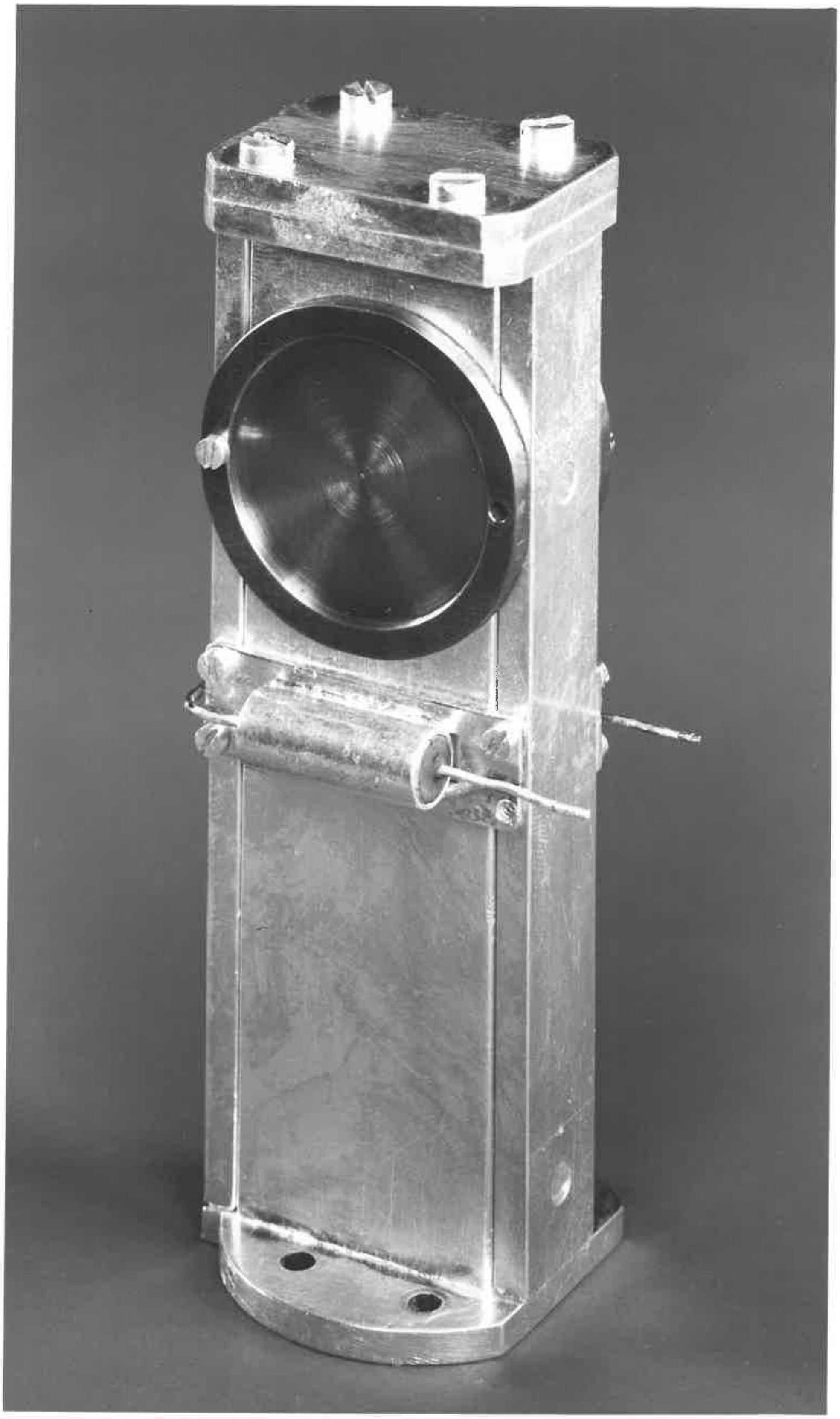


Fig. 3.2 The Double Cavity

the TE_{105} mode was designed and constructed (see fig. 3.2). This cavity allowed the two irradiated crystals to be inserted along its length, one at half a wavelength from the bottom and the second at two wavelengths. Thus, each crystal was in a maximum of the microwave magnetic field. The bottom of the cavity was made removeable to allow access to the bottom crystal position. In the region of the lower crystal two soft iron discs, which can be seen in the photograph, were attached to the outside of the cavity with their centres lining up with the position of the crystal inside the cavity. These discs enhanced the static magnetic field at the position of the lower crystal. Thus the resonant absorption in this crystal occured at a lower value of the external static magnetic field and so the spectra from the two crystals were separated by about 100 gauss depending on the thickness of the two discs used. The inhomogenuity of the magnetic field over the volume of the crystal was minimised by having the cavity centred between the magnet pole faces which were also as close as possible to the cavity. Since the diameter of the discs were about 15 times larger than the cross-section of a typical crystal, field fringing effects were minimised. Further, the iron discs were ridged on the edges to help flatten the field distribution.

3.3 Method for Heating Cavities

The previously described cavities and the crystals inside them had to be heated in as short a time as possible, and so a special oven was used which enabled them to be held at an exactly known elevated temperature for a known time. This type of heating was required when looking for residual radicals, to observe slow transformations of free radicals or for comparing the behaviour of two crystals under identical conditions (in this case using the double cavity). Fig. 3.3 shows a photograph of the thermostatically controlled oven with the

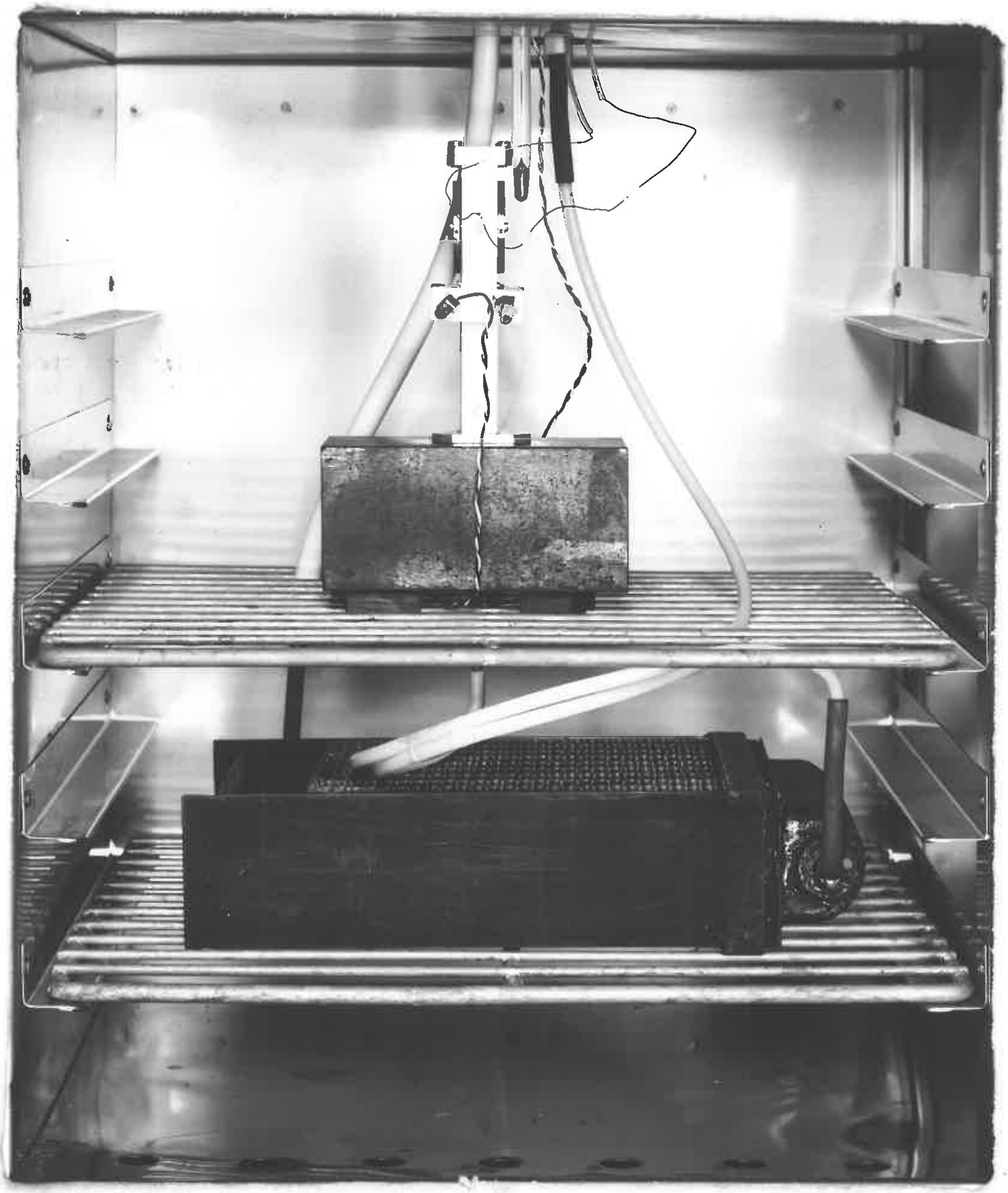


Fig. 3.3 An Interior View of the Oven

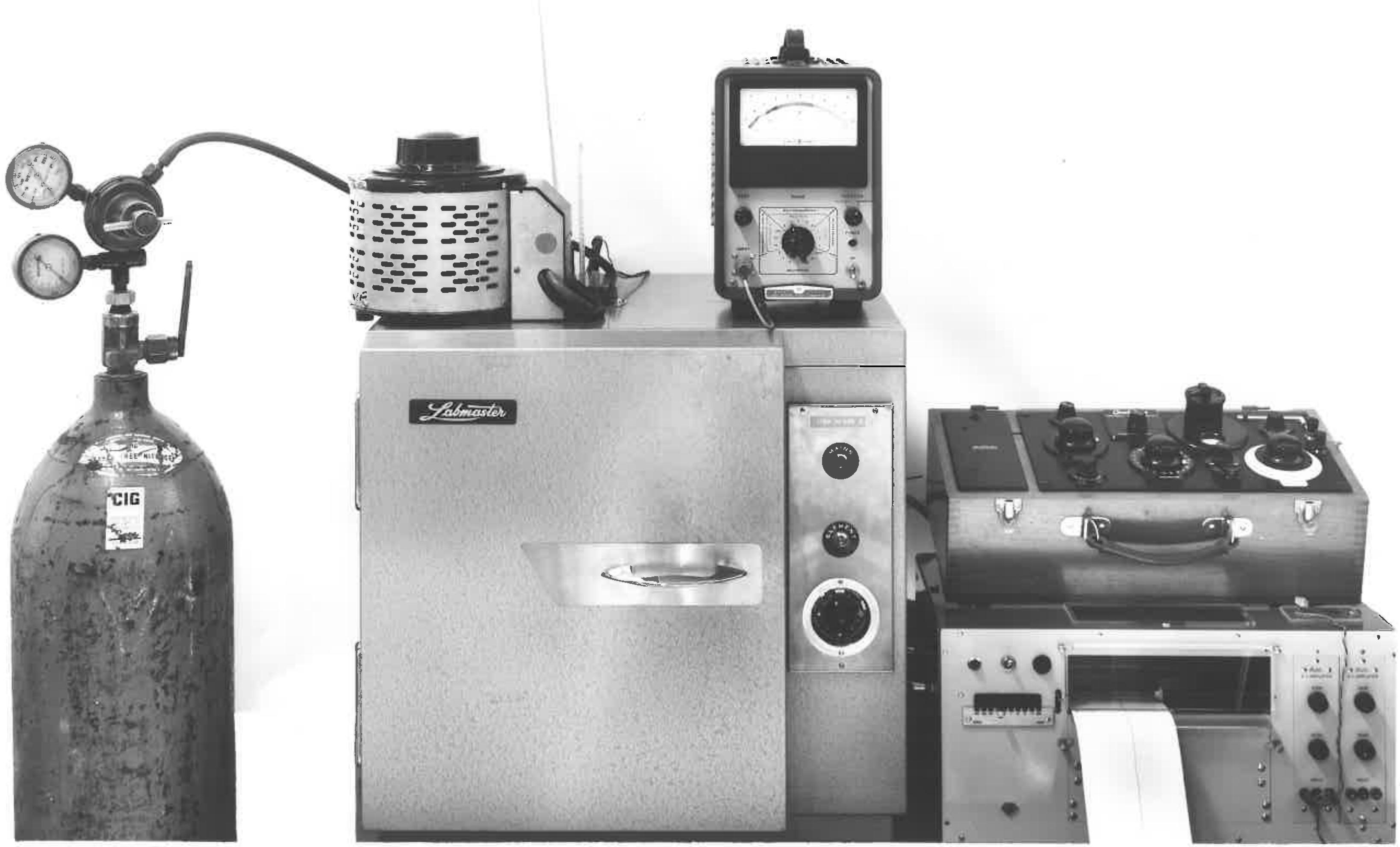


Fig. 3.4 The Oven and Auxiliary Apparatus

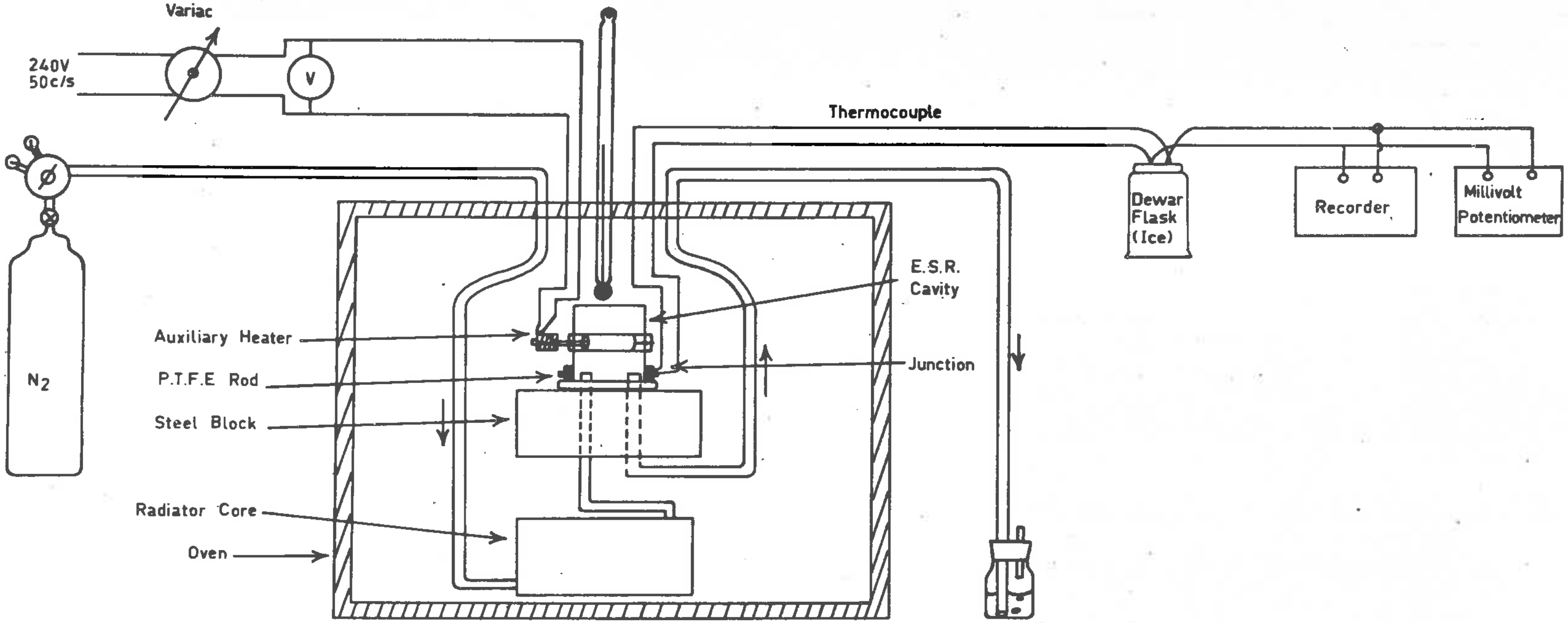

Variac
240V
50c/s
V
N2
Thermocouple
Dewar Flask (Ice)
Recorder
Millivolt Potentiometer
E.S.R. Cavity
Auxiliary Heater
P.T.F.E Rod
Junction
Steel Block
Radiator Core
Oven

Fig. 3.5

double cavity in position whilst fig. 3.4 shows an overall photograph of the oven and temperature measuring equipment. Fig. 3.5 reproduces the schematic layout of the oven. The resonant cavity being used, with the crystal or crystals mounted in it, was placed upside down on a steel block (2" x 3" x 2") perforated by two copper tubes. High purity, dry nitrogen gas was passed into the oven to a small automotive radiator core, via PTFE tubing. This core allowed the gas to reach oven temperature before it flowed into the cavity whence it passed out of the oven to a bubbler to give a rough indication of the flow rate. The cavity flange was coated with silicone grease to seal the cavity and allow good thermal contact with the steel block. Since this block had a large thermal capacity, the cavity when placed on it attained the oven temperature in a short time. The temperature of the cavity was measured with a chromel-alumel thermocouple junction pushed into a neat fitting hole on the side of the cavity on which the PTFE rod, holding the crystal, was mounted. The potential produced by this junction, with the reference junction at 0°C, was measured with a recorder using an amplifier having a sensitivity of ±10mV. Thus a minimum variation in cavity temperature of ±1°C could be observed. The thermostat controlling the oven held the temperature to this degree of accuracy. The oven air temperature was also monitored with a mercury thermometer having its bulb near the centre of the oven. If the crystal was heated to a temperature in the region of 150°C auxiliary heaters were attached to the larger flat sides of the cavity and an AC voltage applied to them. This allowed the cavity to be quickly raised to the required temperature after which the supplementary power was switched off.

As an extra check for the performance of the double cavity the outputs from two thermocouple junctions, one in the position of each crystal, were recorded simultaneously during a heating up of this cavity. The recorded outputs for such a run indicated that each crystal reached the same temperature in the same time.

After a cavity was removed at the end of a heating, it was allowed to cool to room temperature before the ESR spectrum was recorded. The spectrum was usually recorded twice after each heating was completed.

3.4 Variable Temperature Cavities

For determining the kinetics of free radical reactions, apparatus was designed and built to allow the specimen to be heated to a particular temperature and held steadily at this temperature for several hours while observations were made of the ESR spectrum. During the heating period, the signal level of the ESR spectrum had to be recorded at frequent intervals. Further, it was felt that it might be necessary to irradiate some of these crystals at liquid nitrogen temperature and be able to bring them to an intermediate temperature between LNT and room temperature. To fulfill these requirements it was decided to build two ESR cavities; one in which the crystals could be irradiated at LNT and subsequently warmed to a temperature above the irradiation temperature without removing them from the cavity, and the second in which crystals irradiated externally to the cavity at room temperature could be placed and subsequently heated to a temperature up to 200°C. In the following two sections the high and low temperature cavities mentioned above will be described.

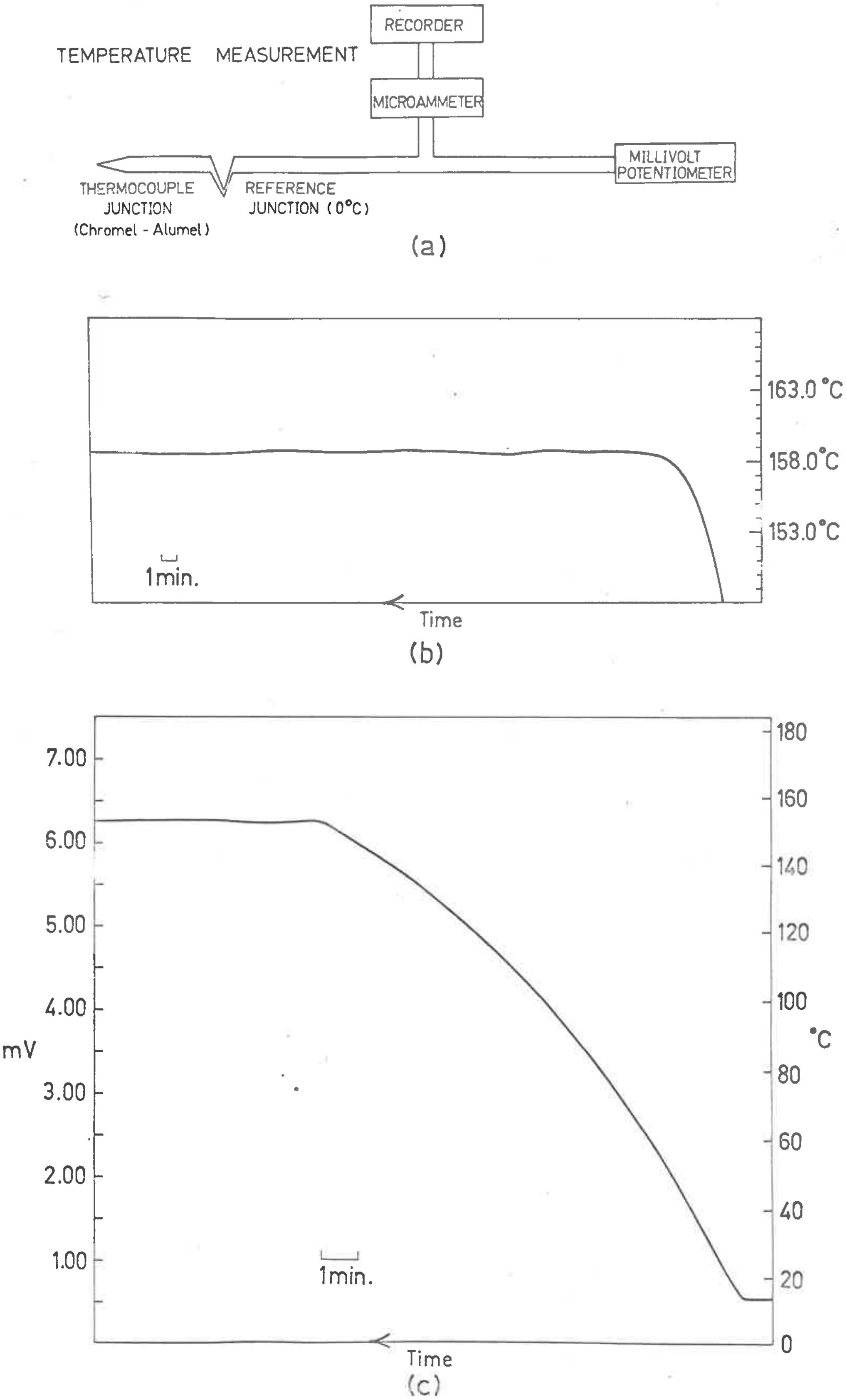
3.4.1 High Temperature Cavity

A high temperature ESR cavity, resonating in the TE_{102} mode, was built to suit the spectrometer described in Appendix A and a photograph of it is shown in fig. 3.6. The waveguide assembly of the spectrometer allowed a vacuum jacket to enclose the cavity and waveguide from the mounting plate down. The flange midway on this jacket allowed the lower part of the jacket to be removed for access to the cavity. The top end of the waveguide was sealed with a thin section of greased mica inserted between the two flat waveguide flanges. The system was pumped through the waveguide above the mounting plate via a LNT vapour trap with a rotary pump. The pressure obtained at the waveguide was about 10^{-3}mm Hg during the heating of the cavity. The copper resonant cavity was permanently joined to the German-silver waveguide using a sleeve of oversize waveguide. The bottom of the cavity was removeable to allow access to the specimen. When this cavity was built and silver-plated it was matched to the microwave line according to the procedure described by Cavenett (1964). The coupling hole, initially undersize, was increased until a VSWR of 0.85 was obtained; the value being kept below 1 because the presence of a crystal in the cavity would increase the coupling.

To provide a source of heat to the cavity, three heaters were made using the wire-wound cores of commercial resistors and mounting each of these inside a ceramic tube. These three heaters were attached to the larger sides of the resonant cavity by a push fit into three copper tubes. The power for the series-connected heaters was supplied by a regulated DC power supply whose output voltage was adjustable from 5 to 40 volts. Thus a maximum of 20W could be delivered to the heaters resulting in the temperature of the cavity being raised to a maximum of 200°C.

The temperature of the cavity was measured using a chromel-alumel thermocouple junction placed on the side just above the PTFE rod holding the specimen (see fig. 3.6). These two thermocouple leads as well as the two heaters leads passed through Kovar seals in the mounting plate. The thermocouple potential was measured by detecting the out-of-balance current obtained when this potential was compared with that obtained from a Cambridge millivolt potentiometer set to a voltage corresponding to the temperature required. A schematic diagram of the apparatus

Fig. 3.6 The High Temperature Cavity


TEMPERATURE MEASUREMENT
RECORDER
MICROAMMETER
MILLIVOLT POTENTIOMETER
THERMOCOUPLE JUNCTION (Chromel - Alumel)
REFERENCE JUNCTION (0°C)
163.0 °C
158.0 °C
153.0 °C
1min.
Time
7.00
6.00
5.00
4.00
3.00
2.00
1.00
mV
180
160
140
120
100
80
60
40
20
0
°C
1min.
Time

(a)

(b)

(c)

Fig. 3.7

for measuring the temperature is shown in fig. 3.7(a). Fig. 3.7(b) shows a typical recording of the temperature variations of the cavity when running at 150°C. To maintain the temperature variations to less than 1°C, the heater voltage was adjusted manually as required. It was found that a manually controlled heat input to a cavity having a large thermal capacity and well isolated from its surroundings by the use of low-conductivity German-silver waveguide and cooled to some extent by radiation, yielded a very stable temperature within the cavity. Thus it was not necessary to have a feed-back temperature controller to maintain the cavity at a given temperature. Fig. 3.7(c) shows the finite time involved for the cavity to reach the required temperature from room temperature. The rate of increase was approximately 10°C/minute. So, if the free radical destruction temperature was chosen such that the reaction was not fast then the loss of free radicals in the last 10°C rise to this temperature would be small.

3.4.2 Low Temperature Cavity

This cavity which is shown in fig. 3.8 was designed along similar lines to the high temperature cavity except that one needed to irradiate the crystal with X-rays inside the cavity at LNT. In designing the cavity one had to take into account the low penetrating power of X-rays as this was the only available source of high energy radiation in this laboratory. The path of the X-ray beam had to be through materials of low mass absorption coefficient to be of sufficient intensity when they reached the crystal. The crystal was mounted over a small hole in the centre of the removeable cavity bottom so that it was located as close as possible to the X-ray tube window. The vacuum jacket had a beryllium window fixed to the centre of its closed end. Vacuum sealing at the other end of the jacket was made with an accurately machined metal to metal cone. The distance between the crystal and window was kept to a minimum without allowing the cavity to touch the jacket. The reason for such a long vacuum jacket was to allow a low

Fig.3.8 The Low Temperature Cavity

Fig.3.9 The Low Temperature Cavity Positioned on the X-ray Tube.

temperature gradient to exist along the waveguide from the point where it is in contact with the liquid nitrogen to the cavity. Thus, combining this with the low thermal conductivity of the German-silver wave-guide, a small amount of heat applied to the cavity was sufficient to hold the cavity at an intermediate temperature. To allow the window in the jacket to be in close proximity to the X-ray tube and at the same time the whole assembly to be maintained at LNT, a special liquid nitrogen container was designed and constructed from polystyrene foam. To prevent the liquid nitrogen from running through this material, a polythene bag was made to fit the inside shape exactly. A shallow depression in the bottom of the dewar allowed the vacuum jacket to be located whilst the weight of the apparatus held the beryllium window against the polythene to minimise the liquid nitrogen path between these two surfaces. When the apparatus was mounted above the X-ray tube (fig. 3.9) and evacuated the container was filled with liquid nitrogen. At the completion of the irradiation the whole assembly was transferred very quickly from this dewar to the glass dewar designed to allow the cavity to be mounted between the poles of the magnet. The method of heating the cavity and recording the temperature were similar to those used for the high temperature cavity.

However, as it was pointed out earlier, this cavity was designed to overcome the low penetrating power of X-rays as well as annealing the crystals at a temperature above LNT. Even taking the greatest precautions, X-rays were absorbed owing to the presence of a greater amount of liquid nitrogen under the beryllium window than originally estimated and in fact, was, the major factor in making the cavity unsatisfactory to use. Also later on in the project it was felt that low temperature irradiations and observations without annealing were not of as great interest as those at room temperature or above. For these reasons this cavity was not modified. In its present form though, the low-temperature cavity is perfectly suitable for examining any specimen at a controlled temperature between LNT and room temperature and also for examining crystals irradiated at low temperature if a source of more penetrating radiation is available. This is in fact the case now in this University with the recent acquisition by the Department of Physical and Inorganic Chemistry of a Co^{60} γ-ray irradiation facility.

3.5 Choice of Radiation for Kinetics Studies

For kinetics studies of free radicals in single crystals one needs to produce a uniform free radical concentration with as little other damage as possible so that the influence, if any, of radiation induced impurities on the free radical reaction is least. If these crystals are to be irradiated with high energy, electro-magnetic radiation then one has available either γ- or X-rays. If either of these ionising radiations are used their interaction within the crystal is via secondary electrons mostly produced by photoelectric absorption. Thus one would expect the effects of either of these ionising radiations to be unspecific. Without any other information available then the choice of radiation is to be the one conveniently available. The most energetic source of radiation available in this laboratory was MoK_{α} radiation with a wavelength of 0.71Å. This source of X-rays is suitable when one considers the mass absorption coefficient for a typical organic crystal. For example the mass absorption coefficient for glycine is calculated to be about 2 cm^2 per gm. for MoK_{α} radiation and so the intensity of the incident X-rays is reduced to 50% only after reaching a thickness of 2.2mm. Using radiation in the vicinity of 1.54Å the distance is reduced to 0.3mm. If the longer wavelength X-rays from the molybdenum anode tube are filtered out then one can expect a more uniform distribution of free radicals will be obtained across the crystal. Since the X-ray beam is only incident on one side of the crystal at a time the procedure of turning the crystal over at half the irradiation time was adopted to allow the crystal to receive an equal dosage on all sides.

Also available for simple irradiations were the γ-irradiation facilities at the Australian Atomic Energy Commission (AAEC), Lucas Heights. In this case crystals were placed inside a spent hollow fuel element which was emitting γ-radiation. Using this facility one had the advantage that the crystals received the same dosage from all directions.

The X-ray beam was produced using a sealed X-ray tube (Phillips type 25295/62) with a molybdenum target. Operating conditions used for the tube were generally 35 KVP anode voltage and 20 ma. tube current. Apparatus was designed for holding the crystals during irradiation at room temperature. The crystals were placed on the metal foil window which formed the bottom of the holder; several holders being made up with different windows (including beryllium and aluminium). The top of the holder was greased and pushed on so that the crystals were sealed from the ozone that may be present. The complete holder was then held several mm. above the X-ray tube window and could be rotated about an axis parallel to the beam. The crystals were rotated regularly and turned over at half the irradiation time so that they were uniformly irradiated. The cover and the top of the holder were lined with lead for shielding.

For most irradiations, the X-ray beam was filtered. The longer wavelengths were filtered using 0.005" aluminium foil as the window in the crystal holder. This filter reduced the intensity of X-rays with wavelengths around 1.5Å to 20% whereas those with wavelengths around 0.71Å (the K_α line for molybdenum radiation) were only reduced to 85%.

3.6 Crystal Preparation

The preparation of single crystals of organic solids for irradiation was carried out in a simple manner. All of the crystals, except N-acetylglycine, were grown from commercial, high purity samples by slow evaporation of an aqueous solution in double distilled water. N-acetylglycine was synthesised according to Vogel (1956) and the product recrystallized twice from distilled water. The purity was checked by observing the melting point (208°C) and also comparing the infrared spectrum with that listed under the ASTN system.

The deuterium-substituted crystals used in this project were prepared in a similar manner. The ordinary compound was dissolved in heavy water (purity 99.9%) and this solution was then evaporated to dryness in a dessicator using phosphorous pentoxide as a drying agent. The residue was redissolved in heavy water and again evaporated to dryness. The evaporation of the third recrystallization solution was allowed to proceed slowly in the dessicator. The resulting single crystals were kept in a dessicator to prevent them coming in contact with water vapour and possibly allowing the exchange reaction to proceed in reverse.

CHAPTER 4

FREE RADICAL REACTIONS

4.1 Introduction

This chapter will be devoted to the experimental testing of some of the predictions on free radical reactions discussed in Chapter 2.2. This constitutes a major portion of the work and includes reaction kinetics of free radical recombination and conversion reactions, activation energies of these reactions and the behaviour of different radical species in an irradiated crystal.
As a prelude to this the chapter discusses the reproducibility of free radical reactions.

4.2 Selection of Systems for Study

Prelimary investigations were made on a number of organic crystals to determine the temperature at which free radicals produced in these crystals begin to disappear or transform to a new radical. All crystals in these particular investigations were irradiated with filtered X-rays in this laboratory using doses ranging from 5 to 8 Megarads. A visual examination of each crystal after irradiation revealed in nearly every case that its colour had changed from colourless to either a yellow or light purple colour. More will be said about this in Chapter 6.5. Those organic crystals investigated are listed in table 4.1. The table also includes a list of the free radicals at present known to be produced in these crystals by high energy radiation. The ESR spectra from those crystals with known radicals were carefully compared with the spectra reported in the literature. This was done by recording the ESR spectrum of the particular irradiated crystal where the static magnetic field was in a specified direction with respect to the crystal axes. Only in one case (β-succinic acid) was the ESR spectrum substantially different from

TABLE 4.1

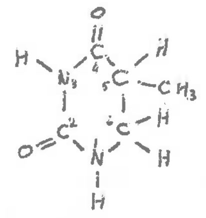
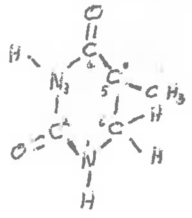
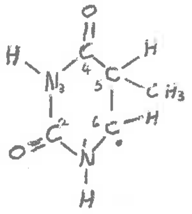
A Listing and Classification of Radicals in Selected Organic Crystals

Compound	Formula	Initial Radical(s) Produced	Kenide Name for Radical	Type of Radical	Reference
Glycine	$\mathrm{NH_3^+{-}CH_2{-}COO^-}$	$\mathrm{NH_3^+{-}\dot{C}H{-}COO^-}$	Kenoglycine	Host	Morton (1964b)
		and	and		
		$\mathrm{\dot{C}H_2\ {-}COO^-}$	Kenoacetic acid	Impurity	Morton (1964b)
D_3-glycine	$\mathrm{ND_3^+{-}CH_2{-}COO^-}$	$\mathrm{\dot{C}D_2{-}COO^-}$	Deuterated kenoacetic acid	Impurity	Morton (1964b)
L-α-alanine	$\mathrm{CH_3{-}CH(NH_2){-}COOH}$	$\mathrm{CH_3{-}\dot{C}H{-}R}$	α-kenopropionic acid	Impurity	Miyagawa & Gordy (1960)
dl-α-alanine	$\mathrm{CH_3{-}CH(NH_2){-}COOH}$	$\mathrm{CH_3{-}\dot{C}H{-}R}$	α-kenopropionic acid	Impurity	Miyagawa & Itoh (1962)
Deuterated L-α-alanine	$\mathrm{CH_3{-}CH(ND_2){-}COOD}$	$\mathrm{CH_3{-}\dot{C}H{-}R}$ $\mathrm{(R{\equiv}COOD\ or\ COO^-)}$	Deuterated α-kenopropionic acid	Impurity	Miyagawa & Itoh (1962)
Malonic Acid	$\mathrm{HOOC{-}CH_2{-}COOH}$	$\mathrm{\dot{C}H_2{-}COOH}$	Kenoacetic acid	Impurity	Hors field et al (1961b)
		and			
		$\mathrm{HOOC{-}\dot{C}H{-}COOH}$	Kenomalonic acid	Host	Horsfield et al (1961b)
D_4-malonic	$\mathrm{DOOC{-}CD_2{-}COOD}$	Two Unknown Species	-	-	Present work
Succinic Acid	$\mathrm{HOOC{-}CH_2{-}CH_2{-}COOH}$	$\mathrm{HOOC{-}CH_2{-}CH_2{-}CO\dot{O}}$ *	β-kenoxycarbonyl propionic acid	Host	Present work
		and	and		
		$\mathrm{HOOC{-}CH_2{-}\dot{C}H{-}COOH}$	Kenosuccinic acid	Host	Heller & McConnell (1960)
D_2-Succinic Acid	$\mathrm{DOOC{-}CH_2{-}CH_2{-}COOD}$	$\mathrm{DOOC{-}CH_2{-}CH_2{-}CO\dot{O}}$ *	Deuterated kenoxycarbonyl propionic acid	Host	Present work
		and	and		
		$\mathrm{DOOC{-}CH_2{-}\dot{C}H{-}COOD}$	Deuterated kenosuccinic acid	Host	Pooley & Whiffen (1962)
N-Acetylglycine	$\mathrm{H_3C{-}CO{-}NH{-}CH_2{-}COOH}$	$\mathrm{H_3C{-}CO{-}NH{-}\dot{C}H{-}COOH}$	Acetylkenoglycine	Host	Miyagawa et al (1960)

* See Text

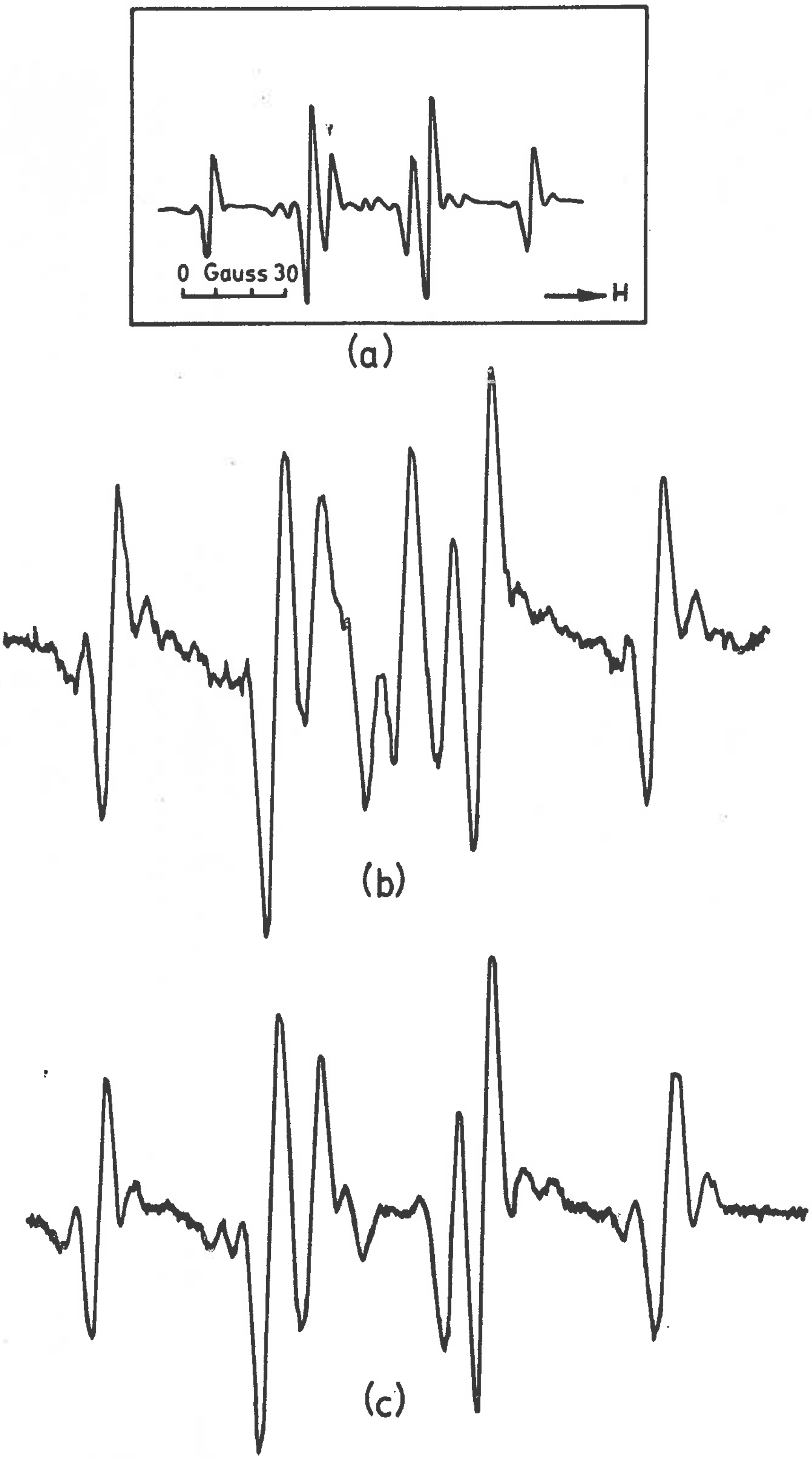
TABLE 4.1 (Cont.)

A Listing and Classification of Radicals in Selected Organic Crystals

Compound	Formula	Initial Radical(s) Produced	Kenide Name for Radical	Type of Radical	Reference
Deuterated N-acetylglycine	$H_3C\text{-}CO\text{-}ND\text{-}CH_2\text{-}COOD$	$H_3C\text{-}CO\text{-}ND\text{-}\dot{C}H\text{-}COOD$	Deuterated acetylkenoglycine	Host	Miyagawa et al (1960)
Glyclyglycine	$^{+}H_3N\text{-}CH_2\text{-}CO\text{-}NH\text{-}CH_2\text{-}COO^{-}$	$^{+}H_3N\text{-}CH_2\text{-}CO\text{-}NH\text{-}\dot{C}H\text{-}COO^{-}$	Glyclykenoglycine	Host	Lin & McDowell (1961)
Methylmalonamide	$H_2N\text{-}CO\text{-}CH(CH_3)\text{-}CO\text{-}NH_2$	$CH_3\text{-}\dot{C}H\text{-}CO\text{-}NH_2$	α-kenopropionamide	Impurity	Cole & Heller (1965)
		$H_2N\text{-}CO\text{-}\dot{C}(CH_3)\text{-}CO\text{-}NH_2$	Methylkenomalonamide	Host	Cole & Heller (1965)
Maleic Acid	$HOOC\text{-}CH{=}CH\text{-}GOOH$	$HOOC\text{-}CH_2\text{-}\dot{C}H\text{-}COOH$	Kenosuccinic acid	Impurity	Cook et al (1967)
Dihydrothymine			5-keno-6-hydrothymine ($\dot{C}_5$)	Host	Bernhard & Snipes (1967)
			6-keno-5-hydrothymine ($\dot{C}_6$)	Host	Bernhard & Snipes (1967)

the spectrum previously reported (McConnell and Heller, 1960). Fig. 4.1(a) reproduces the spectrum they obtained when the static magnetic field was parallel to the C-axis. Pooley and Whiffen (1961) also obtained this spectrum which is attributable to kenosuccinic acid. In this work freshly irradiated β-succinic acid gave the ESR spectrum shown in fig. 4.1(b) for the same orientation of the crystal with respect to the magnetic field. On annealing this crystal at 80°C for a number of hours the final spectrum obtained is that shown in fig. 4.1(c). This observation clearly shows that two free radicals are produced in freshly irradiated succinic acid since the final spectrum is very similar to the reported spectrum. To check whether the presence of the extra radical species observed here was contingent on impurities in the specimens used, succinic acid crystals grown from two different commercial batches were irradiated using both γ-rays and X-rays. Furthermore the use of unfiltered X-rays from the molybdenum anode tube did not alter the production rate of this unknown radical. In fact in every case this radical was produced in the same proportions with kenosuccinic acid. One can offer no explanation at present of the discrepancy between these results and those of Pooley and Whiffen, and Heller and McConnell. Table 4.2 lists the approximate temperature where the concentration of free radicals decreases to half in 30 minutes for those crystals where the free radicals can be thermally annealed out.

During the preliminary investigations free radical transformations were observed in glycine and D_3-glycine ($ND_3^{\pm}CH_2$-COO^-) after irradiation at room temperature. Ghosh and Whiffen (1960) and later Simmons (1966) both reported that a new radical appeared in glycine after it was irradiated and allowed to age at room temperature for several days. The radicals listed in table 4.2



(a)

(b)

(c)

Fig. 4.1 E.S.R. Spectra of Irradiated Succinic Acid.

TABLE 4.2

A table listing observed free radical destruction reactions

Compound	Radical	Temperature Convenient for Annealing
Glycine	$NH_3^+-\dot{C}H-COO^-$ unknown species (after conversion)	150°C
D_3-glycine	$^*R-CO\dot{O}$ (After conversion)	150°C
L-α-alanine	$CH_3-\dot{C}H-R$	160°C
dl-α-alanine	$CH_3-\dot{C}H-R$	160°C
Malonic Acid	$\dot{C}H_2-COOH$ $HOOC-\dot{C}H-COOH$	65°C 75°C
D_4-malonic Acid	Unknown species	55°C
Succinic Acid	$HOOC-CH_2-CH_2-CO\dot{O}$ $HOOC-CH_2-\dot{C}H-COOH$	80°C 105°C
D_2-succinic acid	$DOOC-CH_2-CH_2-COO^{\bullet}$ $DOOC-CH_2-\dot{C}H-COOD$	90°C 105°C
N-acetylglycine	$H_3C-CO-NH-\dot{C}H-COOH$	125°C
Deuterated N-acetylglycine	$H_3C-CO-ND-\dot{C}H-COOD$	125°C
Glyclyglycine	$^+H_3N-CH_2-CO-NH-\dot{C}H-COO^-$	Survives up to the decomposition temperature of the crystal
Methylmalonamide	$CH_3-\dot{C}H-CO-NH_2$ $H_2N-CO-\dot{C}(CH_3)-CO-NH_2$	Not determined 160°C
Dihydrothymine	$\dot{C}_5$	165°C

*See Text

for both forms of glycine are those radical species remaining after the conversion is complete. Both of these conversion reactions will be mentioned later in this chapter.

Those radicals marked with an asterisk in both tables 4.1 and 4.2 have not been formally identified. However, because of the very simple nature of the ESR spectra obtained (a very strong single line in each case when all the magnetic centres were equivalent) it can very well be proposed that these radicals are peroxy radicals; the unpaired electron residing on an oxygen atom. This type of radical has been reported to exist in irradiated oxalic acid (Moulton et al, 1967). It will be recalled from Chapter 2 that this project is primarily concerned with free radical behaviour and hence ESR was used as a means of assaying the free radical concentration as a function of time. Thus the unknown identity of several radical species does not hinder the testing of most predictions of the hypothesis. In respect to the kinetics, activation energies, and isotopic phenomena, knowledge of their identity is desirable but not essential. In fact detailed ESR spectroscopy was not engaged in during the course of this project.

The organic single crystals eventually chosen for the majority of the experiments in this project were glycine, L- and dl-α-alanine, malonic acid, succinic acid and N-acetylglycine. These compounds were picked first because of their simplicity. They are the simpler molecules of their respective groups and the crystal structure and hydrogen bonding has been determined for all of them. These crystals have fairly high melting points and are stable below this point. Secondly, the preparation of good quality large single crystals is quite easy (as described in the previous chapter). With regard to the experiments requiring deuterated crystals these five compounds were suited to the preparation of such crystals by recrystallization from heavy water. This procedure is very much simpler then that required to prepare crystals in which the hydrogen atoms bonded to the carbon atoms are exchanged for deuterium atoms. Unfortunately these particular deuterated compounds were not readily available, commercially. An exception to this is malonic acid, in which, all hydrogen atoms can be replaced during repeated recrystallization from heavy water (Halford and Anderson, 1936). Lastly, it may be mentioned again that most of the radical species formed in the above named crystals have been determined (see table 4.1).

The experiments discussed in this chapter and the following two chapters have generally involved these five compounds and their deuterated counterparts.

4.3 Reproducibility of Free Radical Reaction Rates.

It is of interest to examine the variation of rate of production of the free radicals in crystals chosen from different batches which have been similarly irradiated. If one needs crystals with equal concentration of free radicals which is the case if one of the methods for determining the activation energy of the free radical reaction is used, then one needs to ascertain whether this can be achieved by similar irradiations. It may be that the free radical production rate depends upon the concentration of impurities in the crystals which may vary between crystals taken from different batches.

The reproducibility of a free radical reaction rate is of such interest as to warrant investigation. Most reactions in solids are notorious for their lack of reproducibility. Galwey (1967) has reviewed solid state reactions occuring below the melting point of the solid especially thermal decomposition reactions. The growth rate of nucleation in this type of reaction generally increases with reaction temperature and may lead to self-heating that is, the rate of heat liberated from the exothermic reaction increases the reaction temperature because the sample is raised in temperature above its surroundings. The main point in regard of this sort of reaction is that it proceeds by nucleation and so the rate generally varies considerably from sample to sample. One point of interest regarding free radical reactions in organic crystals is that there is every hope that here one can study a solid state reaction free of the troubles in lack of reproducibility associated with nucleation and self-catalysis. Because the rate of free radical destruction might still vary between crystals grown from different batches where the concentration of impurities differed, it was felt that a study of the reproducibility of the free radical reaction rate was needed.

In the course of these investigations one can also find out whether the annealing of crystals and the presence of radiation induced impurities in the crystals alter the reaction rates of free radical reactions. On these grounds two series of experiments were devised, one to take account of the effect of radiation effects and the other on the effect of annealing the crystal after it is irradiated. Now during irradiation the induced damage and the concentration of radicals increase together with time of irradiation. To test the influence of these impurities on the reaction rate for free radical destruction one only needs to check whether or not the relative rates of destruction for isothermal annealing is what is predicted by the reaction order in crystals subjected to different irradiation doses on the assumption of an invariable rate constant. As radical destruction generally obeys second-order kinetics (as discussed in section 4.4) one can expect that if the radical concentration is double that in another similar crystal then the relative rate constant will be doubled too. In fact this is what one wants to investigate in the experiment. The question of previous thermal annealing can be examined by preirradiating and annealing the crystals. These crystals are reirradiated with unirradiated crystals and their reaction rates compared as discussed earlier in this section. The effect on the production rate of radicals with previous irradiation and annealing can also be examined.

4.3.1 Methods for Comparing Reaction Rates.

If the concentration of a particular radical species in an irradiated single crystal is to be compared with the concentration of the same radical species in another crystal then it is necessary to irradiate both of these crystals uniformly with the same dosage of radiation. First two crystals of the particular organic compound were chosen (preferably from different batches) with the same weight and habit. Next it was necessary for the crystals to be irradiated uniformly. To enable this to be done the γ-irradiation facilities at the Australian Atomic Energy Commission Establishment, Lucas Heights were used. The crystals were placed inside a spent hollow, reactor fuel element providing a dose rate of approximately 1.5 Megarads per hour. The dose over the volume of the two crystals was uniform. However, for comparing the variation of rate for the conversion reaction in glycine crystals the matched crystals had to be irradiated in this laboratory using X-rays. This was necessary because the reaction occurs at room temperature and crystals could not be returned to the laboratory from Lucas Heights quickly enough. For the glycine crystals to receive as uniform a dose of X-rays as is practicable from an X-ray tube, both crystals were rotated during the irradiation time and turned over at half time.

To check the concentration of free radicals produced in the matched crystals, each crystal was mounted similarly on separate PTFE rods. The only convenient way of mounting the crystals was to shape a slot in the PTFE rod for a prefered direction of the crystal, for it was found that those glues freely available decomposed at high temperatures and could not be used when the cavity with crystal was upside down during a heating in the oven. After the mounting the two crystals were, in turn, fixed in the resonant cavity which also held a copper sulphate standard having a known number of spins. The ESR spectrum of the first crystal and the standard were recorded. Now the spectrum from the second crystal, replacing the first crystal in the cavity and the same standard (whose position had not been altered) were recorded. The same instrumental settings of the spectrometer were used and the alignment of the second crystal after being replaced in the cavity was made as close as possible to that of the first crystal. The heights of several corresponding lines from each of the first derivative spectra were compared after taking into account any gain variations in the spectrometer. Thus relative free radical concentrationscould be accurately compared. If the absolute concentration of free radicals in each crystal was required then a double integration had to be carried out. A CDC 3200 computer program was written to compute the first and second integrals from the first derivative ESR spectrum using Simpson's Rule. The second integration gives the area under the absorption curve which is proportional to the number of free radicals.

For the reaction rates of free radicals in two crystals to be compared the crystals were mounted in the double cavity along with a standard in the top position. The initial ESR spectrum from each crystal and the standard were recorded twice. The cavity with crystals was then heated (the heating interval being noted) according to the technique described in section 3.3 and the new ESR spectra recorded using the same instrumental settings. At the completion of the series of heatings reaction curves were plotted for each crystal and their slopes compared.

To check the behaviour of a conversion reaction in two matched crystals it was necessary to examine the shape of each spectrum at various stages of the conversion to see whether the shape remains identical. As one wanted to examine the complete shape of the spectrum from each crystal after a heating, an alternative technique was necessary. This came about because the usual standard composed of powdered zinc selenide doped with manganese (which is described in section 4.4.1) obscured the outer lines of the free radical spectrum. An alternative standard was needed and the only suitable one was copper sulphate as its spectrum is separated from the free radical spectrum. However, this standard cannot be heated without affecting it and so the two crystals had to be heated in a separate cavity. The method of recording the spectra from both crystals is the same as that used to measure relative concentration in two matched crystals which has been described earlier. After the spectra were recorded both crystals were mounted in the other cavity ready for the next heating in the oven. To remount each crystal accurately the PTFE rod was slotted at the end opposite to the crystal to allow it to be located by the guide pin situated in the hole of the cavity wall.

As mentioned in the last section one would like to observe any effect of preirradiation and annealing of the crystals on the reaction rate of destruction and production of free radicals. The technique as just described can be used to check relative concentration and compare reaction rates in two crystals where one crystal has previously been preirradiated and the radicals thermally destroyed. To prepare a pair of such crystals one needs to irradiate one crystal with a known dose and then thermally anneal at a temperature where the free radical reaction is slow. The time chosen was such that no residual radicals were able to be detected. Now this crystal and the other unirradiated crystal were carefully irradiated together to receive the same dose of radiation that the annealed crystal received the first time. X-rays were used in these irradiations for convenience.

The experiments to examine the effect of radiation induced impurities were undertaken also using the double cavity and oven. A pair of crystals of which one had been exposed to X-rays for twice as long as the other were prepared. The initial relative concentrations were determined for each crystal according to the method described earlier in this section. Comparitive rate constants were obtained from the slopes of the two reaction curves which were compiled from data obtained when the two crystals were heated identically at the same temperature for various intervals. The reason for the choice of one irradiation time being twice the other was that these results were to be compared to those obtained from the pairs of crystals where one crystal was preirradiated and annealed. It was expected that the preirradiated crystal when irradiated a second time with the same dose of X-rays would also contain twice as much radiation induced impurity as the other crystal.

4.3.2 Results and Discussion

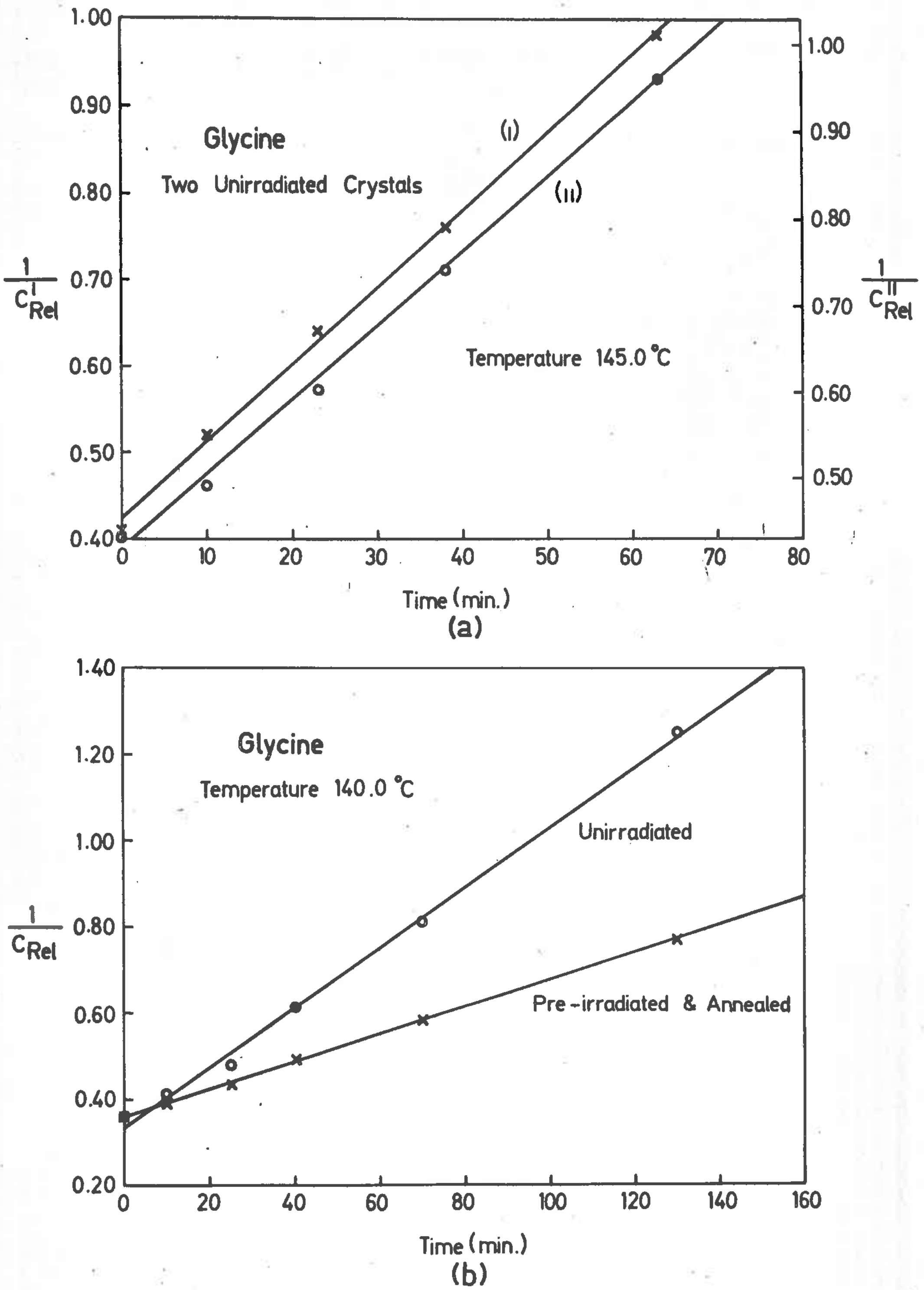
From the results (shown in table 4.3) the conclusion can be drawn that the production rate of free radicals and the reaction rate constants can be reproduced in a given pair of crystals of a particular compound. Fig. 4.2(a) shows a typical pair of reaction curves for the destruction of free radicals in a matched pair of glycine crystals annealed at 146°C. The comparitive rate constants for glycine were obtained directly from the slope of the two curves and after being corrected for slight differences in radical concentrations are given as a ratio. All other results in table 4.3 were determined in the same way. The free radical conversion reaction which takes place in glycine at 50°C was found to be reproducible in matched crystals. This was checked using the technique mentioned in section 4.3.1 of examining the two spectra, which were initially identical, at various stages of reaction to observe whether both spectra remained the same in shape and intensity.

TABLE 4.3

A comparison of reaction rates in matched irradiated crystals.

Compound	Radical(s)	Rel. Conc. of Radicals	Ratio of Rate Constants	Ratio of Rates Corrected for Diff. in Concs
Glycine	$NH_3^+\text{-}\dot{C}H\text{-}COO^-$ and Unknown	1.04	0.96	0.99
L-α-alanine	$CH_3\text{-}\dot{C}H\text{-}R$	1.04	1.08	1.12
Malonic Acid	$\dot{C}H_2\text{-}COOH$	1.04	1.07	1.11
Succinic Acid	$HOOC\text{-}CH_2\text{-}CH_2\text{-}COO^\bullet$	1.06	1.08	1.14
N-acetyl-glycine	$H_3C\text{-}CO\text{-}NH\text{-}\dot{C}H\text{-}COOH$	1.04	0.94	0.98

The results on the influence of radiation induced impurities on the reaction rate of free radical recombination are given in table 4.4. As it was pointed out in section 4.3 if the relative concentration of free radicals is increased by n times in one crystal with respect to another and the reaction obeys second-order kinetics then the relative rate constant for the two crystals will also be increased by a factor of n. The results given in table 4.4 for L-α-alanine indicate that this in fact holds to within 5% since this reaction


Glycine
Two Unirradiated Crystals
(I)
(II)
Temperature 145.0 °C
$\frac{1}{C^{I}_{Rel}}$
$\frac{1}{C^{II}_{Rel}}$
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0
10
20
30
40
50
60
70
80
Time (min.)
Glycine
Temperature 140.0 °C
Unirradiated
Pre-irradiated & Annealed
$\frac{1}{C_{Rel}}$
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0
20
40
60
80
100
120
140
160
Time (min.)

(a)

(b)

Fig. 4.2

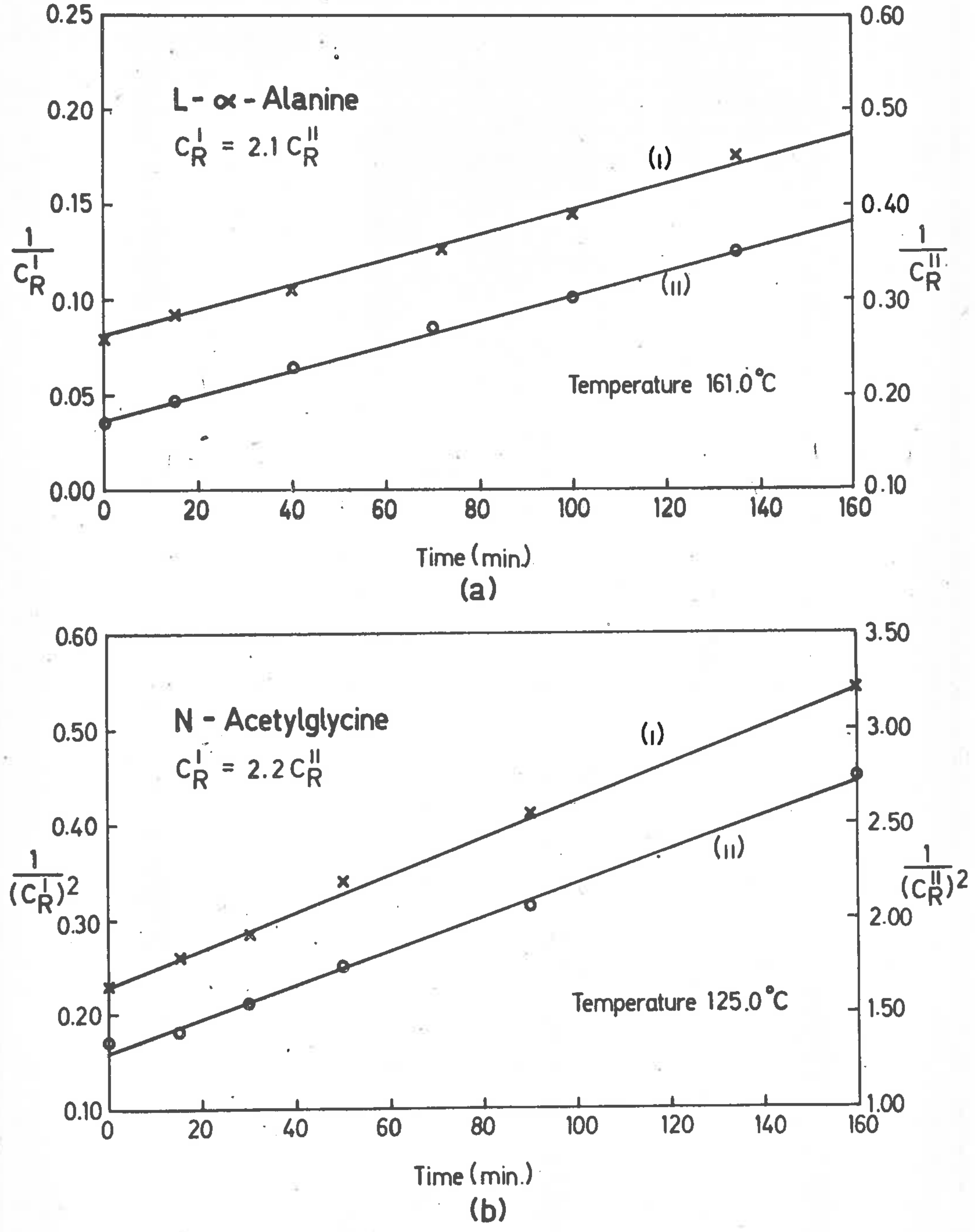

L - α - Alanine
$C_R^I = 2.1\,C_R^{II}$
Temperature 161.0 °C
(I)
(II)
$\frac{1}{C_R^I}$
$\frac{1}{C_R^{II}}$
0.00
0.05
0.10
0.15
0.20
0.25
0.10
0.20
0.30
0.40
0.50
0.60
0
20
40
60
80
100
120
140
160
Time (min.)
(a)
N - Acetylglycine
$C_R^I = 2.2\,C_R^{II}$
Temperature 125.0 °C
(I)
(II)
$\frac{1}{(C_R^I)^2}$
$\frac{1}{(C_R^{II})^2}$
0.10
0.20
0.30
0.40
0.50
0.60
1.00
1.50
2.00
2.50
3.00
3.50
0
20
40
60
80
100
120
140
160
Time (min.)
(b)

Fig. 4.3

actually obeys second-order kinetics (see table 4.6). Fig. 4.3(a) reproduces the reaction curves for the pair of L-α-alanine crystals used in this experiment where one crystal was irradiated twice as long as the other using the same dose rate. Note that the scale factor for $^1/_{C''_R}$ in fig. 4.3(a) is twice that for $^1/_{C'_R}$. In the case of N-acetylglycine where the free radical destruction obeys third-order kinetics the relative rate constant is 4.5 which is within 6% of the expected value of 4.8. The reaction curves for N-acetylglycine are shown in fig. 4.3(b) where it is to be noted that the vertical scaling factors for each curve differ by 5. These results allow the conclusion that reaction kinetics for a particular free radical destruction is still rigidly adhered to when the concentration is doubled. The effect of extra damage on a conversion reaction was not observed. The method by which this was confirmed is discussed in section 4.4.2. The conclusion can now be drawn that the extra induced impurities do not affect the free radical reaction.

TABLE 4.4

The effect of radiation induced impurities on the reaction rate.

Compound	Relative Concentrations of Radicals C'_R/C''_R	Relative Rate Constant K''/k'	Expected Rel. Rate Constant
L-α-alanine	2.1	2.0	2.1
N-acetylglycine	2.2	4.5	4.8

The results of the experiments conducted on pairs of crystals in which one crystal of each pair has been preirradiated and annealed are listed in table 4.5. These experiments, as it was mentioned in section 4.3 were to check for any alteration in the rate of production and reaction rates of free radicals in those crystals subject to this rather severe treatment. Fig. 4.2(b) reproduces the reaction curves for the destruction of the two radical species in ordinary and preirradiated glycine crystals and it is evident that the relative rate constant is different from the expected value that is, the reaction rate in the preirradiated crystal has been reduced by this treatment. It made no difference if the unirradiated crystal was annealed before irradiation with the preirradiated crystal. The reaction rate for the conversion reaction in a pair of glycine crystals prepared similarly to those above was observed. This experiment was carried out in the same way as the rate of conversion was compared for two matched glycine crystals.

TABLE 4.5

The effect of preirradiating and annealing on the reaction rate of free radical destruction.

Compound	$\frac{\text{Rel. Conc. in Unirrad. Crystal}}{\text{Rel. Conc. in Preirrad. Crystal}}$	Relative Rate Constants	Expected Relative Rate Constant
Glycine	1.02	0.48	1.02
L-α-alanine	1.05	0.53	1.05
N-acetylglycine	0.98	0.25	0.96

One can conclude from the results on the production of free radicals that the rate of production is not altered in any way irrespective of how the single crystals are prepared or what is done to them prior to irradiation. Free radical production is not a structure sensitive phenomenon and catalytic processes appear not to be involved.

It can be stated that the free radical reaction (which includes destruction and conversion reactions) is to be regarded as a well behaved and reproducible reaction in the solid state. The effects of self-nucleation and variation of reaction rate do not appear to be evident during these reactions. The reproducibility of this reaction allows those experiments on activation energy and investigation of the kinetic isotope effect to be undertaken with confidence. Extreme lack of reproducibility in these reactions would have made the observation of the isotope effect less conclusive. However, the effect of annealing and recooling a crystal after irradiation does alter the reaction rate. One can conclude that it is the annealing and recooling of the crystal that affects the rate because the presence of extra secondary radiation damage after the crystal is reirradiated can be ruled out. This is arrived at from the fact that reaction kinetics are unaltered when the concentration of radicals and radiation damage is doubled. It appears that what really matters is the cooling of a crystal which has been irradiated and then held at an elevated temperature. The microscopic cracking caused by the aggregation of impurities when hot, apparently ruptures the crystal when it is cooled to room temperature and becomes more brittle than it is at a high temperature. Thus, some radicals when formed during the reirradiation of the crystal are "trapped" on the boundaries that were produced by microscopic cracking. The less likelihood of these radicals being released from these sites on warming would inhibit the rate of radical destruction since less radicals become available for migration in the crystal at a given temperature. At this stage one can note that a crystal is annealed to some extent when it is heated to a sufficient temperature for the free radicals to destroy each other. It is to be noted that the complete annealing of a crystal after irradiation did not affect the conversion rate of radicals in glycine. This is to be expected if the conversion reaction is a unimolecular reaction and a transport mechanism is not necessarily involved. These boundaries that may be introduced by the irradiating and annealing of the crystal can have no influence on the rate of reaction if only one radical is involved.

4.4 Reaction Kinetics.

In Chapter 2.2 it was proposed that ordinary reaction kinetics are expected to be obeyed when free radicals react to destroy each other. This is expected if the unpaired electrons on two adjacent radicals are paired up to form a saturated chemical species. Reaction kinetics for a molecular reaction of this type are expected to be second-order. Thus the determination of kinetics would indicate the number of radicals involved in the reaction. As the theory of reaction kinetics is well established only the results will be given here. For a second-order reaction the concentration [A] of a particular reactant at a given temperature is related to time t by the expression

$$k = {}^{1}/_{t}\left({}^{1}/_{[A]_t} - {}^{1}/_{[A]_e}\right)$$

where $[A]_e$ is the concentration of radicals at $t = 0$ and k is the rate constant. If in fact the reaction follows first-order kinetics the expression

$$k = {}^{1}/_{t} \log_e\left({}^{[A]_o}/_{[A]_t}\right)$$

is obeyed and one can rule out that free radicals need to be in pairs before they can be destroyed. A monomolecular reaction involves only one molecule of a particular species. In the case of a radical conversion only one radical is expected to be involved and so first-order kinetics should be obeyed.

Experimentally, the reaction kinetics for a particular reaction can be determined in several ways. Two of these will be briefly described. The first of these methods involves measuring the concentration of the reacting species [A] at various times for a given temperature. After having obtained this data one can plot three curves as a function of time using an expression $f([A(t)])$ as the quantity for the vertical axis. This quantity $f([A(t)])$ can be either of the quantities, $\log_e\left(\frac{[A(t)]}{[A]_o}\right)$, ${}^{1}/_{[A(t)]} - {}^{1}/_{[A]_e}$ or ${}^{1}/_{[A(t)]^2} - {}^{1}/_{[A]_e^2}$ which are linear with time for first, second and third-order kinetics, respectively.

If the reaction being studied does obey second-order kinetics then the curve of $f([A(t)]) = {}^{1}/_{[A(t)]} - {}^{1}/_{[A]_0}$ as a function of time will be the only linear curve of the three. This situation is shown in fig. 4.4 where this curve is linear but the other two are not. Similarly if the reaction followed first-order kinetics the expression $-\log_e\left(\frac{[A(t)]}{[A]_0}\right)$ as a function of time will be the only linear curve of the three curves plotted.

One can also determine the order of a reaction from the curve of concentration $[A(t)]$ as a function of time. The time for the concentration of the reacting species to be reduced to one half and to one quarter of the initial concentration $[A]_0$ are determined from this curve. These times, denoted as $t_{\frac{1}{2}}$ and $t_{\frac{3}{4}}$ respectively, obey one of the three following relationships depending on which order this reaction follows. The relationships are :-

$t_{\frac{3}{4}} = 2\ t_{\frac{1}{2}}$ for a first-order reaction,

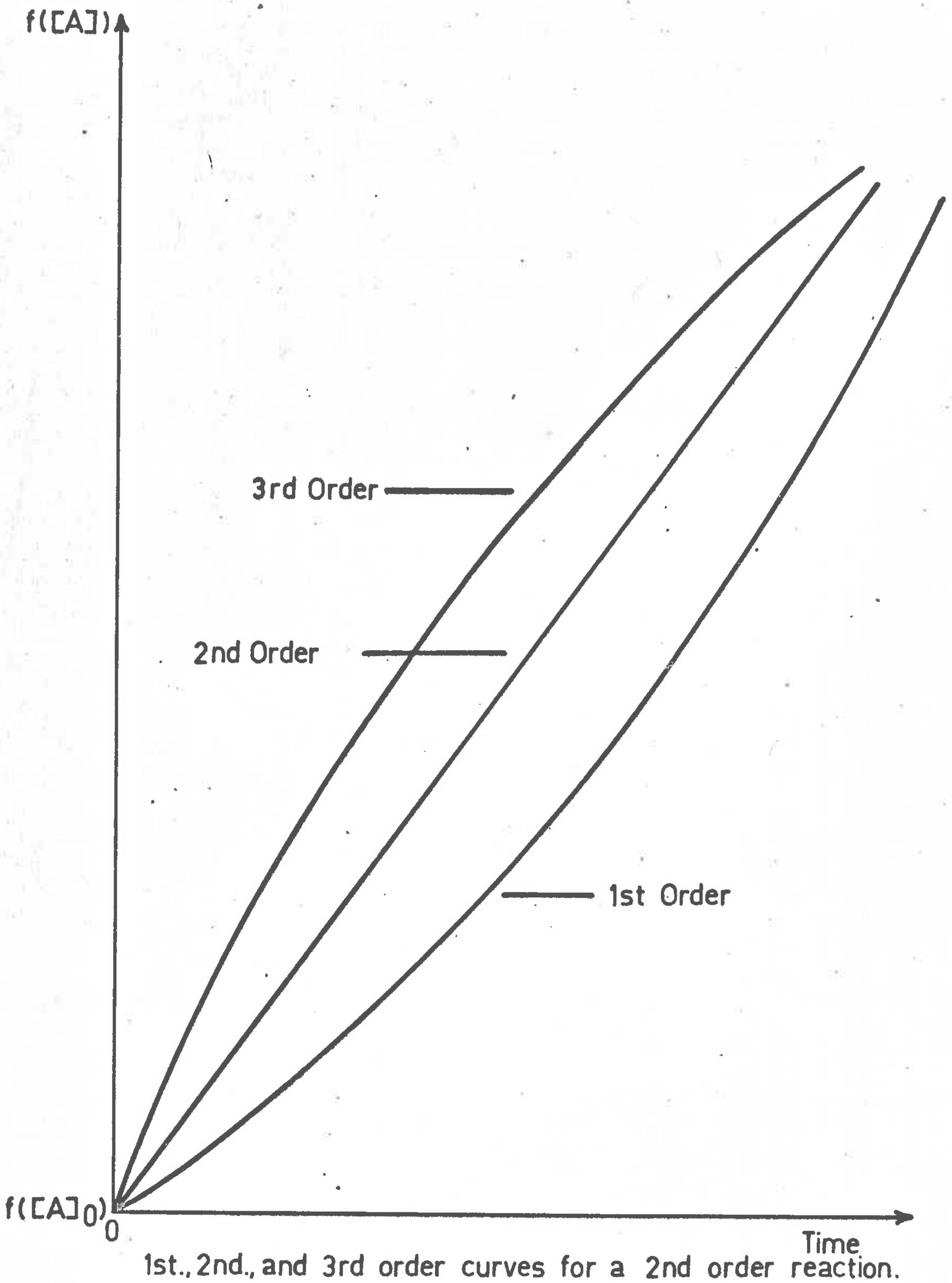
$t_{\frac{3}{4}} = 3\ t_{\frac{1}{2}}$ for a second-order reaction,

and $t_{\frac{3}{4}} = 5\ t_{\frac{1}{2}}$ for a third-order reaction.

For determining the reaction order for free radical destruction in the present work the first method was used exclusively as it is more accurate. To determine the kinetics of a radical conversion a novel method which is described in the next section is used.

4.4.1 Experimental Procedure.

The apparatus usually used for determining the kinetics of free radical destruction was the variable temperature cavity described in Chapter 3.4.1. It was most suitable for following reactions for times up to several hours. If a reaction had to be followed for many hours the small resonant cavity and oven were used. The technique used with the variable temperature ESR cavity was as

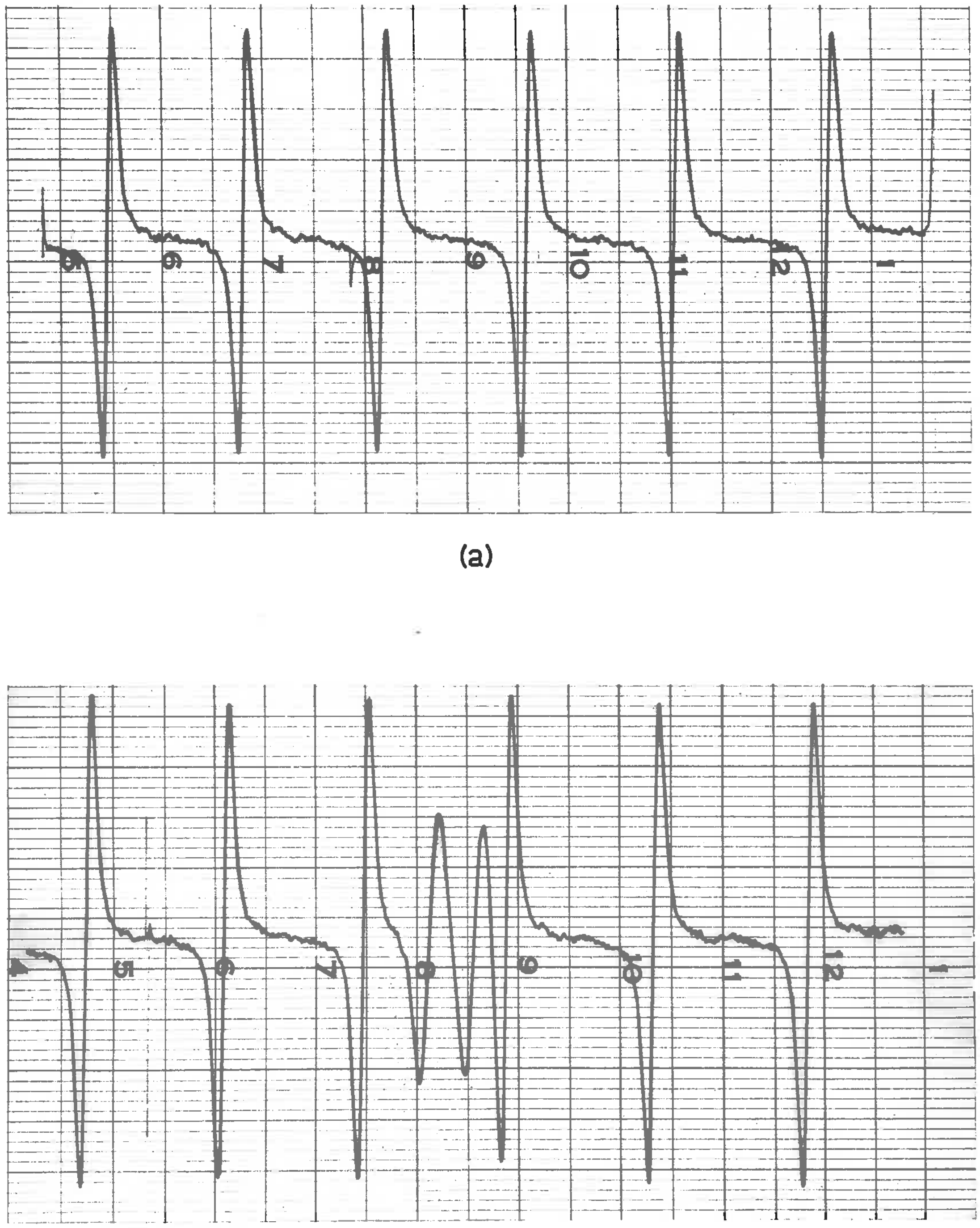


1st., 2nd., and 3rd order curves for a 2nd order reaction.

Fig. 4.4

follows. The crystal was mounted on a $\frac{1}{8}$" diameter by $\frac{1}{2}$" PTFE rod with the chosen crystal axis mounted parallel to the magnetic field. PTFE rod was most suitable for mounting the crystal because of its favourable dielectric properties and its ability to withstand temperatures to 200°C without bending or decomposing. The crystal was next coated with a thin layer of high purity silicone grease, to prevent evaporation in the vacuum at high temperatures. (The possibility of contamination from the silicone diffusing into the crystal is very unlikely because silicones are immiscible with most substances. At a temperature of 170°C the silicone grease did not flow sufficiently to expose the crystal; however, at the end of each experiment the silicone grease was removed and the crystal examined under X20 magnification for any signs of evaporation or other effects). After this mounting and greasing procedure the crystal and PTFE rod were then inserted in the cavity and opposite the crystal was mounted a standard composed of a powdered zinc selenide crystal doped with a small percentage of manganese. The ESR signal from the standard is shown in fig. 4.5 (a). The spectrum is that of the familiar six strong lines due to the manganese ion. The anisotropic splitting is removed by using the powdered material; the hyperfine splitting between two successive lines is 70 gauss (Cavanett, 1964). Fig. 4.5 (b) shows a typical ESR spectrum when both standard and irradiated crystal are included in the cavity. The centre portion of the free radical spectrum is completely unaffected by the presence of a standard and hence measurements can be taken from these centre lines for estimating the relavive concentration of free radicals as a function of time when the cavity is heated.

Since the incident microwave power was set so that no ESR saturation occurred at room temperature the first derivative of the ESR spectrum would alter in



(a)

(b)

Fig.4.5

proportion to the change in free radical concentration. Appendix C outlines the way the height of a first derivative spectrum can be used to measure relative concentrations. The amount of standard material was selected so that its signal at the elevated temperature was approximately one third full scale deflection on the recorder. It is pointed out here that when most paramagnetic materials are warmed the ESR signal decreases. This arises from the distribution of electrons between the two states (given by $^{N_1}/_{N_2} = \exp(^{-\Delta E}/_{kT})$ changing as the temperature increases. The ratio $^{N_1}/_{N_2}$ approaches more closely to unity as T increases and hence less nett absorption takes place. However, as the temperature of the cavity can be maintained to within $\pm\frac{1}{2}$°C no variation in standard or free radical signal can be expected.

After the sample was mounted in the cavity, the waveguide assembly was then mounted between the poles of the magnet and evacuated to a pressure of 10^{-2} mm. Hg with a rotary pump. The cavity was heated with a variable DC power supply and the temperature measured by a thermocouple junction as described earlier. After allowing several minutes for the cavity to settle to the required temperature, the combined ESR spectrum was recorded. The amplitude of the magnetic field sweep was adjusted to the same as the total splitting of the standard spectrum and the time of sweep set at 4 minutes. Since the sweep time can be made recurrent the free radical spectrum was able to be recorded every $4\frac{1}{2}$ minutes ($\frac{1}{2}$ minute was required for the sweep control to return to its initial conditions). The time of 4 minutes was found to be most suitable for accurately reproducing narrow lines generally encountered with free radical spectra. Each time when the magnetic field passed through the centre of the free radical spectrum a mark was put on the temperature chart by shorting the input to the recorder amplifier. Thus the time when each spectrum was recorded was known exactly.

After a series of spectra were obtained at a particular temperature it was then necessary to determine the relative concentration of the free radicals at the time when the spectra were recorded. First, the heights of the two outermost lines of the standard on both sides of the free radical spectrum were measured and an average value of their height obtained. Next a suitable line was selected near the centre of the free radical spectrum and its height measured. Thus the normalised height of the free radical line could be calculated giving the relative concentration C_R at that time. (The line chosen to give C_R was measured for each spectrum). The relative concentration was determined each time the spectrum was recorded and the terms $-\log_e C_R$, $^1/_{C_R}$ and $^1/_{C_R^2}$ were calculated and first, second and third-order curves plotted, respectively. To make these tedious calculations easier a computer program was written for the CDC 3600 computer. Heights of four of the six standard lines, the height of the free radical line and the time were punched onto cards to provide input data. The output was plotted directly by the machine and each set of points for a particular order were fitted to a straight line by the least squares method. Thus the 3 curves could be compared at a glance to check which set of points lay closest to a straight line.

A difficulty arises in determining the reaction kinetics of a free radical conversion which generally is avoidable in the case of free radical destruction because two different radical species will be present for most of the time during the conversion and, in general, the two spectra will overlap to a considerable extent. Now for kinetics to be determined with the above technique an isolated line from either spectrum is necessary. However, it is difficult to find an orientation of the crystal where one line from either spectrum is sufficiently separated. An alternative method for determining the kinetics of a radical conversion was developed, based on the fact that first-order kinetics leads to the time dependant spectrum shape being independant of the initial concentration, which is not true for second-order kinetics. The proof of this statement follows. Initially one can start with the overall spectrum being represented by $f_1(H) + f_2(H)$ where $f_1(H)$ represents the shape of the spectrum due to one free radical species. Now for a first-order reaction $C = C_o e^{-kt}$ and so after time t the new shape is given by $f_1(H)e^{-kt} + f_2(H) + \beta f_2(H)(1-e^{-kt}) = F(H,t)$ where β is a conversion factor representing the efficiency of radical I into radical II. The quantity $f_2(H)$ takes into account the fact that some of the radicals, II, may have already been formed. If the initial concentration is n times greater, then the initial spectrum can be represented by $nf_1(H) + nf_2(H)$, and after the same time t the new shape is $nf_1(H)e^{-kt}+nf_2(H)+n\beta f_2(H)(1-e^{-kt})=nF(H,t)$. Hence if a conversion obeys first-order kinetics the shape of the spectrum remains independant of concentration. It is only the intensity of the spectrum that is altered when two crystals differing only in concentration are heated in parallel. Now if the conversion reaction was to follow second-order kinetics then $C = \frac{Co}{Cokt+1}$ and after time t the new shape is

$$f_1(H)\left[\frac{Co}{Cokt+1}\right] + f_2(H) + \beta f_2(H)\left\{1-\left(\frac{Co}{Cokt+1}\right)\right\} = G(H,t)$$

If the initial concentration is n times then after time t the shape becomes

$$f_1(H)\left(\frac{nC_o}{nC_o kt+1}\right) + nf_2(H) + \beta f_2(H)\left\{1-\left(\frac{nC_o}{nC_o kt+1}\right)\right\} \neq nG(H,t)$$

This means that the shape of the spectrum does alter with concentration if the conversion obeys second-order kinetics. If, in the actual experiment, the corresponding parameters representing the shape of the combined spectrum from each of the two crystals (one having n times as many radicals as the other) show a constant ratio between them the conversion is first-order kinetics. Both crystals must be identically heated at the same temperature.

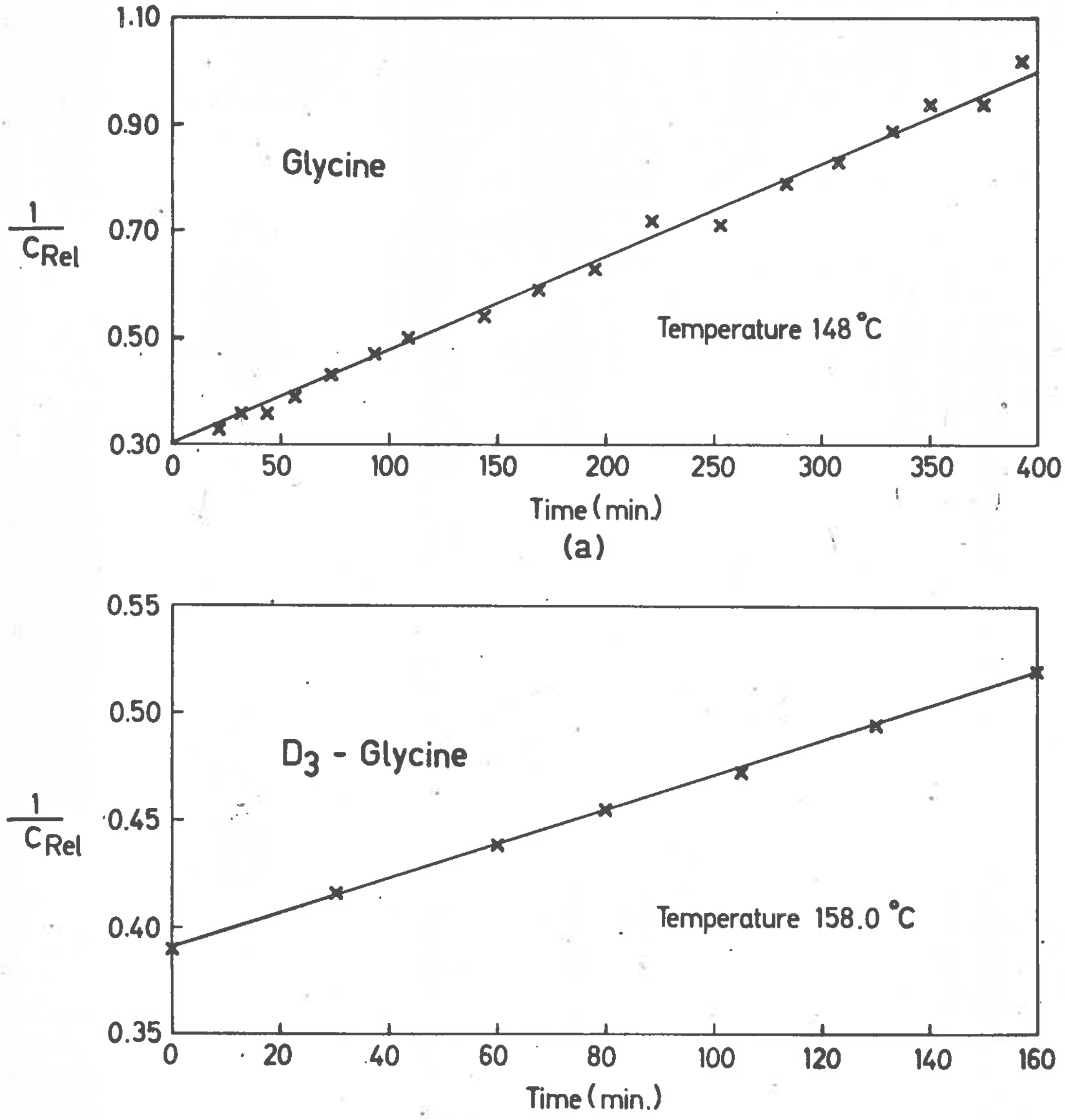
4.4.2 Results.

This section tabulates the results determined during the course of this project for reaction kinetics of free radical reactions in different irradiated crystals and selected deuterated crystals. These results will be discussed in Chapter 7 but some comment at this stage is needed to clarify some of the observations. The second-order reaction kinetics curves for radical destruction in each of the crystals listed in table 4.6 are shown in figs. 4.6 to 4.10. In the case of succinic acid kinetics were determined separately for the destruction of the two different radical species present. For glycine the two final radicals disappeared together and apparently obey second-order kinetics because of the near equality of the concentrations of the two radicals. An exception to free radical destruction obeying second-order kinetics is that exhibited by the radicals in N-acetylglycine. The 3 curves reproduced in fig. 4.11 clearly reveal that this reaction follows third-order kinetics. Fig. 4.12(a) shows third-order kinetics for radical destruction in deuterated acetylglycine. No reaction kinetics were determined for ketomalonic acid produced in irradiated malonic acid because of the physical appearance of the irradiated crystal above 75°C. At this temperature the crystal gradually became a hard, white powder and it was felt that no confidence could be attached to further measurements made on the system. For irradiated D_4-malonic acid the spectrum from each radical could not be sufficiently separated to check whether one radical disappeared without affecting the other radical. Thus kinetics were observed on the whole spectrum.

TABLE 4.6

A list of free radical destruction reactions studied to determine the kinetics of the reactions

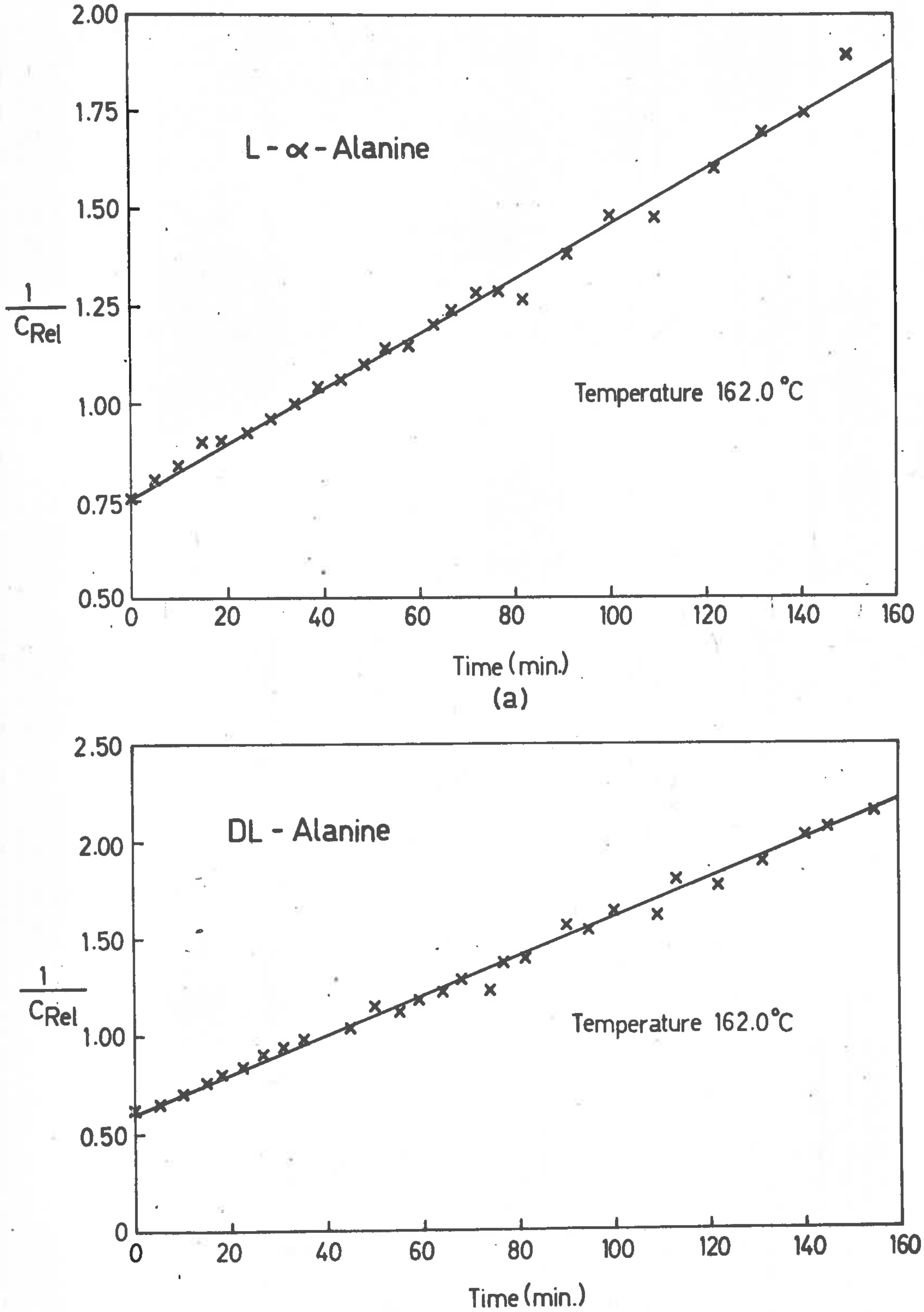
Compound	Formula	Radical(s)	Kinetics Determined	Reference
Glycine	$NH_3^+-CH_2-COO^-$	$NH_3^+-\dot{C}H-COO^-$ and unknown species	Apparently second-order (See Text)	Present work
D_3-glycine	$ND_3^+-CH_2-COO^-$	$R-CO\dot{O}$	Second-order	Present work
L-α-alanine	$CH_3-CH(NH_2)-COOH$	$CH_3-\dot{C}H-R$ (R=COOH or COO^-)	Second-order	Present work
dl-α-alanine	$CH_3-CH(NH_2)-COOH$	$CH_3-\dot{C}H-R$ (R=COOH or COO^-)	Second-order	Present work
Malonic acid	$HOOC-CH_2-COOH$	$\dot{C}H_2-COOH$	Second-order	Present work
		$HOOC-\dot{C}H-COOH$	Not determined (See Text)	Present work
D_4-Malonic Acid	$DOOC-CD_2-COOD$	Two unknown radicals	Second-order (See Text)	Present work
β-Succinic Acid	$HOOC-CH_2-CH_2-COOH$	$HOOC-CH_2-CH_2-CO\dot{O}$ (Radical A)	Second-order	Present work
		$HOOC-CH_2-\dot{C}H-COOH$ (Radical B)	Second-order	" "
D_2-Succinic Acid	$DOOC-CH_2-CH_2-COOD$	$DOOC-CH_2-CH_2-CO\dot{O}$	Second-order	Present work
		$DOOC-CH_2-\dot{C}H-COOD$	Second-order	" "
N-Acetylglycine	$H_3C-CO-NH-CH_2-COOH$	$H_3C-CO-NH-\dot{C}H-COOH$	Third-order	Present work
D_2-Acetylglycine	$H_3C-CO-ND-CH_2-COOD$	$H_3C-CO-ND-\dot{C}H-COOD$	Third-order	Present work
n-Octadecyl Disulphide (polycrystalline)	$C_{18}H_{37}-S-S-C_{18}H_{37}$	Alkyl Type Radical and RS· Type Radical	Second-order	Truby, MacCallum and Hesse (1962)


Glycine
Temperature 148 °C
1/C_Rel
1.10
0.90
0.70
0.50
0.30
0
50
100
150
200
250
300
350
400
Time (min.)
D3 - Glycine
Temperature 158.0 °C
0.55
0.50
0.45
0.40
0.35
0
20
40
60
80
100
120
140
160
Time (min.)

(a)

(b)

Fig. 4.6


L - α - Alanine
Temperature 162.0 °C
$\frac{1}{C_{Rel}}$
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0
20
40
60
80
100
120
140
160
Time (min.)
DL - Alanine
Temperature 162.0°C
$\frac{1}{C_{Rel}}$
2.50
2.00
1.50
1.00
0.50
0
0
20
40
60
80
100
120
140
160
Time (min.)

(a)

(b)

Fig. 4.7

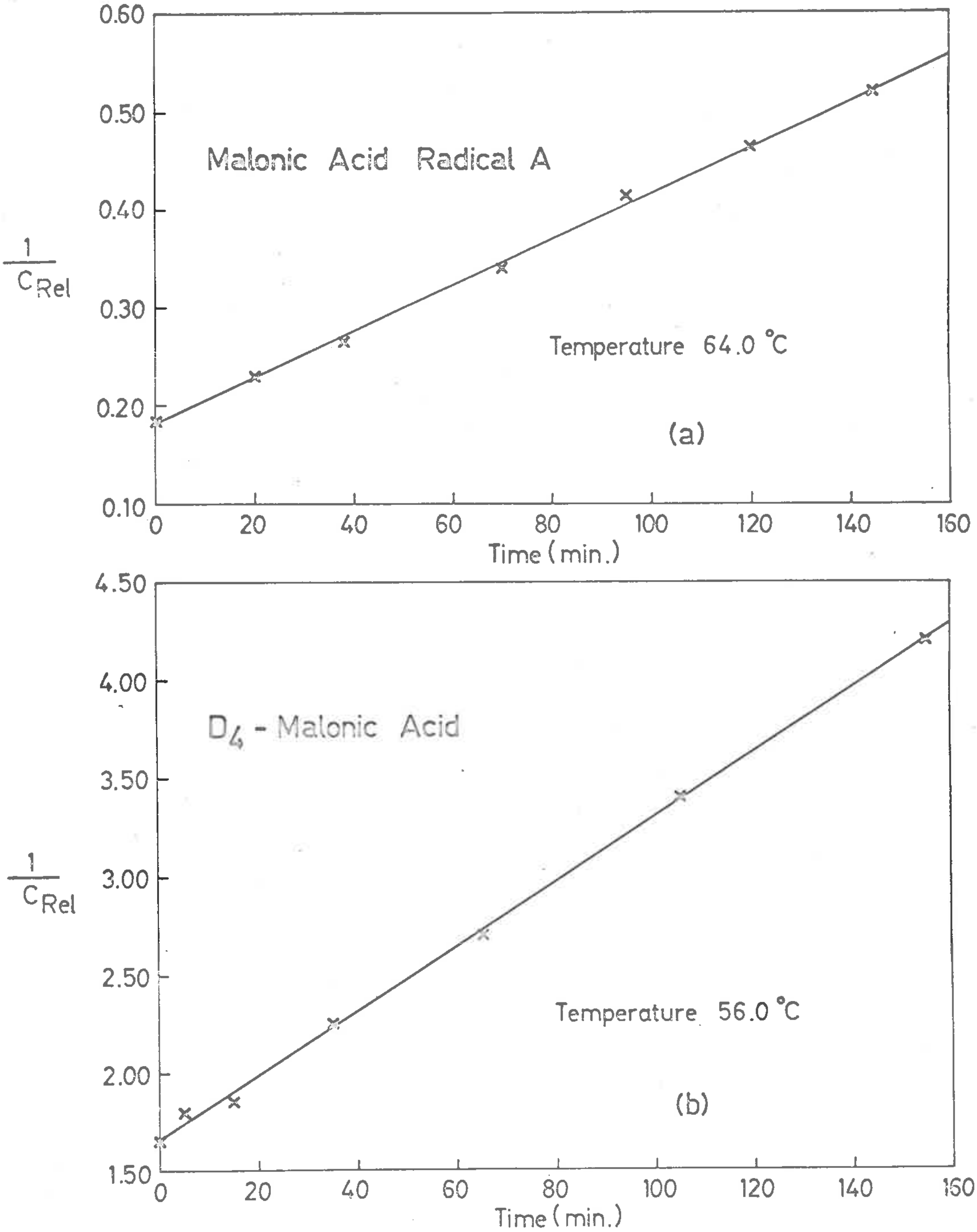
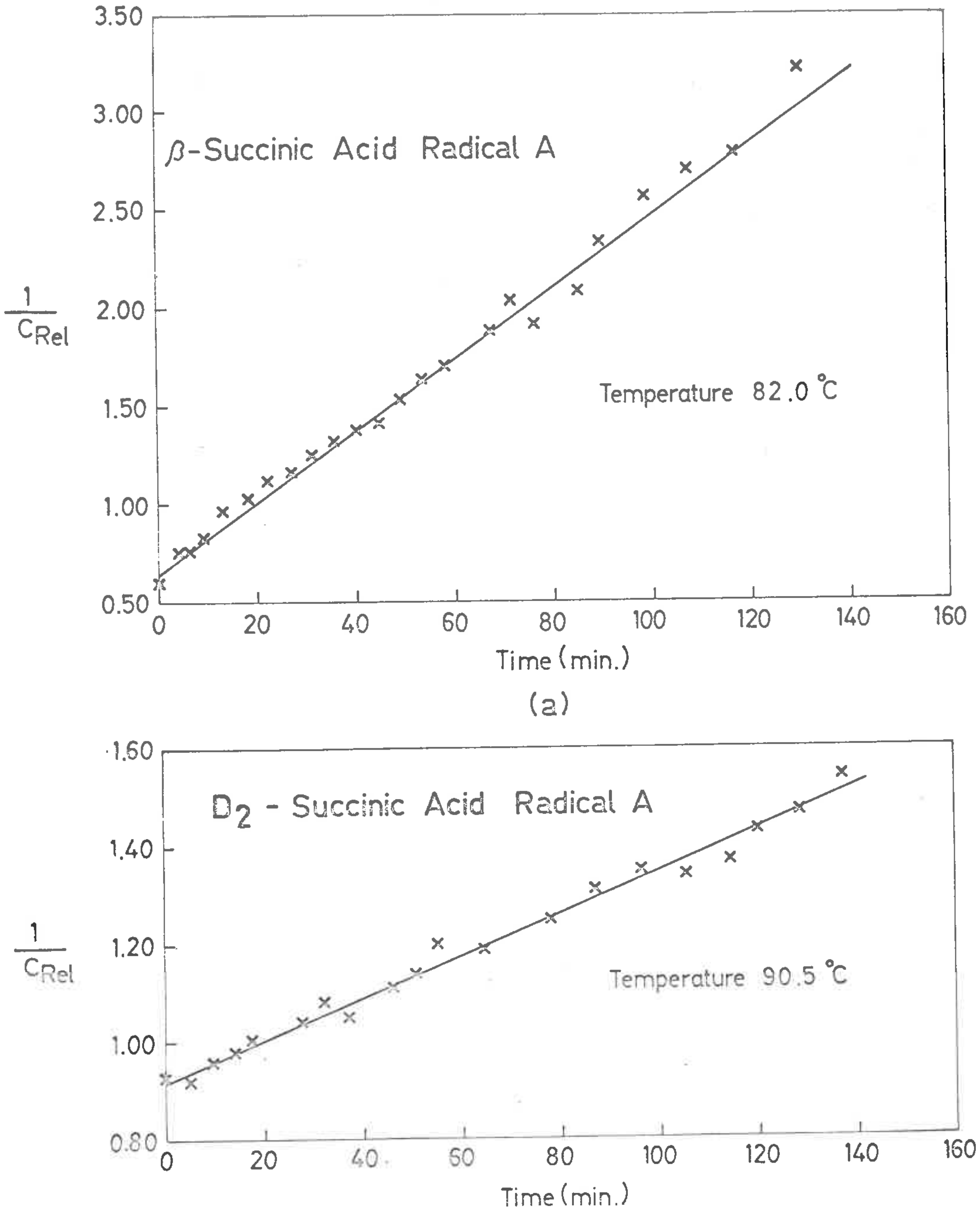

Malonic Acid Radical A
Temperature 64.0 °C
(a)
1/C_Rel
0.60
0.50
0.40
0.30
0.20
0.10
0
20
40
60
80
100
120
140
160
Time (min.)
D_4 - Malonic Acid
Temperature 56.0 °C
(b)
1/C_Rel
4.50
4.00
3.50
3.00
2.50
2.00
1.50
0
20
40
60
80
100
120
140
160
Time (min.)

Fig. 4.8

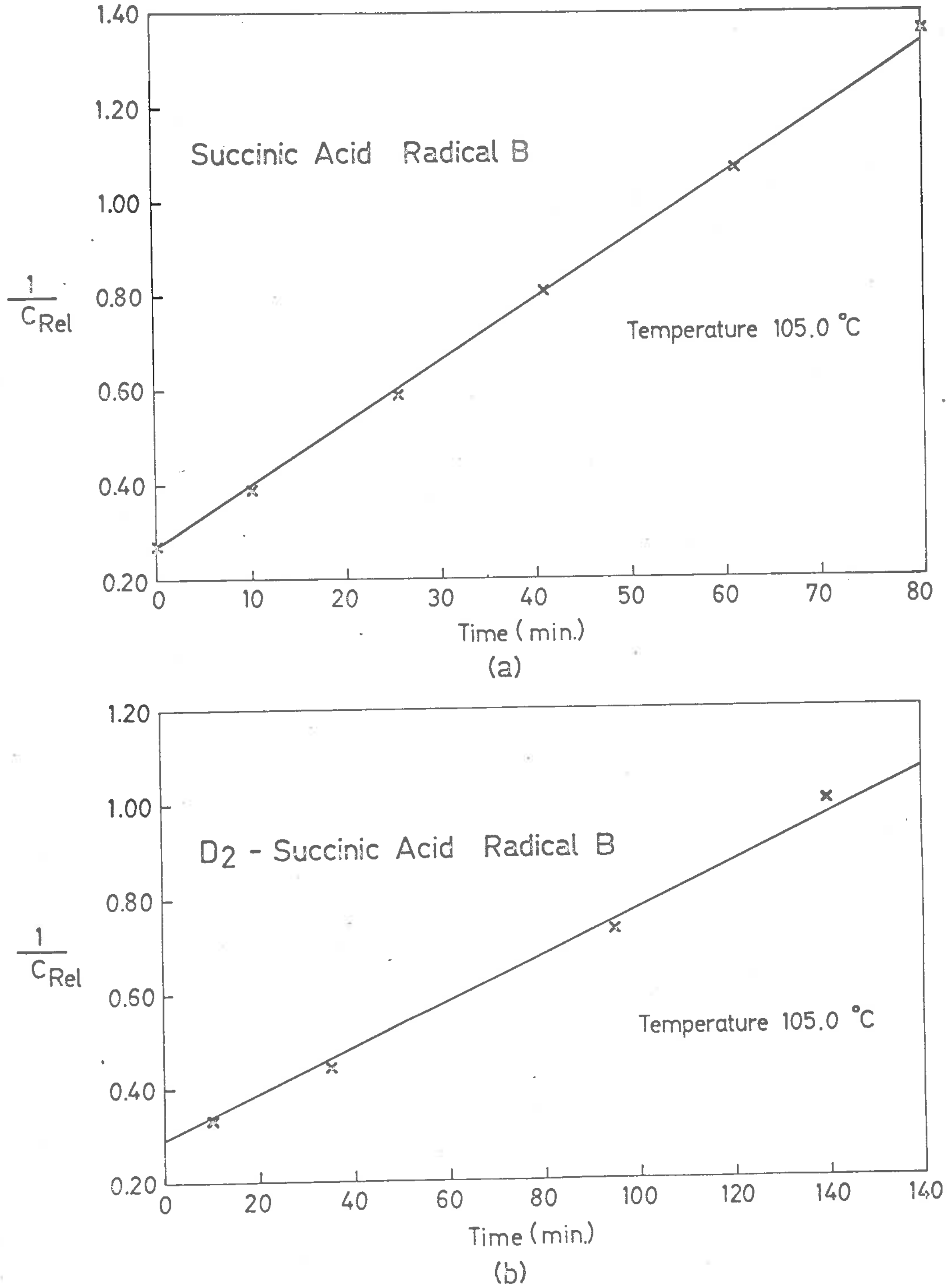


β-Succinic Acid Radical A
Temperature 82.0 °C
$\frac{1}{C_{Rel}}$
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0
20
40
60
80
100
120
140
160
Time (min.)
D₂ - Succinic Acid Radical A
Temperature 90.5 °C
$\frac{1}{C_{Rel}}$
1.60
1.40
1.20
1.00
0.80
0
20
40
60
80
100
120
140
160
Time (min.)

(a)

(b)

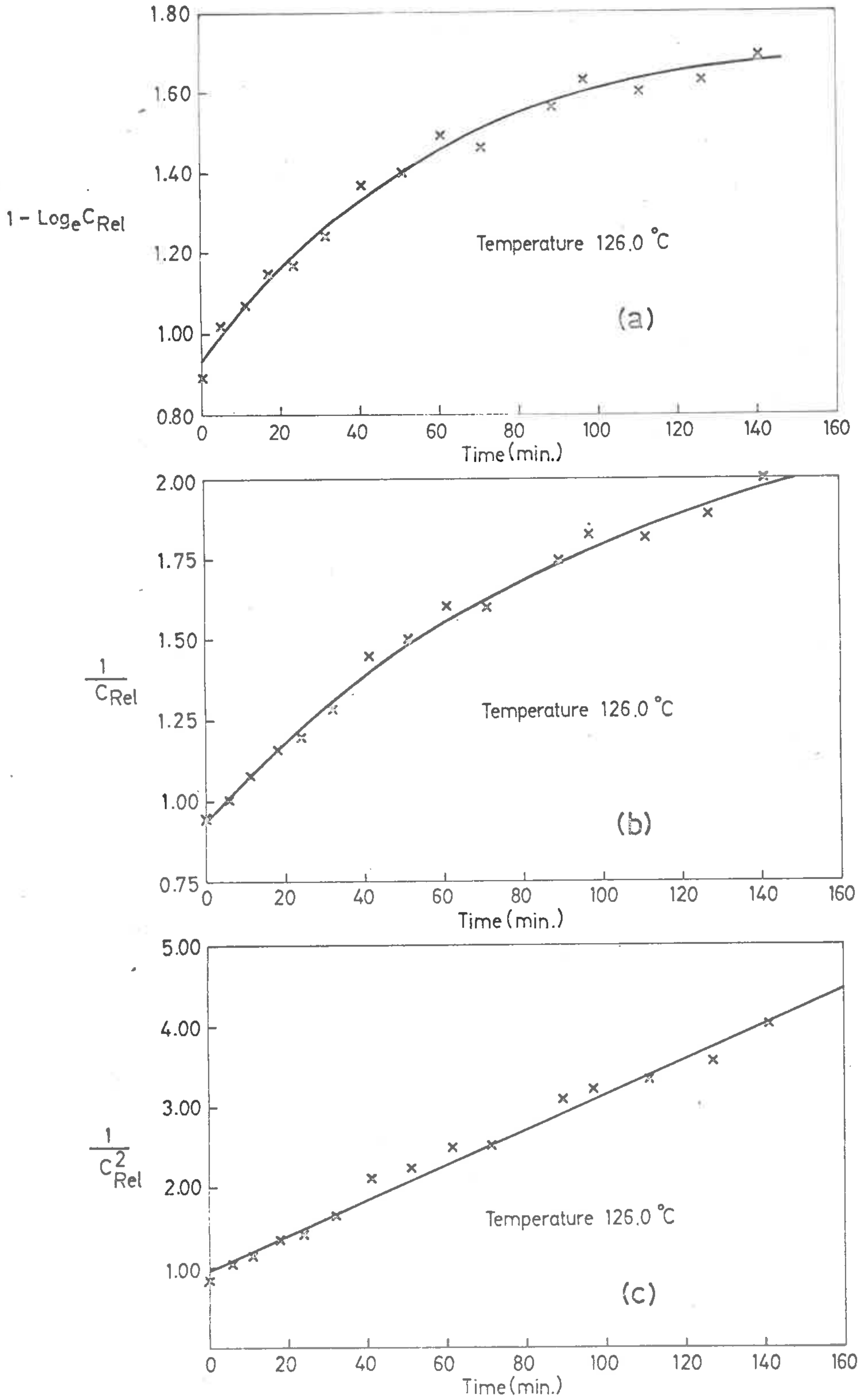
Fig. 4.9


1.40
1.20
1.00
0.80
0.60
0.40
0.20
$\frac{1}{C_{Rel}}$
Succinic Acid Radical B
Temperature 105.0 °C
0
10
20
30
40
50
60
70
80
Time (min.)
1.20
1.00
0.80
0.60
0.40
0.20
$\frac{1}{C_{Rel}}$
D_2 - Succinic Acid Radical B
Temperature 105.0 °C
0
20
40
60
80
100
120
140
140
Time (min.)

(a)

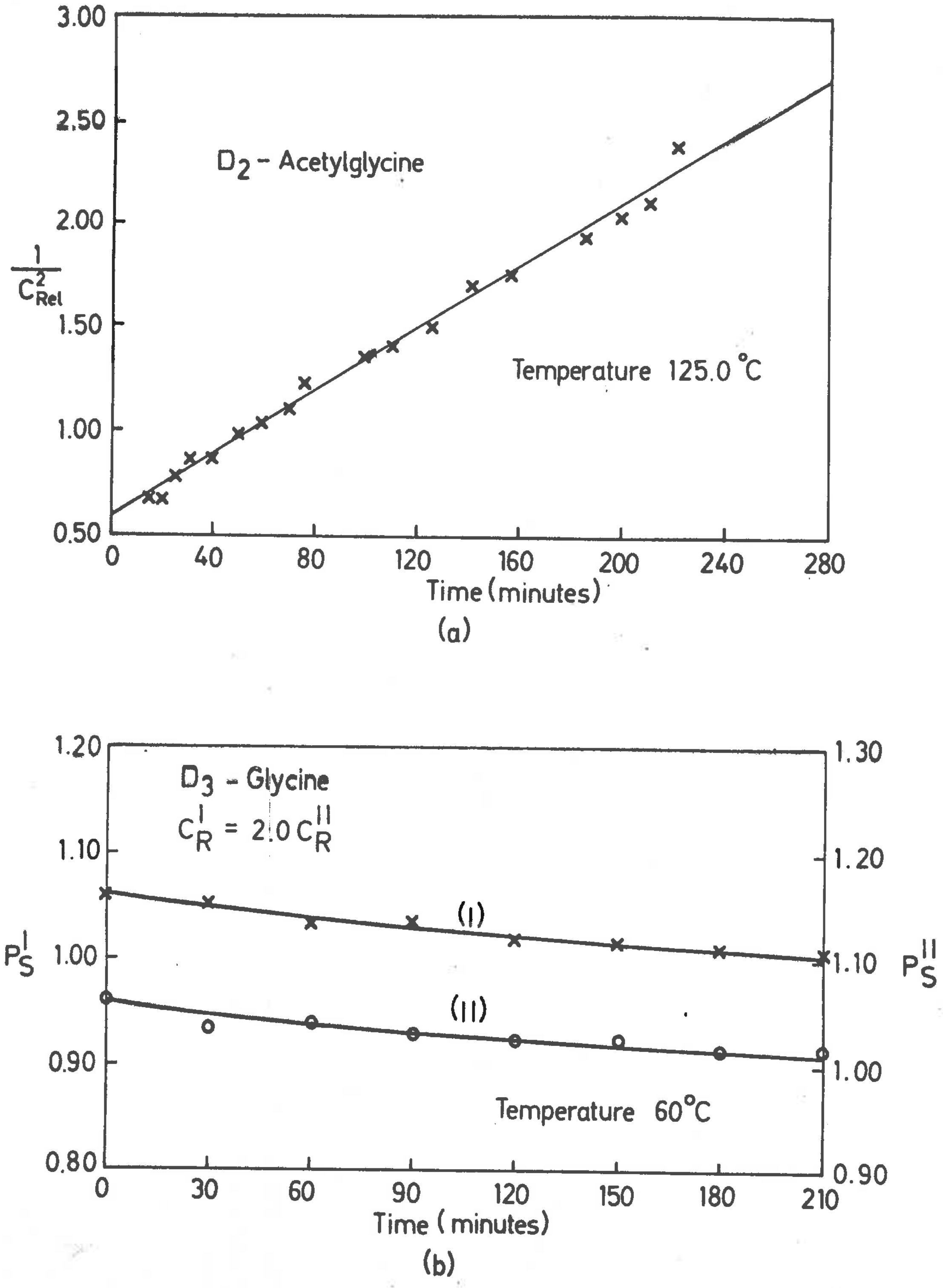
(b)

Fig.4.10



Acetylglycine

Fig.4.11


D2 - Acetylglycine
Temperature 125.0 °C
1/C²Rel
3.00
2.50
2.00
1.50
1.00
0.50
0
40
80
120
160
200
240
280
Time (minutes)
D3 - Glycine
CᴵR = 2.0 CᴵᴵR
(I)
(II)
Temperature 60°C
Pᴵs
Pᴵᴵs
1.20
1.10
1.00
0.90
0.80
1.30
1.20
1.10
1.00
0.90
0
30
60
90
120
150
180
210
Time (minutes)

(a)

(b)

Fig 4.12

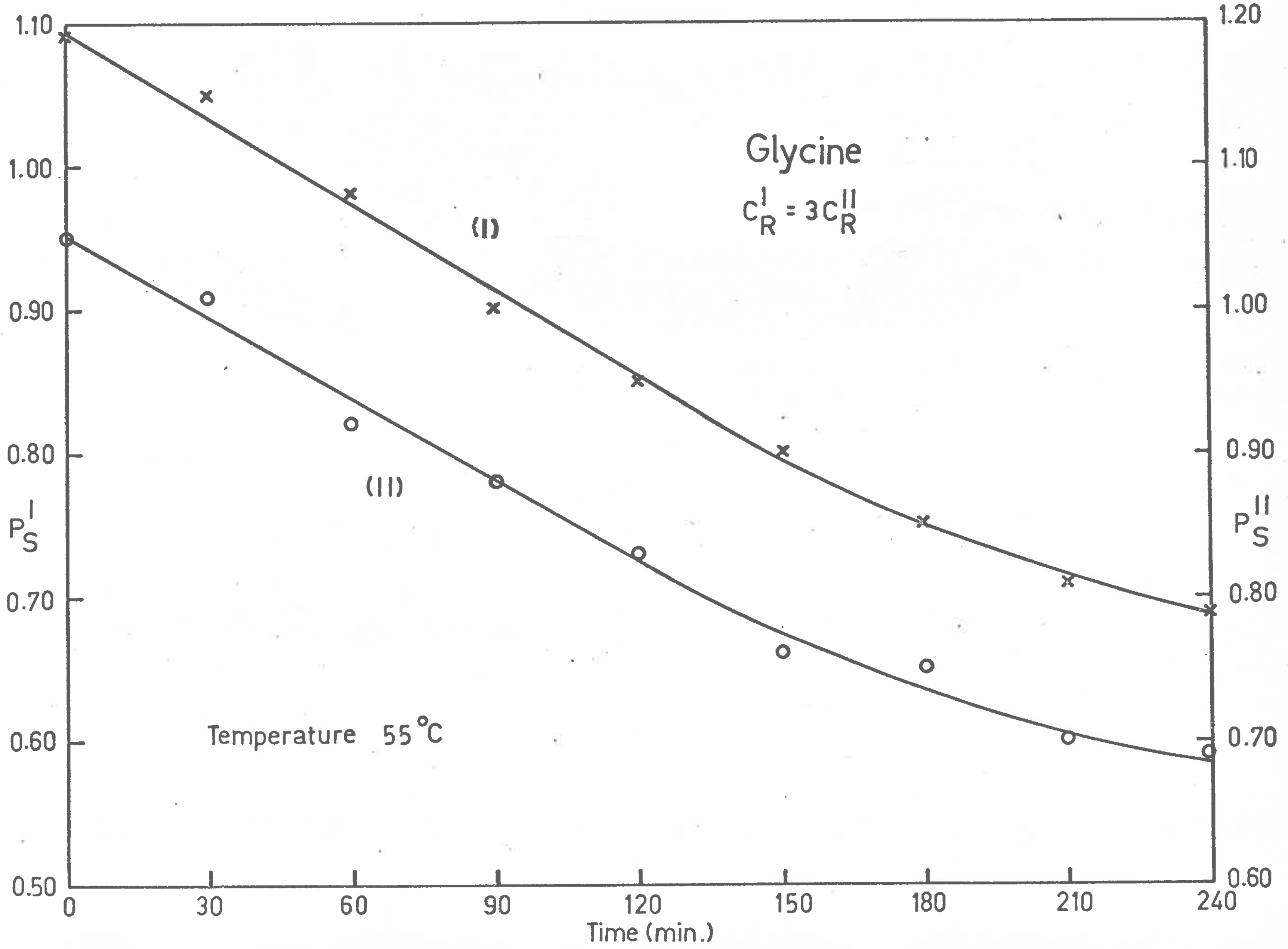

1.10
1.00
0.90
0.80
0.70
0.60
0.50
P_S^I
1.20
1.10
1.00
0.90
0.80
0.70
0.60
P_S^{II}
Glycine
$C_R^I = 3C_R^{II}$
(I)
(II)
Temperature 55 °C
0
30
60
90
120
150
180
210
240
Time (min.)

Fig. 4.13

The kinetics observed for free radical conversions in glycine and D_3-glycine are listed in table 4.7. Also included are the kinetics recently reported for the conversion in irradiated dihydrothymine. Earlier in this chapter a new method was described for determining the kinetics of a free radical conversion where the spectrum from each radical could not be separated easily.

TABLE 4.7

Reaction kinetics observed for 3 radical conversions.

Compound	Radicals Involved in the Conversion	Kinetics Determined	Reference
Glycine	$\dot{C}H_2-COO^- \rightarrow$ Unknown	First-order	Present Work
D_3-glycine	$\dot{C}D_2-COO^- \rightarrow R-COO^{\cdot}$	First-order	Present Work
Dihydrothymine	$\dot{C}_6 \rightarrow \dot{C}_5$	First-order	Bernhard and Snipes (1967).

In this case a number of measurements representing the shape of the spectrum were taken. The heights of various lines in the spectrum were measured from a baseline. The ratio of two heights from opposite sides of the baseline were then calculated. This procedure was repeated with the other heights to obtain different ratios while the same ratios were calculated for the spectrum from the other crystal which contained n times the number of radicals. In this way one could represent the shape of the ESR spectrum from each crystal. Now the two crystals were heated together such that both spectra altered only a small amount and the same measurements were made on the new spectra. These heatings were repeated in equal intervals until the conversion was complete. The ratios calculated from the two spectra after each heating were each plotted as a function of time. If two curves representing corresponding ratios from each spectrum of the two crystals are compared and are essentially the same then it can be said that the shape of the spectrum from the two crystals has not altered. Such a pair of curves from two crystals of glycine of the same weight where one crystal had three times the number of radicals as the other, initially, is shown in fig. 4.13. Similarly, a pair of curves for deuterated glycine are given in fig. 4.12(b) where the difference in initial concentration was a factor of two. The comparison of the two curves is helped by the fact that they are linear in the early stages of the conversion as a result of small changes involved if the conversion rate is slow. Any small error that may be present in the two corresponding ratios for the two initial spectra arises from the positioning of the baseline that is drawn in, and the initial mounting of the two crystals in the cavities with respect to the static magnetic field.

As has already been mentioned in section 4.3.2 the negligible effect of radiation induced impurities on the free radical conversion rate was confirmed from these kinetics experiments. As one crystal was irradiated for three times as long as the other this crystal had three times as much secondary damage and as the data were consistent with first-order kinetics with no change in rate constant, this indicates that secondary damage has little effect on the rate of conversion. This is perfectly understandable for a unimolecular reaction as was pointed out earlier.

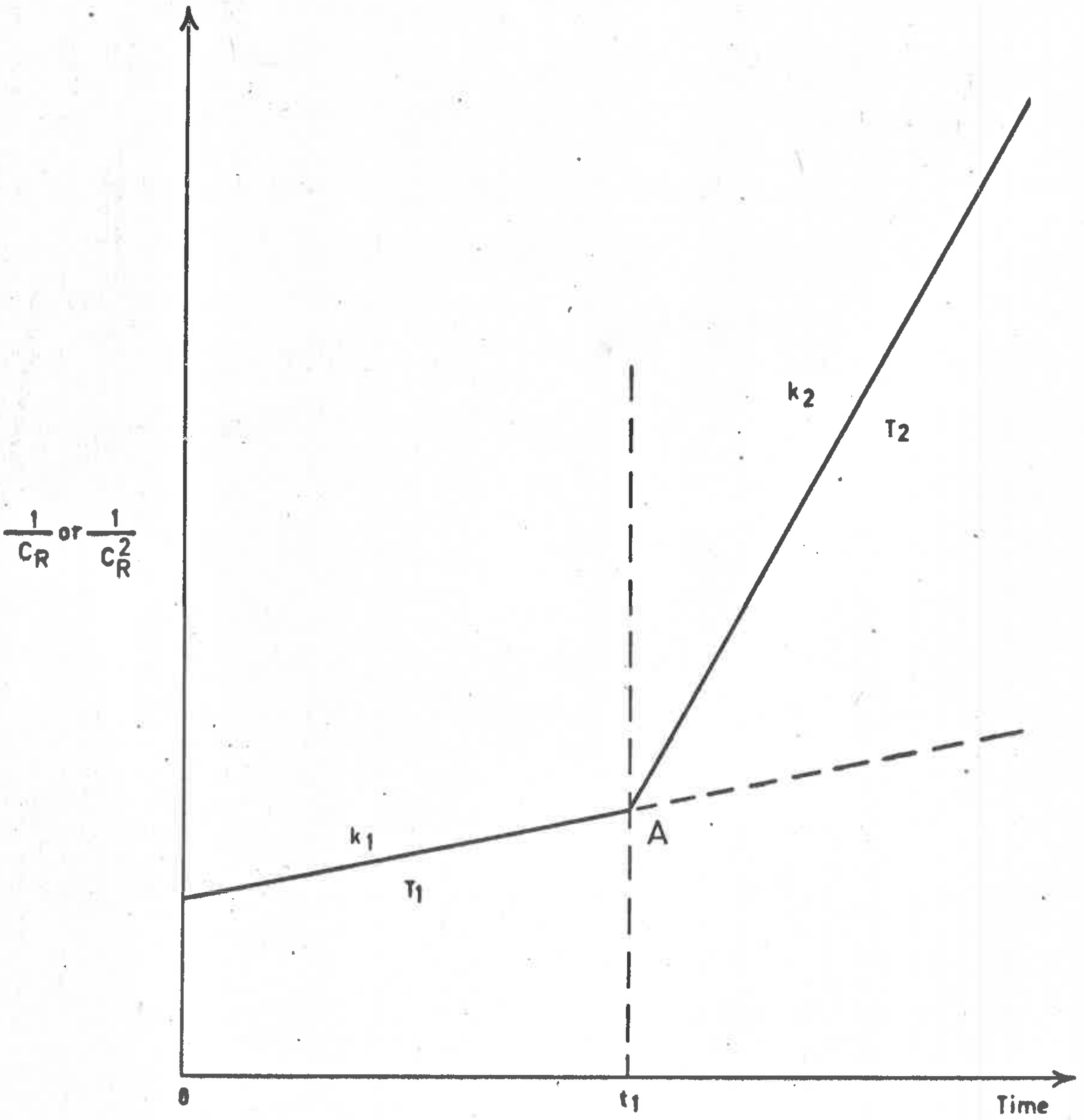
4.5 Activation Energy of the Free Radical Reaction

As it has been established that free radical reactions obey the familiar laws of reaction kinetics very well, one can expect to go further and determine an activation energy associated with the reactions since the well known Arrhenius equation can be applied to determine this energy. A knowledge of the activation energy for this type of reaction will be useful for comparing with activation energies that one hopes will be determined for molecular diffusion in organic crystals. These are available, in some cases, from experiments involving nuclear magnetic resonance (Andrew, 1954) and radioisotope tracer studies. In particular self diffusion in cyclohexane (Hood and Sherwood, 1966) and anthracene (Lee et al, 1965; Sherwood and Thomson, 1960) have been studied using C^{14} as a tracer.

4.5.1 Methods of Determining Activation Energies

A knowledge of the reaction order enables one to determine the activation energy of the reaction by measuring the rate constant as a function of T. In the present situation this involves using a number of matched single crystals all uniformly irradiated so that each contains the same number of free radicals and heating them separately under identical conditions except for the temperature. Each successive crystal is heated at a higher temperature such that the reaction rate is about 10% faster than for the previous crystal. The lowest temperature used must not be too low otherwise the rate becomes very slow and the reaction has to be followed a long time. The highest temperature also should not be so high that the reaction will be too fast. Now having obtained the free radical reaction rates, denoted as k, from the slopes of the curves for different temperatures one is in a position to plot a curve of $\log_e k$ as a function of $^1/_T$ where T is the absolute temperature. The slope of this curve will yield $\frac{E\alpha}{R}$ and so the activation energy $E\alpha$ in calories per mole. can be calculated.

An alternative method uses only one crystal which is a great advantage. The rate constant for free radical destruction is quite reproducible from crystal to crystal yet even small variations are encountered. In this method, a rate constant k_1 can be determined if the crystal is heated at a temperature T_1 over



Determining Activation Energy

Fig. 4.14

a period of time. Now if the temperature is quickly raised to a new point T_2 at a time t_1 the rate constant will be increased to k_2. The reaction curve for a crystal heated in this way will resemble that shown in fig. 4.14. If one extends the first linear segment of the curve past t_1 (shown as a dashed line) it can be seen that the two lines now originating from A effectively represent reaction curves for two samples of radicals, whose initial concentrations are the same, reacting at two different temperatures. If one now plots $\log_e k$ as a function of $^1/_T$ and a line is drawn through the two points then the activation energy can be determined from the slope.

4.5.2 Results

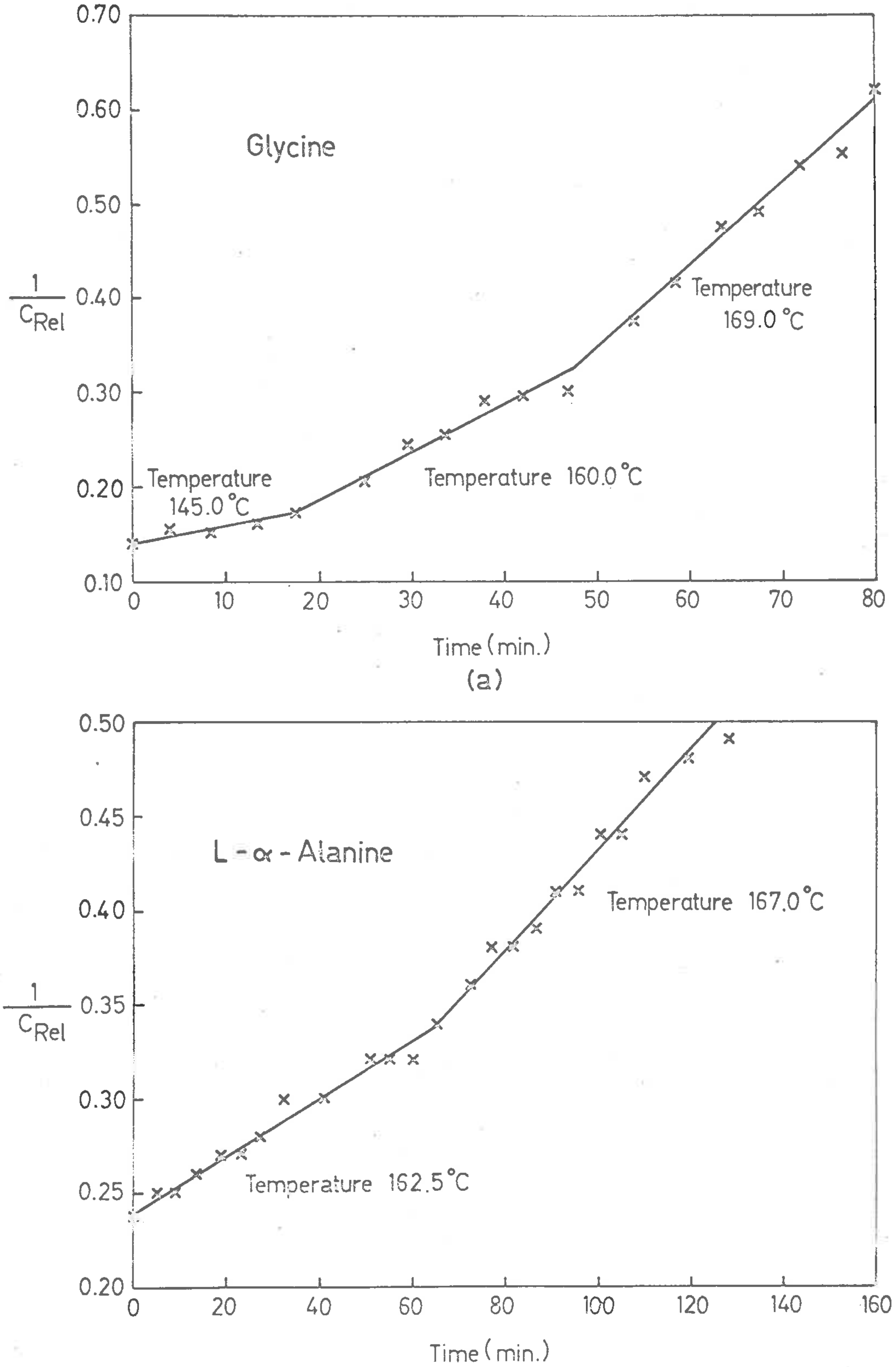
The activation energies were determined for eight free radical reactions using the second method. These experiments were conveniently done using the high temperature cavity where the time to raise the cavity temperature from T_1 to T_2 was about three minutes. This method was accurate and much simpler than the alternative method which was tried on one free radical reaction (glycine) with little success. As it was necessary to have five or six crystals, containing equal concentrations of free radicals, so that rate constants can be determined for six different temperatures a problem arose in finding a suitable temperature range. With the free radical destruction in glycine, the reaction rate was very slow at the lower temperature (150°C) requiring a long time to follow the reaction to determine the rate constant accurately while at the high temperature end (165°C) the reaction rate was too fast to trace for any sufficient time. Thus six points on the $\log_e k$ as a function of $^1/_T$ curve could not be suitably spaced over a wide enough temperature range. In view of this the second method was used exclusively.

TABLE 4.8

A list of activation energies determined for free radical reactions.

Compound	Radical	Activation Energy (eV)	Reference
Glycine	$NH_3^+-\dot{C}H-COO^-$ and Unknown	1.0	Present work
D_3-glycine	$R-COO^{\bullet}$	0.5	Present work
L-α-alanine	$CH_3-\dot{C}H-R$	2.1	Present work
Malonic Acid	$\dot{C}H_2-COOH$	2.7	Present work
Succinic Acid	$HOOC-CH_2-CH_2-COO^{\bullet}$	1.0	Present work
	$HOOC-\dot{C}H-CH_2-COOH$	2.3	Present work
N-acetylglycine	$H_3C-CO-NH-\dot{C}H-COOH$	2.6	Present work
Dihydrothymine	$\dot{C}_6 \rightarrow \dot{C}_5$ (conversion)	1.0	Bernhard and Snipes (1967)

The activation energies are listed in table 4.8 with values ranging from 0.5 eV to 2.7 eV. Fig. 4.15(a) and (b) show typical reaction curves for glycine and L-α-alanine from which the activation energies were calculated. In the case of glycine three rates were determined from the one crystal giving values of the activation energy of the free radical destruction as 1.1 eV and 1.0 eV. The experimental error associated with the activation energies listed in the table depends on the accuracy of determining the two slopes of the reaction curve which is the largest error involved in the estimation. A careful judgement of what is involved leads the author to estimate that the standard error of the activation energy is of the order of 10%. This is borne out by an examination of the reproducibility of these energies in repeated experiments which show that the energy is repeatable to within 10%.


0.70
0.60
0.50
0.40
0.30
0.20
0.10
$\frac{1}{C_{Rel}}$
Glycine
Temperature 145.0 °C
Temperature 160.0 °C
Temperature 169.0 °C
0
10
20
30
40
50
60
70
80
Time (min.)
0.50
0.45
0.40
0.35
0.30
0.25
0.20
$\frac{1}{C_{Rel}}$
L - α - Alanine
Temperature 162.5 °C
Temperature 167.0 °C
0
20
40
60
80
100
120
140
160
Time (min.)

(a)

(b)

Fig. 4.15

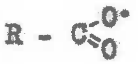
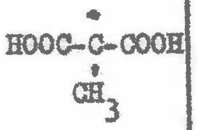
4.6 Other Aspects of Free Radical Reactions

In this section it is proposed to examine some other aspects of free radical reactions. A review of all conversion reactions reported to date is included with particular attention being paid to the nature of the phenomena involved and whether they conform to the general predictions of the kenon hypothesis. Further one also needs to examine the order of annealing of radicals in a particular crystal when more than one radical species is present. As it was outlined in Chapter 2 the behaviour of radicals in this situation provides evidence verifying some of the predictions arising from the model. The first reactions to be considered are conversion reactions.

All conversion reactions known to date in compounds irradiated at LNT or room temperature are listed in table 4.9. This table also lists the class of radicals involved in each compound and one can see that in all cases except one, the primary radical involved is an I-radical which is in agreement with the hypothesis. The conversion reaction in dihydrothymine is consistent with the hypothesis and appears to be a metastable conversion of the radical state. In the present work only two conversion reactions were examined, viz. glycine and deuterated glycine. The transformation observed in D_3-glycine at 60°C is shown in figs. 4.17(b) and (c). Fig. 4.17(b) shows the ESR spectrum for a freshly irradiated crystal when the static magnetic field is parallel to the C-axis while fig. 4.17(c) shows the final spectrum seen for the same orientation after the conversion is complete. Several workers have reported alterations in the ESR spectrum of ordinary glycine and it would be appropriate at this stage to review this work on glycine in respect of the appearance of the new radical after ageing. Ehrenberg, Ehrenberg and Zimmer (1957) were the first to mention the unusual

TABLE 4.9

A List and Classification of Conversion Reactions

Compound	Initial Radical	Final Radical	Type of Conversion Between Groups	Temperature of Conversion Reaction	Reference
Glycine $(NH_3^+CH_2COO^-)$	$\dot{C}H_2-COO^-$	Unknown species	I → Unknown	50°C	Present work and Simmons (1966)
D_3-glycine $(ND_3{}^+CH_2COO^-)$	$\dot{C}D_2-COO^-$	 $R - C\genfrac{}{}{0pt}{}{O^{\cdot}}{O}$	I → H	60°C	Present work
Dihydrothymine	$\dot{C}_6$	$\dot{C}_5$	H → H'	120°C	Bernhard and Snipes (1967)
Monofluoroacetamide (CH_2FCONH_2)	$\dot{C}H_2-CO-NH_2$	$\dot{C}HF-CO-NH_2$	I → H	-70°C	Iwasaki and Toriyama (1967)
Glycollic Acid $(HO-CH_2-COOH)$	$\dot{C}H_2-COOH$	$HO-\dot{C}H-COOH$	I → H	-100°C	Hawke and Rawson (1965)
Methyl Malonic Acid $(COOH-CH(CH_3)-COOH)$	$CH_3-\dot{C}H-COOH$	 $HOOC-\underset{CH_3}{\overset{\bullet}{C}}-COOH$	I → H	50°C	Cole and Heller (1965)

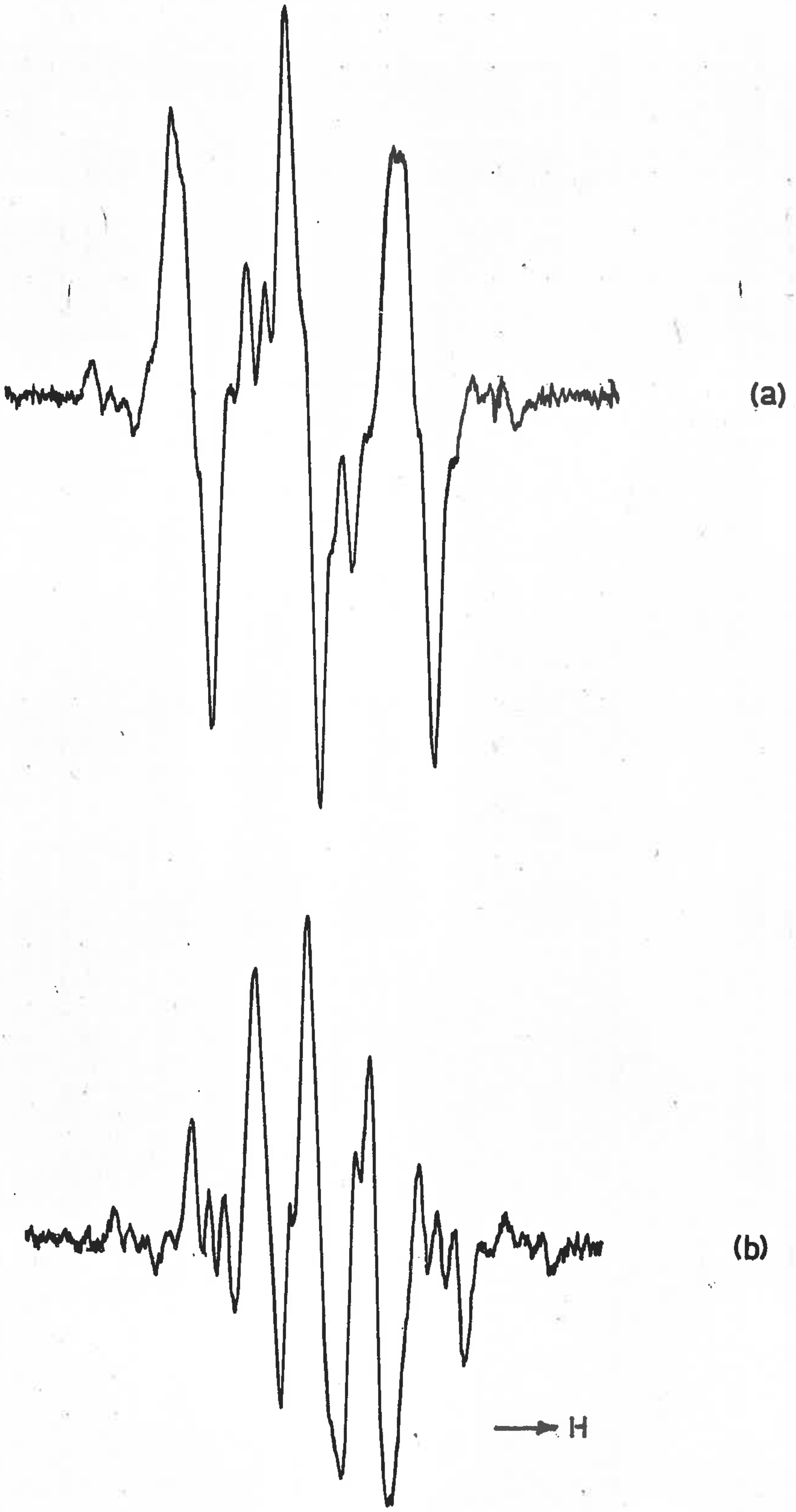


Fig. 4.16 E.S.R. Spectra of Irradiated Glycine.

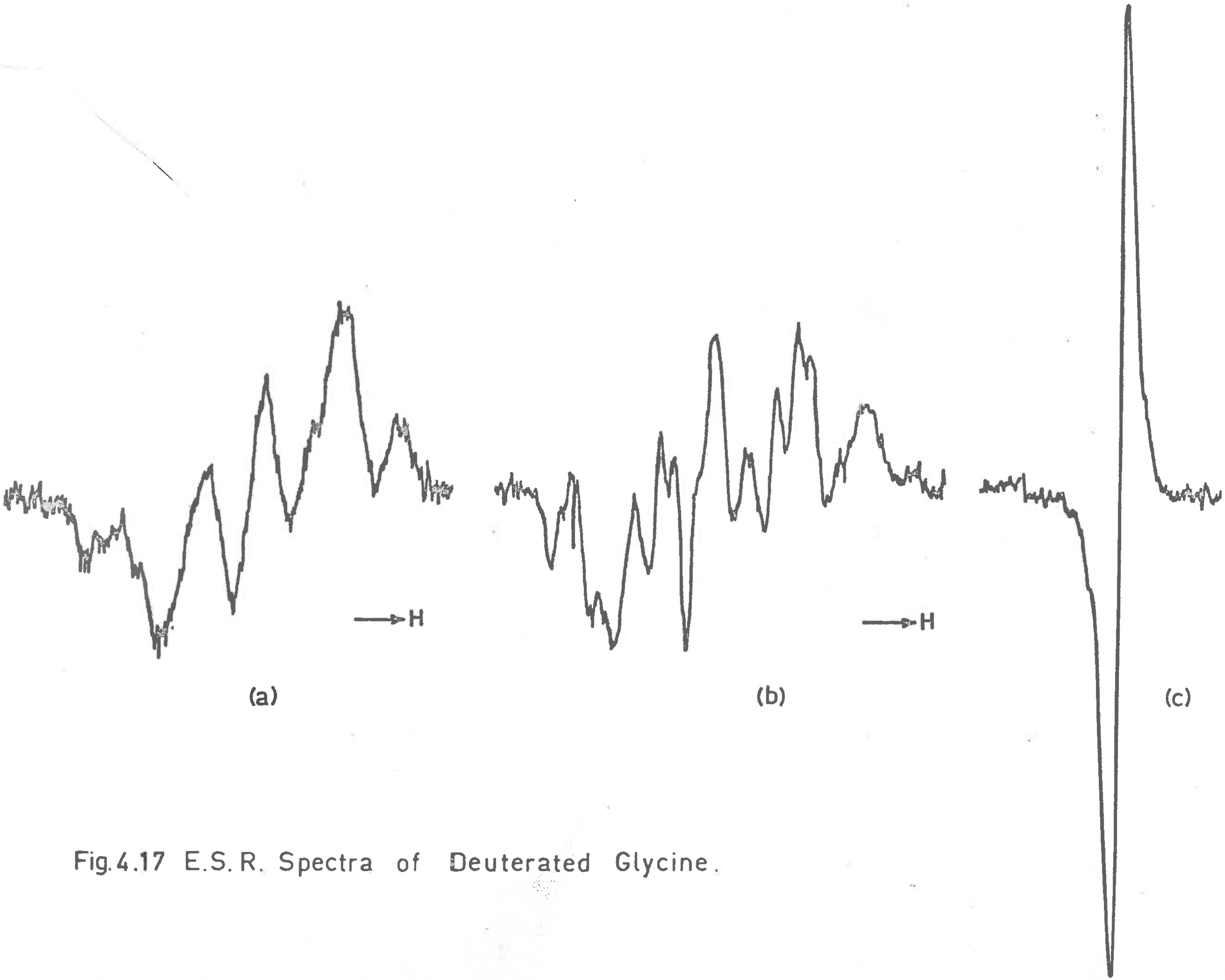


Fig. 4.17 E.S.R. Spectra of Deuterated Glycine.

behaviour of the glycine spectrum when the crystal aged. They found that the area under the ESR absorption curve remained essentially constant indicating that the number of radicals remained the same. Ghosh and Whiffen (1960) were the first to report that a new species existed in glycine if left at room temperature for several weeks. In 1964, Morton established that the two radicals produced in freshly irradiated glycine at room temperature were kenoglycine and kenoacetic acid. This removed the conflicting interpretations as to the identity of the two initial radicals proposed by Ghosh and Whiffen (1959) and Koski and Weiner (1963). Simmons (1966) also reported that an unidentified radical appeared in glycine at the same time kenoacetic acid disappeared when the crystal aged. During this change kenoglycine remained essentially unaltered in concentration. In the present work the spectrum from a freshly irradiated crystal of glycine was carefully observed when annealed at 50°C. This observation of the spectrum led to the conclusion that kenoacetic acid is transformed into an unknown radical while kenoglycine remained essentially unaltered in any way. Fig. 4.16(a) shows the ESR spectrum of freshly irradiated glycine when the static magnetic field is parallel to the C-axis and fig. 4.16(b) shows the final spectrum for the same orientation after the conversion reaction is finished. The outer lines of both of these spectra show that the spectrum due to kenoglycine is the same in intensity. Thus two radicals were clearly present at the end of the conversion. This was also checked by examining the ESR spectrum under the usual conditions where power saturation was not present and when saturation is present. The latter spectrum was significantly altered in shape to reveal that two different radical species must be present with different spin-lattice relaxation times. (This technique of altering the microwave power was also used to check that two radical species were present in irradiated succinic acid). These observations on glycine now show that kenoacetic acid (an I-radical) transforms into an unknown radical while kenoglycine (an H-radical) remains unaltered. This radical behaviour in glycine is consistent with the ideas of the hypothesis.

Turning now to the final aspect on free radical reactions, viz. the order of annealing of radicals in a crystal, one finds that only vague reports have been made to date about these reactions. In malonic acid it was reported by McConnell et al (1960) that one radical species could be annealed out in the presence of the other species. In this work four compounds were examined for this radical behaviour and all the results are listed in table 4.10. These results will be discussed in the last chapter but some comment will be made to clarify the observations.

TABLE 4.10

A list of I- and H- radical reactions

Compound	First Radical to Disappear	Radical Remaining
Glycine	Kenoaminoacetic acid disappears with the unknown radical	
Malonic Acid	Kenoacetic Acid (an I-radical)	Kenomalonic Acid (an H- radical)
Succinic Acid	β-kenoxycarbonylpropionic Acid (an H-radical)	Kenosuccinic Acid (an H- radical)
Methylmalonamide	Methylkenomalonamide (an H- radical)	α-kenopropionamide (an I- radical)

In glycine the end result of the conversion reaction was again two radicals. Now when a glycine crystal at this stage was annealed at 150°C both radicals disappeared at the same time which suggested that they were destroying each other. This reaction proceeded until a small fraction of the unknown radical was left over. Ghosh and Whiffen (1960) also reported a stable, unknown radical in glycine at 160°C.

The behaviour of the ESR spectrum of methylmalonamide at 150°C revealed that methylkenomalonamide (an H-radical) disappeared without affecting the concentration of α-kenopropionamide (an I-radical).

The results for free radical destruction in irradiated succinic acid presented a different situation. At 80°C β-kenoxycarbonyl propionic acid disappeared without significantly affecting the concentration of kenosuccinic acid. The small decrease is probably due to kenosuccinic acid beginning to recombine at this temperature. Both of these radicals are H-radicals. Fig. 4.1(b) and (c) show the ESR spectrum for succinic acid freshly irradiated, and after β-kenoxycarbonyl propionic acid had been removed, respectively.

In the last case examined, malonic acid, the behaviour of the two different radicals, kenomalonic acid and kenoacetic acid, was a little more difficult to observe. In contrast to succinic acid the spectra from the two radical overlapped each other considerably. However, careful observation revealed that kenoacetic acid disappeared before kenomalonic acid.

After taking a brief look at the results given above one can see that they are in general agreement with the hypothesis; malonic acid may be an exception in this instance alone as one observes the disappearance of an I-radical without the reduction of the concentration of the H-radical.

CHAPTER 5

ISOTOPIC PHENOMENA

5.1 Introduction

This chapter reports experimental investigations of the predictions of the kenon hypothesis in connection with isotopically substituted phenomena. The first part of the chapter looks at the possible involvement of the deuterium atom in the rate determining step for free radical destruction and in the conversion reactions of free radicals. The remaining portion of the chapter examines the results of experiments related to isotopic mixing in free radicals produced in partially deuterated crystals. In particular, the discovery of gross isotopic mixing involving a large fraction of the molecules in OO' - dideuterosuccinic acid is reported.

5.2 Kinetic Isotope Effect and the Free Radical Reaction Rate

The hypothesis is that free radicals are able to migrate through the crystal lattice by the transfer of hydrogen atoms. If a deuterium atom replaces the hydrogen atom in this transfer an isotope effect will occur on the radical state migration. Therefore, the rate of free radical destruction would be changed too if the mobility of the free radical is what limits the reaction rate. The theory of the isotope effect will be briefly summarised. Consider for example a C-H bond in the hydrogen atom involved in the transfer of the radical state. The zero point energy associated with this bond for an equilibrium state is 8.3 kcal. per mole (Wiberg, 1964). If a deuterium atom replaces the hydrogen atom in this particular bond the zero point energy is about 6.0 kcal. per mole since the vibrational frequencies are altered due to the larger (reduced) mass

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of the vibrational system. Thus a difference of 2.3 kcal. per mole is expected between the dissociation energies for bonds to hydrogen and deuterium. This assumes that the C-H or C-D bond is completely broken in the activated state and no new bond to the hydrogen or deuterium is formed, that is, the stretching and bending vibrational frequencies have gone to zero in this state. Therefore there will be no contribution from the zero point energy arising from the hydrogen or deuterium in this activated state. The rate ratio for the two reactions under these conditions at 400°K will be approximately

$$K_H/K_D = \exp\left(\frac{2300}{1.99 \times 400}\right) = 20$$

This situation is shown in an energy diagram in figure 5.1. However, bond breaking and bond making to hydrogen or deuterium will occur simultaneously. As a result the zero point energy of the deuterium atom in the activated complex will be reduced again due to the larger (reduced) mass. Thus the height of the barrier which the deuterium atom has to overcome when forming the activated complex is less than in the situation where bond forming is not occuring at the same time. This results in a reduction of the isotope effect. The ratio K_H/K_D at 400°K now lies in the range of 5 to 7 (Wiberg, 1955). Thus if a deuterium atom is involved in the radical state transfer the free radical destruction rate will also be slower by this factor if the migration of the radical is the rate determining process. Although the effect on the rate constant in free radical destruction is measurable the same does not apply to the activation energy of the reaction. The differences in energies for reactions which are controlled by a hydrogen or deuterium atom are small. If $K_H/K_D = 5$ at $T = 400$°K then $\Delta E = 1.5$ kcal. per mole or 0.06 eV. Now as a typical activation energy for free radical

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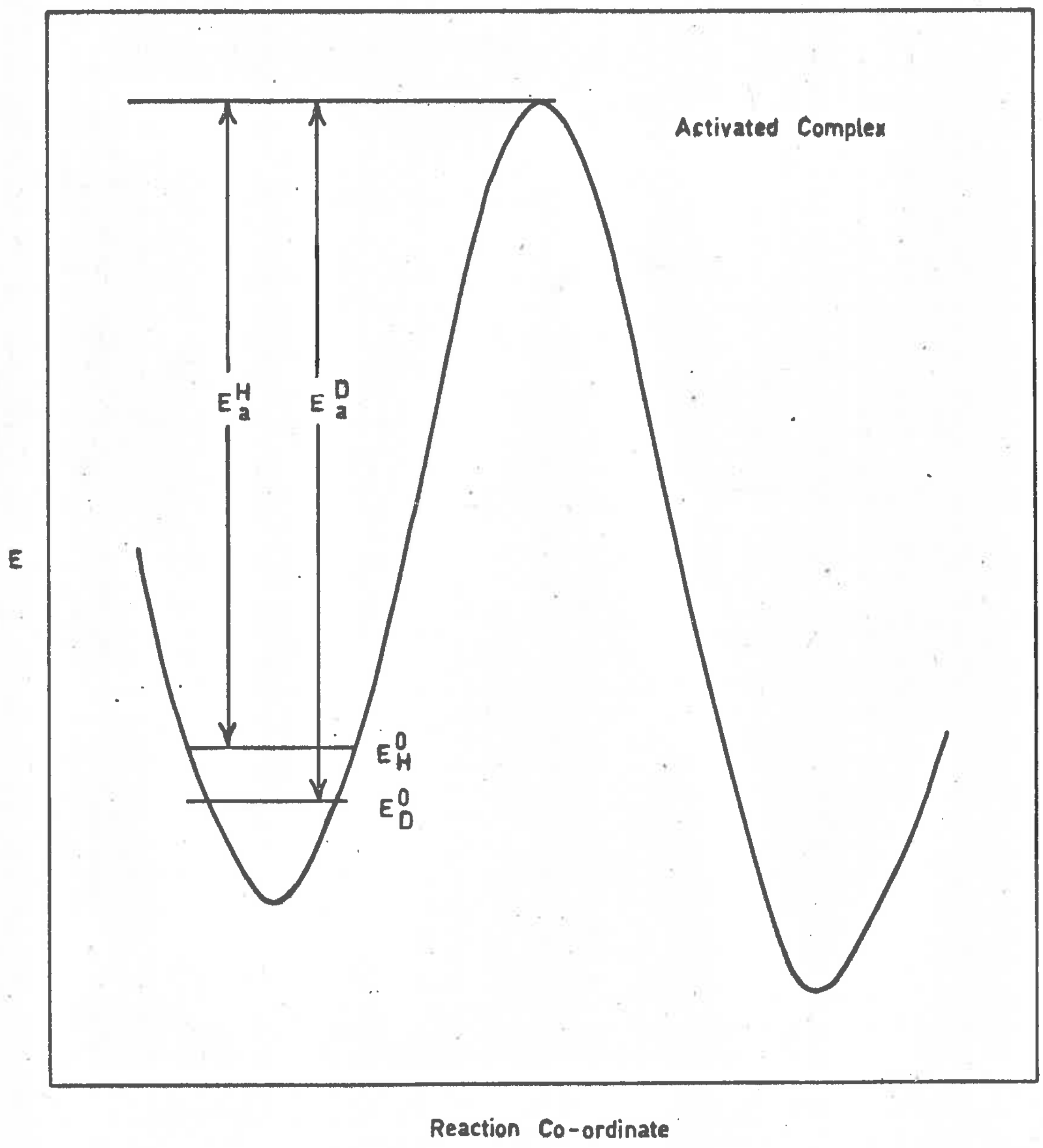
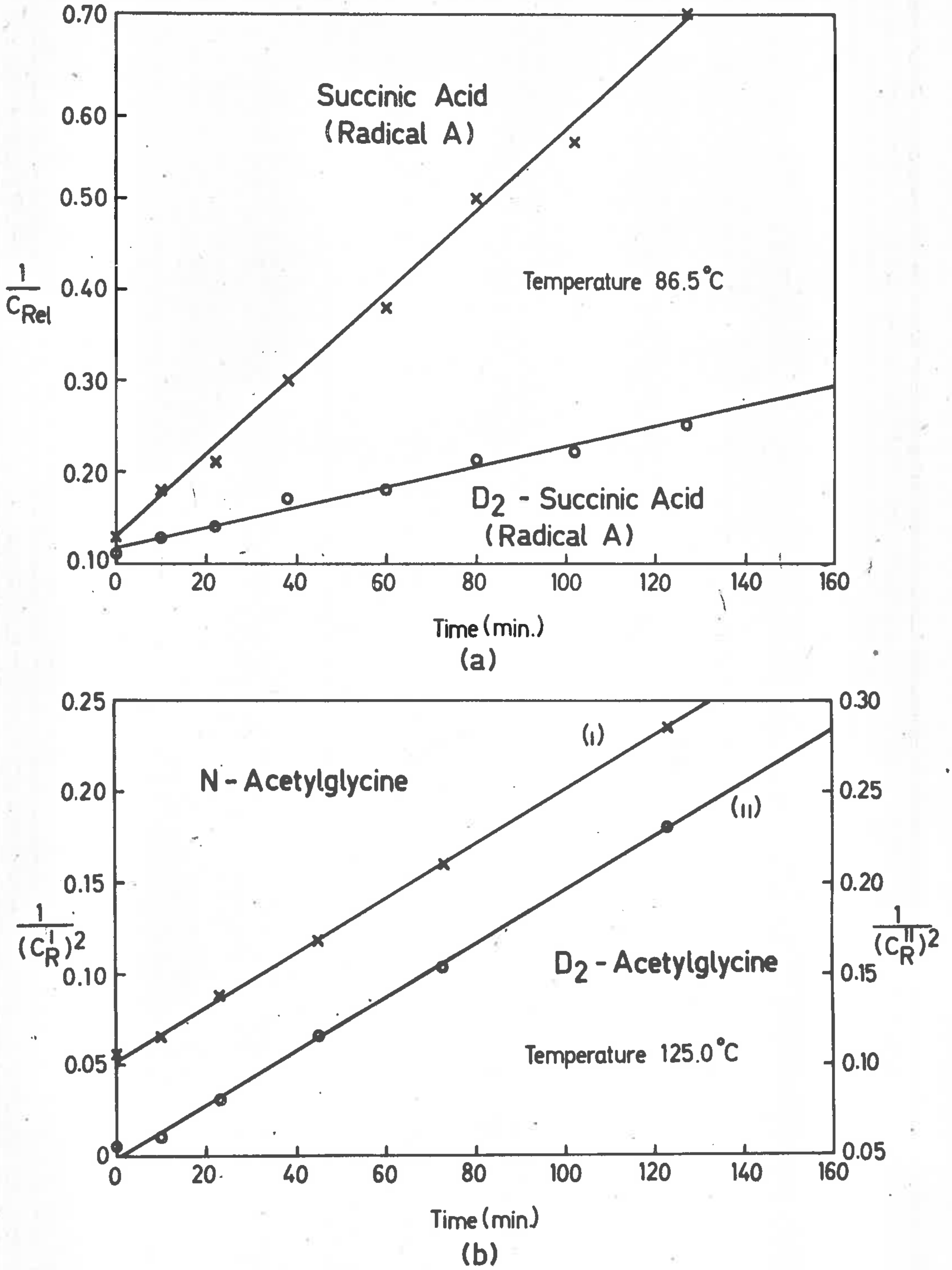


Kinetic Isotope Effect

Fig. 5.1


0.70
0.60
0.50
0.40
0.30
0.20
0.10
$\frac{1}{C_{Rel}}$
Succinic Acid
(Radical A)
Temperature 86.5°C
D2 - Succinic Acid
(Radical A)
0
20
40
60
80
100
120
140
160
Time (min.)
0.25
0.20
0.15
0.10
0.05
0
$\frac{1}{(C_R^{I})^2}$
0.30
0.25
0.20
0.15
0.10
0.05
$\frac{1}{(C_R^{II})^2}$
(I)
(II)
N - Acetylglycine
D2 - Acetylglycine
Temperature 125.0°C
0
20
40
60
80
100
120
140
160
Time (min.)

(a)

(b)

Fig. 5.2

destruction is 46 kcal. per mole, the difference only amounts to 3% which is distinctly less than the available experimental accuracy.

As already mentioned in Chapter 4.2 the deuterium atoms can replace the polar hydrogen atoms in organic molecules by simple recrystallization from heavy water; repeated recrystallization ensuring that most of the polar hydrogen atoms are replaced in the crystals. Crystals having deuterium substituted for hydrogen in C-H bonds would also be suitable but were not readily available. If two matched irradiated crystals, one of which is deuterated, are annealed together then their reaction rates can be compared. The method for comparing rates was identical to that used for comparing reaction rates in matched crystals having the same initial number of free radicals. In this case one ordinary and one deuterated crystal of the same compound were carefully chosen and irradiated with X-rays. After observing the intial free radical spectra so that intial relative concentration could be compared, each crystal was mounted in the double cavity and the cavity heated according to the procedure described in Chapter 4.3.2.

5.2.1 Results

In all, six free radical reactions were examined to see whether the kinetic isotope effect occurs. These results are shown in table 5.1. Figure 5.2(a) shows the deuterium isotope effect on the destruction of β -kenoxycarbonyl propionic acid (radical A) in irradiated D_2 - succinic acid. The rate constant, obtained from the slope of the reaction curve for this reaction, was less by a factor of 4.5 than the rate constant for the same radical in ordinary succinic acid. To arrive at this factor one had to accurately compare the intial relative concentration of free radicals in the two crystals. In this case, ESR spectra from both crystals were

TABLE 5.1

FREE RADICAL REACTIONS STUDIED FOR THE DEUTERIUM ISOTOPE EFFECT

Compound	Radicals on which Reaction Rates were compared	Type of Free Radical Reaction	Relative Rate Constant	Isotope Effect
N-acetyl-glycine	$H_3C\text{-}CO\text{-}NH\text{-}\dot{C}H\text{-}COOH$ and $H_3C\text{-}CO\text{-}ND\text{-}\dot{C}H\text{-}COOD$	Destruction	1.1	No
Malonic Acid	$\dot{C}H_2\text{-}COOH$ and unknown radicals	Destruction	0.8	No (See Text)
Succinic Acid	$HOOC\text{-}CH_2\text{-}CH_2\text{-}CO\dot{O}$ and $DOOC\text{-}CH_2\text{-}CH_2\text{-}CO\dot{O}$ (Radical A)	Destruction	4.5	Yes
	$HOOC\text{-}CH_2\text{-}\dot{C}H\text{-}COOH$ and $DOOC\text{-}CH_2\text{-}\dot{C}H\text{-}COOD$ (Radical B)	Destruction	1.0	No
Glycine	$\dot{C}H_2\text{-}COO^-$ and $\dot{C}D_2\text{-}COO^-$	Conversion	Not Determined	Yes (See Text)
Dihydro-thymine	$\dot{C}_5$ and $\dot{C}_6$	Conversion	1.0	No

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essentially of the same shape. Only a small difference in the spectrum from irradiated D_2 - succinic acid was observed due to proton-deuteron exchange occuring in kenosuccinic acid (radical B) during irradiation (see next section). The comparison of intial spectra revealed that the intial concentrations were the same. After radical A was completely removed by annealing, a second comparison on the remaining spectra showed that the concentration of radical B in the two crystals was equal. However, no isotopic effect was observed in the reaction rate for the destruction of radical B at the higher temperature where these radicals react. Figure 5.2(b) reproduces the reaction curves for free radical destruction in N - acetylglycine and deuterated N - acetylglycine at 125°C and reveals no isotopic effect in the reaction rate. (Note that the vertical scales in figure 5.2(b) have been displaced for clarity.) Comparison of intial spectra revealed that the intial concentrations of free radicals were the same in the two crystals after they were irradiated uniformly. The two lines comprising the ESR spectrum from the deuterated crystal were, however, slightly narrower due to the magnetic moment of the deuteron being smaller than the proton resulting in less inhomogeneous broadening.

In the case of the glycine conversion, the conversion rate was observed to be slower in D_3 - glycine after each crystal was heated equally so that radicals in the glycine crystal were completely converted. The radicals in D_3 - glycine were not completely converted at this stage as further heating still altered the spectrum. However, little work has been published on the identity of the free radicals in irradiated D_3 - glycine. Box et al (1966) have identified the radical produced in D_3 - glycine when it is irradiated at LNT and allowed to warm to 165°K as being $\dot{C}H_2\text{-COO}^-$ or $\dot{C}H_2\text{-COOD}$ (kenoacetic acid). In the present work it was observed that after a crystal was irradiated at LNT and stored at dry ice temperature (ESR spectrum as shown in figure 4.17(a)) the spectrum slowly altered when the crystal was observed at room temperature. The final spectrum (figure 4.17(b)) resembled that obtained when a crystal was irradiated at room temperature, initially. On heating at 55°C a crystal which had been irradiated at room temperature, the spectrum was altered (as mentioned in Chapter 4.6) indicating that the radicals, in this case, were being converted (figure 4.17(c)). This conversion reaction was compared with the one in ordinary glycine (described in Chapter 4.6) and was noted to be slower. The question that arises here is whether the radicals are, electronically, the same in the two conversions. In ordinary glycine the radical that is converted is kenoacetic acid ($\dot{C}H_2 - COO^-$) while the radical transformed in D_3 - glycine appears to be $\dot{C}D_2 - COO^-$. This radical has not been identified in freshly irradiated D_3 - glycine but the possibility of it being $\dot{C}D_2$-COO^- has been mentioned by Morton (1964 b).

For perdeutero-malonic acid ($DOOC$-CD_2-$COOD$), where the identity of the free radicals are unknown, the rate of disappearance of the whole ESR spectrum was compared with the disappearance of the kenoacetic acid spectrum in ordinary malonic acid when the crystals were identically heated at 65°C. Both crystals were uniformly irradiated using the sealed holder and the initial concentrations of radicals were, in fact, checked by double integration and found to be similar. Observations from this experiment indicated that the spectrum from irradiated perdeutero-malonic acid diminished at a faster rate than the kenoacetic acid in ordinary malonic acid. This anomalous result may indicate that the radicals in the deuterated compound are structurally different.

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5.3 Isotopic Mixing as Evidence for Radical Migration

Since the phenomenon referred to as isotopic mixing in Chapter 2.2 has been observed to occur in the radicals of D_2 - succinic acid during the irradiation process (Pooley and Whiffen, 1962) it is worth checking for this phenomenon in other irradiated deuterated organic crystals. Proton-deuteron exchange has also been reported (Itoh and Miyagawa, 1964) in free radicals of an annealed irradiated crystal of L-α-alanine with annealing at a sufficiently high temperature exchanging all protons on the radical. Thus one would like to look for H-D exchange in radicals of other deuterated crystals by ESR techniques and see whether it occurs during the irradiation process or is a result of annealing. In the cases of succinic acid and L-α-alanine it would be of great interest to see whether the exchange is confined to the radicals only or whether it has extensively involved the molecules of the host crystal as well as the radicals. Evidence of the latter situation would be strong evidence in favour of kenon migration. One can establish the extensiveness of isotopic mixing in a crystal by examining the infrared absorption spectrum. If any alteration in the spectrum is seen as a result of proton-deuteron exchange then the mixing must occur in the molecules of the crystal as well as the free radicals because infrared absorption spectroscopy is notoriously insensitive to detecting small contaminants in a specimen.

5.3.1 Experimental Method

If a sufficient number of the molecules in the crystal each have one or more hydrogen atoms bonded to carbon atoms exchanged with deuterium atoms, then its infrared spectrum can be altered because if a hydrogen atom in a C-H bond is replaced by a deuterium atom the stretching, bending and wagging frequencies will be reduced by a factor of about $\sqrt{2}$. Thus new bands in the spectrum will appear with a corresponding decrease in intensity of the bands associated with the C-H bond. These vibrational frequencies due to the C-H and C-D bonds lie in a frequency region of 2000 to 600 cm^{-1}. Thus looking for an alteration in the infra-red spectrum before and after irradiation will show whether or not isotopic mixing is occuring to any considerable extent in the crystal.

Samples of deuterium - substituted crystals in suitable form for observing the infra-red spectra were made using the well known KBr disc technique. A quantity of high purity potassium bromide and the organic crystal in the ratio of 100 to 1, both previously ground to some extent with a mortar and pestle, were then mixed and ground further for about 90 seconds using a vibration mill equipped with a steel capsule and ball. The resulting finely divided powder was placed in an evacuable die holder and the assembly evacuated to a pressure of 1 mm Hg. The powder was then pressed for about three minutes with a pressure of two tons per cm^2. Under these conditions the powder flowed to form a solid, translucent disc, 13 mm in diameter. After the disc had been carefully removed from the die holder it was immediately stored in a dessicator containing phosphorous pentoxide. All components used for preparing the discs that were in contact with the powder were also stored in a dessicator while not in use and were warmed in an oven just before use. This precaution was necessary to prevent contamination of the disc with water which would alter the infra-red absorption spectrum. The spectrum was recorded with the use of a commercial grating spectrophotometer (Perkin-Elmer model 237) having a frequency range

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of 4000 to 600 cm^{-1}. This instrument also had a facility for recording differential spectra which was very useful in looking for small changes in the spectrum following irradiation. Very careful preparation of the two discs is needed so that those bands common to each spectrum and having equal intensity cancel out and those bands not having equal intensity or new bands in one spectrum remain. Furthermore for preparing discs for recording differential spectra the irradiated and unirradiated organic samples were prepared from a selected crystal cut in halves and one half irradiated with X-rays.

5.3.2 Results

By utilising the technique just described five partially deuterated crystals were examined either after irradiation or after irradiation and annealing. The results from these experiments are listed in table 5.2. It was concluded that extensive isotopic mixing was observed in D_2 - succinic acid and not in the other four compounds examined. Figure 5.3(a) and (b) show respectively, the infra-red absorption spectra of D_2 - succinic acid before and after irradiation. So that the differential spectra of these two will be directly comparable with the difference of the two spectra the usual compensating KBr disc was omitted from the reference beam in each case. The first point to be raised about this gross isotopic mixing is that this is the first time that such a remarkable phenomenon has been reported. Furthermore, this significant alteration in the infra-red absorption spectrum was consistently reproducible in four different samples. The absorption bands marked with arrows in figure 5.3(b) reflected the strongest changes in the spectrum.

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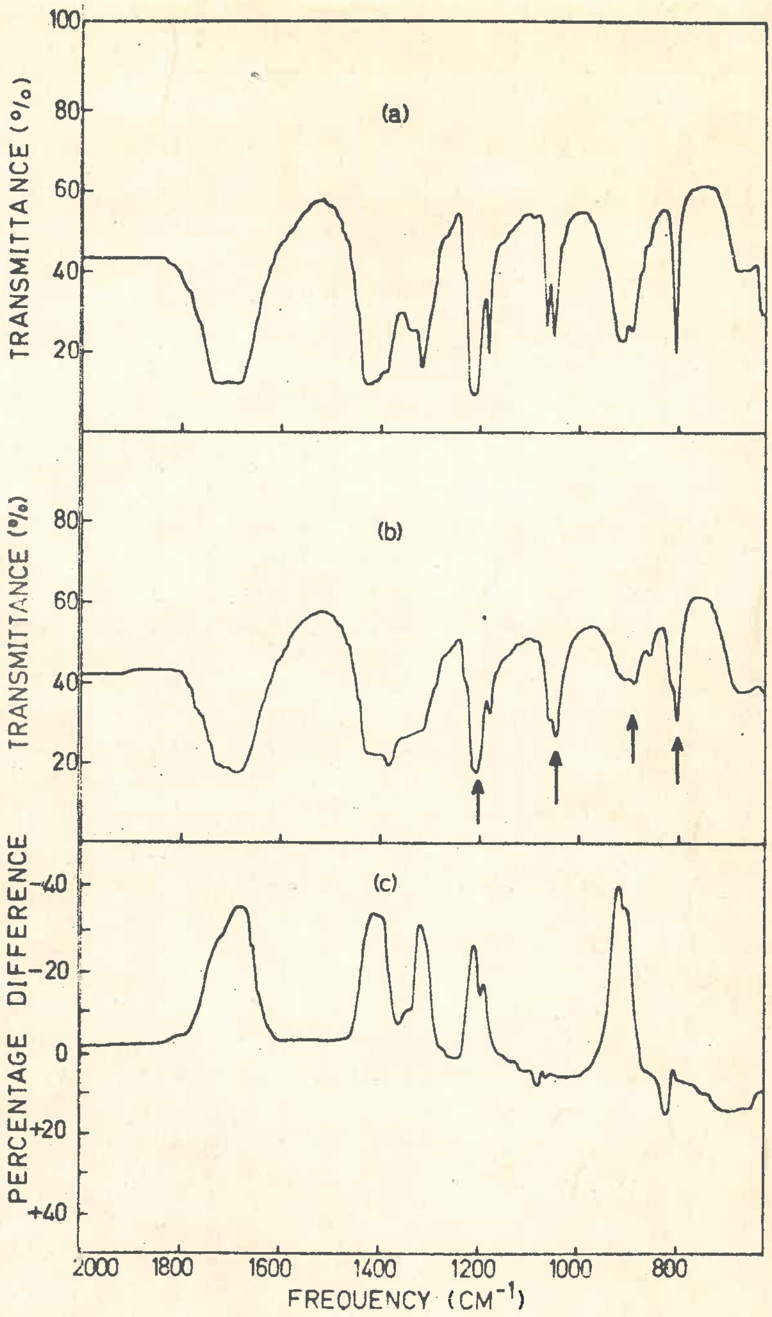

Infrared Absorption Spectra of Irradiated oo'-dideuterosuccinic acid.

Fig. 5.3

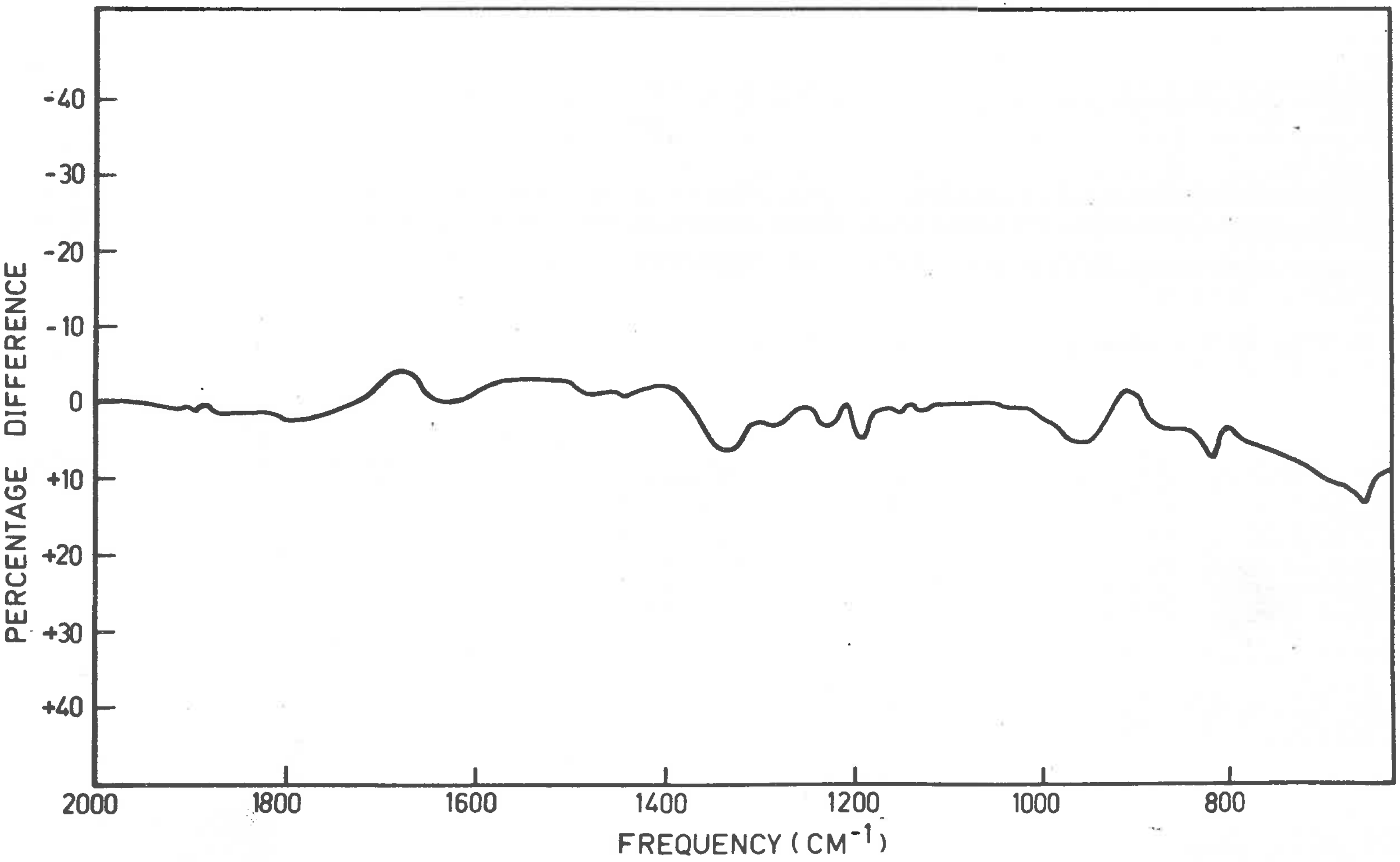
-40
-30
-20
-10
0
+10
+20
+30
+40
PERCENTAGE DIFFERENCE
2000
1800
1600
1400
1200
1000
800
FREQUENCY (CM^{-1})

Fig. 5.4

TABLE 5.2

RESULTS OF EXPERIMENTS TO OBSERVE ISOTOPIC MIXING IN IRRADIATED ORGANIC CRYSTALS

Deuterated Organic Compound	Evidence of H-D Exchange from the Infra-red Spectrum	ESR Evidence for H-D Exchange in the Radical	Reference to ESR Evidence for H-D Exchange
D_3-glycine	No	Possibly Occuring (See Text)	Present Work
L-α-Alanine	No	Yes	Itoh and Miyagawa (1964)
D_2-Succinic Acid	Yes	Yes	Pooley and Whiffen (1962)
D_2-Acetyl-glycine	No	No	Present Work
D_2-dihydro-thymine	No	No	Present Work

Also reproduced (figure 5.3(c)) is the differential spectrum of the irradiated material with the unirradiated D_2 - succinic acid sample in the reference beam. This spectrum clearly shows those alterations marked in figure 5.3(b) as well as other alterations. Also recorded in the same way was the differential spectrum (figure 5.4) for irradiated undeuterated succinic acid with the unirradiated sample in the reference beam. From this curve one can see that X-rays have not produced any significant changes in the undeuterated crystals.

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This at once confirms that the appearance of the phenomenon is contingent upon partial deuteration and must be the result of isotopic mixing. The hypothesis that there is an extensive chemical reaction involving the production of new molecular species or extensive polymerization, can be ruled out from the fact that it should appear in both undeuterated and partially deuterated crystals. Furthermore, visual inspection of the irradiated crystals revealed them to be essentially unchanged in appearance; they remained water clear. It is to be pointed out at this stage that the differential spectrum shown in figure 5.4, has not shown all bands completely cancelled out as one should expect. This degree of incomplete cancellation (viz. plus or minus about four per cent) was also seen in the differential spectrum recorded for two discs prepared from the same unirradiated compound. This was even after care was taken to see that both discs were prepared under identical conditions and were of similar opacity and that neither of the holders did not obscure the beam.

To establish the band assignments in the differential spectrum reproduced in figure 5.3(c), those made by Shimanouchi et al (1960) for the infra-red spectra of four isotopic species of succinic acid were used. Table 5.3 lists the infra-red bands identifiable in the spectrum of DOOC-CH_2-CH_2-COOD together with the nature of the changes in them. One will notice that those changes listed are just what can be expected for isotopic mixing between the H and D positions. The wag, twist and bending frequency vibrations for the molecular groups -CHD- were calculated to a first approximation by taking a mean between the corresponding frequencies for the -CH_2- and -CD_2- groups.

TABLE 5.3

CHANGES IN THE INFRA-RED ABSORPTION SPECTRUM OF OO'-DIDEUTERO-SUCCINIC ACID DUE TO IRRADIATION

Band Frequency	Assignment	Change in Absorption Strength after Irradiation
1435	CH_2 bend	-
1240	CHD bend	+ (?)
1210	CH_2 wag	-
1190	CHD wag	+
1180	CH_2 twist	-
1060	CHD twist	+
1050	OD in-plane def.	- (?)
910	OH out-of-plane def.	+
860	C-C stretching for the $-CH_2-CH_2-$group	- (?)
830	C-C stretching for the -CHD-CHD-group	+
805	CH_2 bending	-

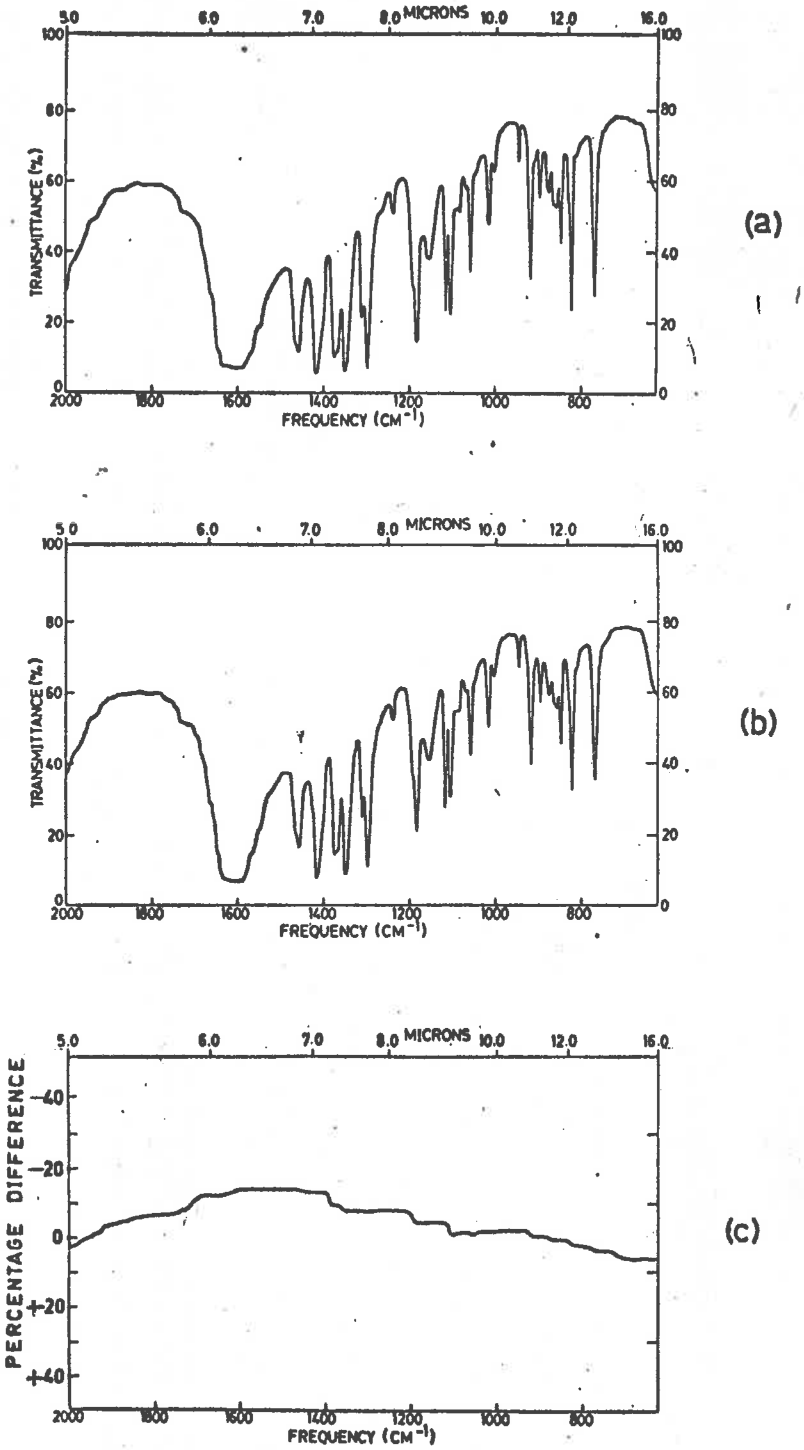

Fig. 5.5 Infrared Spectra of Deuterated Alanine.

In the case of L-α-alanine the infra-red absorption spectra from irradiated and unirradiated partially deuterated crystals superimposed on the spectra of KBr, are shown in figures 5.5(a) and 5.5(b), respectively. The differential spectrum (figure 5.5(c)) of the irradiated and unirradiated samples showed no significant changes in the irradiated sample. The effects of annealing on deuterated L-α-alanine at a temperature below that at which the free radicals can be annealed and for which it is known that isotopic mixing occurs in the free radicals, did not alter the infra-red spectrum. In the case of D_2 - succinic acid, annealing at 100°C for 6 hours did not increase the extent of isotopic mixing. With regard to the three remaining partially deuterated systems listed in table 5.2, the differential spectra were also essentially featureless.

The ESR spectra were observed for the crystal systems listed in table 5.2 immediately after irradiation and after briefly annealing the crystals. Proton-deuteron exchange in the radicals produced in D_2 - succinic acid and L-α-alanine was confirmed. In the case of D_3 - glycine crystals which were irradiated at LNT and allowed to warm to room temperature it was found that the ESR spectrum slowly altered (as already mentioned in the last section). This alteration of the spectrum appears to indicate that H-D exchange is occuring in the radical intially produced (kenoacetic acid). However, a closer examination is required which could not be undertaken in the laboratory at this stage because of inadequate low temperature irradiation facilities.

With the infra-red absorption spectrum revealing evidence of isotopic mixing for a large fraction of the molecules of D_2 - succinic acid as well as the radical, a detailed discussion is called for and will be given in Chapter 7.

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CHAPTER 6

OTHER INVESTIGATIONS

6.1 Introduction

During the project several experimental investigations were carried out which were indirectly related to free radical reactions and the kenon migration hypothesis. These included attempts to detect free radicals by differential thermal analysis, free radical production by hydrogen atom bombardment and attempts to detect microscopic diffusion of the radical state. These experiments and their results will be discussed in this chapter.

6.2 Hydrogen Atom Bombardment

As early as 1961 Ingalls and Wall (1961) observed that free radicals detectable by ESR were produced in finely divided polymers bombarded with hydrogen atoms. More recently Cole and Heller (1965) bombarded a number of organic crystal powders with hydrogen atoms produced by a microwave discharge and found a detectable ESR signal from most of them. The results indicated that the radical species produced by hydrogen atom bombardment were more selective than those produced in the same compounds by X-ray irradiation. Only a C-H bond breakage was observed with hydrogen atom bombardment whereas using high energy radiation either one or both of the C-H and C-C bond breakages resulted in radicals. Snipes and Schmidt (1966) bombarded various powdered amino acids with thermal hydrogen atoms and were able to record ESR spectra from all compounds investigated. Sometimes when powders were used the spectrum altered after they were exposed to air for a short time. This indicated the reactivity of the radicals with oxygen atoms to form peroxy radicals which have a characteristic spectrum exhibiting no hyperfine structure. If these same compounds were irradiated with high energy radiation under vacuum only a slight effect was observed upon exposure to air, suggesting that the oxygen atoms do not penetrate very far below the surface. As all radicals produced by hydrogen atom bombardment in a particular sample are altered when exposed to the air, these radicals must be formed near the surface. Further experimental observations were published by Heller, Schlick and Cole (1967) who concluded that free radicals can only be produced in one of two ways. In the case of a saturated organic molecule a thermal hydrogen atom may abstract a hydrogen atom from a C-H bond or if an olefinic molecule is involved the thermal hydrogen atom could be added to an unsaturated carbon atom. These workers also reported bombarding single crystals with thermal hydrogen atoms with results indicating a very weak ESR signal due probably to the smaller area exposed to the atoms than with the powders.

In this project it was hoped to extend the work on hydrogen atom bombardment of organic compounds to include single crystals, with the aim of developing an alternative method of preparing crystals for kinetic studies. Cole and Heller have made calculations showing that the hydrogen atoms penetrate only the first 10 molecular layers from the surface and hence concluded that the number of free radicals that can be produced is limited. However, it has been proposed in Chapter 2.2 that the free radical state may be mobile at a temperature below where the radicals react. Thus if a crystal is bombarded at an elevated temperature the

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radicals as soon as they are produced may be able to "migrate" away leaving another molecule in its place to be attacked by an incoming hydrogen atom. If this does occur the concentration of free radicals is expected to be higher than at room temperature. If free radicals can be produced in single crystals in sufficient concentration free radical reactions could be compared with the corresponding reactions in those crystals exposed to high energy radiation. Those crystals bombarded by hydrogen atoms might be regarded as "clean" crystals. By this it is meant that no other secondary radiation damage is present with the free radicals as there is when they are irradiated with X-rays.

The basic technique for bombarding organic materials with thermal hydrogen atoms has been outlined in the three papers cited above. This involves using a radio-frequency discharge to produce thermal hydrogen atoms which can then be directed to impringe on the powder at a pressure of about 1 mm of mercury. The bombarding chamber shown in figure 6.1 was designed along similar lines to that of Cole and Heller. No arrangement was made to seal off the powder under vacuum after its exposure to the hydrogen atoms. The right angle bend in the discharge tube at the top of the chamber prevented most of the unwanted UV light from the discharge arriving at the powder. The discharge tube was cleaned, before being used, with the technique described by Cole and Heller. Provision was made to warm the sample above room temperature whilst it was being bombarded with hydrogen atoms. This consisted of a circular copper block having a polished and cleaned top and provided with heating elements (figure 6.2). A chromel-alumel thermo-couple junction was attached to

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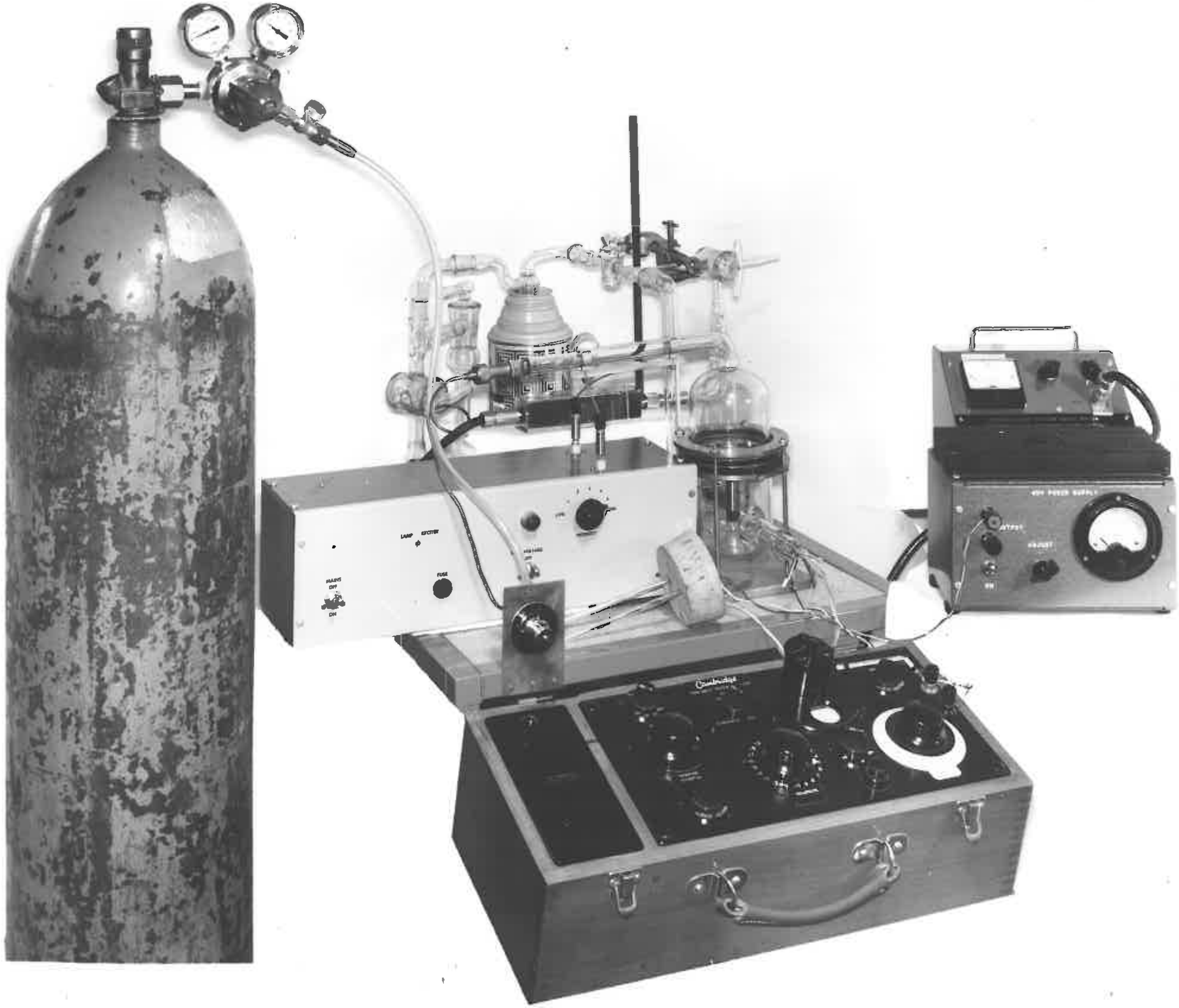

Fig. 6.1 The Apparatus used for Hydrogen Atom Bombardment.

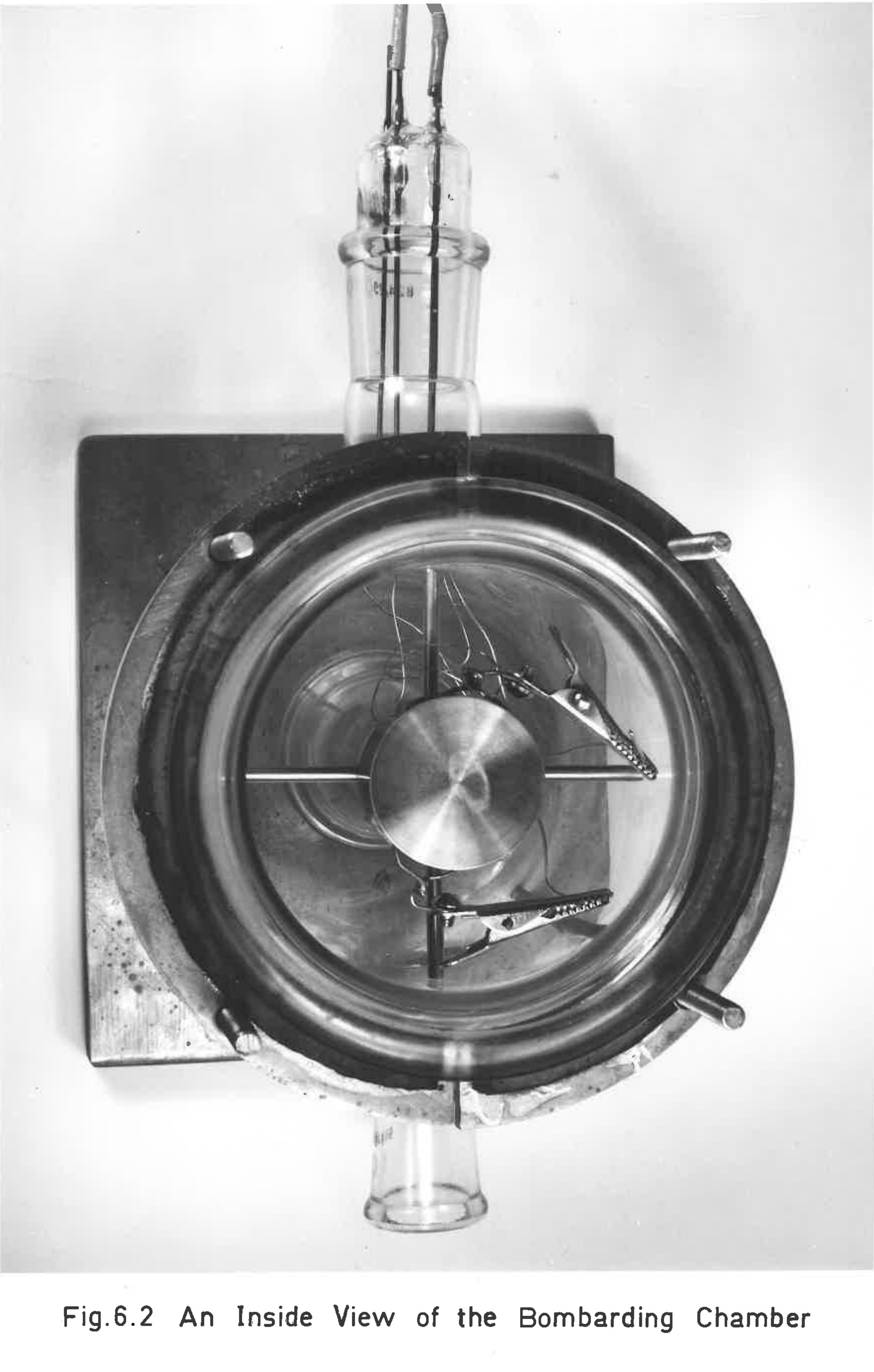

Fig.6.2 An Inside View of the Bombarding Chamber

the side of this block to measure the temperature. After steady conditions were attained at the temperature required the temperature of the block remained within $\pm \frac{1}{2}$°C without it being necessary to adjust the heater voltage. The sample could be expected to be several degrees lower in temperature than the block because of radiation loss but a knowledge of the exact temperature was not necessary.

The first hydrogen atom bombardments were made on glycine, L-α-alanine, dl-malic acid and maleic acid crystal powders at room temperature. Moderate ESR signals were obtained from the first three compounds while no signal was seen from maleic acid. The spectra from the first-mentioned compounds agreed with those produced with X-rays. Since this work began Snipes and Schmidt have reported similar spectra from powdered glycine and L-α-alanine. In L-α-alanine it should be noted that a C-N bond is broken by an impinging hydrogen atom rather than the usual C-N bond. This point was established when the spectrum was identified as being the same as that exhibited by the radical species produced by X-irradiation of the powder. Some powders which were bombarded at room temperature (including methylmalonamide, malonic acid and glycine) were warmed to 60°C whilst the ESR spectra were being observed. It was found that the free radicals reacted at a much lower temperature than if they were produced by X-rays. Finally single crystals of glycine and malonic acid (largest face about 1 cm^2 in area) were bombarded at temperatures above room temperature. The glycine crystal was maintained at 100°C for 4 hours while the malonic acid crystal was at 40°C during bombarding. Both crystals were allowed to cool to room temperature before being removed

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from the vacuum. Immediately after removing from the chamber an ESR spectrum was looked for. Unfortunately in neither crystal could any detectable free radicals be found.

It was felt that the behaviour of free radicals produced in bombarded powders when warmed above room temperature probably results from the radicals being formed near the surface of the crystallites and the inhomogenuity in the distribution of these radicals. The effect of exposure of these powders to air after bombarding has been observed by Heller, Schlick and Cole and this reaction may also influence the free radical destruction. In the case of single crystals exposed to air the concentration of free radicals may be adversely affected.

As it appeared that there were many difficulties in the way of production of "clean" single crystals, uniformly doped with free radicals by this method, investigations were not persevered with.

6.3 Macroscopic Diffusion of the Radical State

In Chapter 2.2 one of the predictions involved the mobility of the radical state by hydrogen atom jumping. If one considers the kenon migrating at a particular temperature so that two radicals reach adjacent sites and react then the average number of lattice sites that the kenon can visit before reacting is about 10^4. This arises from the fact that about 1 in 10^4 radicals are produced in the crystal. Thus with a crystal lattice spacing, a, the average distance x in a straight line the radical state can move before reacting is roughly $\frac{a}{3}\sqrt{10^4}$ from consideration of the random walk problem in 3-dimensions. An upper limit to the diffusion coefficient D can be estimated from the approximate relationship $x = \sqrt{Dt}$

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(Seitz, 1952) where t is the time involved. If it takes about 10 minutes for most of the radicals to recombine then $D = 5 \times 10^{-14}$ $cm^2 sec^{-1}$. This value for D is very small and so it would be very difficult to detect diffusion macroscopically. However, if the radicals were able to visit adjacent lattice sites without mutual destruction, at temperatures high enough to promote mobility, a different situation would exist. In this case the activation energy associated with the annealing would represent the energy barrier that the two free radicals on adjacent sites need to surmount before reacting. If this is the case one can expect the kenon to diffuse for considerable distances at a lower temperature than that at which the radicals recombine at an appreciable rate. Consequently one may have macroscopic diffusion of the kenon occurring in the crystal. In view of these considerations the following experiment was performed. This involved irradiating half of a suitably shaped crystal and warming the crystal to a selected temperature while observing the unirradiated portion of the crystal for an increasing ESR signal. The radicals are expected to diffuse into the unirradiated portion if the kenon migrates without reacting. It should be noted that "macroscopic" diffusion can result either from the radical state mobility due to hydrogen atom jumping or by the diffusion of the whole radical and its detection does not help in distinguishing between these two mechanisms.

To prepare a crystal for this experiment one first needed to choose an elongated crystal with a cross-section of about 1.5 mm^2. This crystal was inserted into a small lead block for half of its length and the assembly mounted in the holder designed to hold the single crystals in the X-ray beam. The crystal was irradiated on both sides of the exposed portion by

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turning the assembly over half-way through the irradiation period. The crystal was then mounted in an ESR cavity such that the signal from the irradiated portion of the crystal was just suppressed. This was done by mounting the irradiated end of the crystal inside a thin copper tube of diameter just larger than the cross-section of the crystal. The tube and crystal were attached to the cavity with a small piece of PTFE. Since the microwave field was excluded from the inside of this tube no ESR signal could be obtained from this part of the crystal. The crystal was moved into the tube until the ESR signal was just undetectable. Then if the radicals were to move out into the unirradiated portion of the crystal after a long period of heating and were of sufficient concentration an ESR signal would be detectable. A standard was included to monitor the sensitivity of the spectrometer and to ensure that the same gain was used. Three different types of crystals were examined because of their suitable shape. These were glycine, partially deuterated glycine and dl-α-alanine. The glycine crystals (both types) were heated in the oven at 100°C for 120 hours while the dl-α-alanine crystal was heated at 130°C for 120 hours. In all three crystal systems no increase in the ESR signal was observed.

From these results an upper limit may be put on the diffusion coefficient. It was estimated that a migration distance, under diffusion, of 0.5 mm could have been detected by this method. Applying the relation $x = \sqrt{Dt}$ one can put an upper bound on D of 5×10^{-9} $cm^2 sec^{-1}$. It can only be said that D is less than this. In general it can be said that careful application should allow one to detect the diffusion of free radicals if their diffusion is significantly larger than the above value.

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Much depends on the choice of a suitable system for study and the lack of time precluded an extensive search for such a system beyond the three cases mentioned above.

6.4 Differential Thermal Analysis

If one considers free radicals being annealed in a crystal and if the radicals recombine in pairs to form a saturated chemical species then it can be expected that each reacting pair releases energy. Usually free energy is expected to be released if a chemical bond is formed between two reacting species. Thus free radical destruction is an exothermic reaction. In a reaction where chemical bonds are formed and energy is released at a sufficient rate, the reaction can be detected by the technique of differential thermal analysis (DTA). To estimate the amount of thermal energy that may be released if all free radicals react, the following calculation was made. In an irradiated 20 mgm sample of glycine say, there are about 6×10^{15} radical pairs that are able to recombine. Now if about 4 eV is associated with each radical pair reacting then the total energy able to be released is about 10^{-3} calories. The most sensitive instrument available at present can detect exothermic reactions which liberate 1 or more millicalories per second from which it is easy to conclude that it is hardly to be expected that one can detect free radical destruction by DTA.

However, several attempts were made to detect radical recombination in glycine, L-α-alanine, malonic acid, succinic acid and N-acetylglycine before the above calculations were made but all results were negative as one would expect.

6.5 Other Observations

This section discusses a phenomenon associated with the free radical recombination in malonic acid irradiated in different organic crystal systems after irradiation.

During the very early stages of this project, irradiations using X-rays from a copper anode were carried out using a different X-ray source and apparatus. This source of X-rays was used until the molybdenum anode X-ray source described in Chapter 3.5 was operational. To enable the crystals to be exposed to the X-rays from the copper anode tube they were mounted in front of the window but open to the atmosphere and any other gases that may be present in the tube housing. This included ozone always present where high voltages exist. When malonic acid crystals were exposed to X-rays under these conditions the free radicals began to destroy each other at a rate convenient to experimental observation when the temperature was raised to 50°C. Both kenoacetic acid and kenomalonic acid were involved in the annealing. However, if the malonic acid crystals were irradiated using the specially made holder to seal the crystals from outside gases such as ozone radical disappearance involving only kenoacetic acid occurred at a similar rate only if the temperature was raised to about 65°C. These experiments were repeated several times with the same results. Other organic crystals were irradiated with both X-ray sources but no difference was observed in the temperature at which the free radicals reacted in the pairs of crystals. It was concluded from these results that ozone present during the irradiation altered the free radical reaction rate in single crystals of malonic acid but no explanation can be offered at this stage as to how this occurs.

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The other observation that will be reported here is the visual examination of the different single crystals immediately after irradiation. In five different crystal systems uniform colouration was observed throughout the crystal. The colour ranged from a bright yellow to a purple in contrast to the colourless appearance before irradiation. Table 6.1 lists the colour each crystal exhibited. The deuterated crystals of the first four compounds gave the same colour.

Table 6.1

Colours Exhibited by Crystals after Irradiation

Crystal	Colour of Freshly Irradiated Crystal
Glycine	Yellow
L-α-Alanine	Yellow
Malonic Acid	Purple
Succinic Acid	Purple
N-Acetylglycine (Deuterated)	Pink
N-Acetylglycine	Colourless

In crystals of malonic acid and succinic acid the colouration at room temperature did not remain for more than several hours after irradiation whereas in the other crystals the colour was persistent. On heating these crystals at 60°C for several hours the colour could be bleached out completely. The temperature at which this occurred was such that no free radical destruction actually took place. For those crystals showing a colouration an examination was made of the absorption spectra of the crystals in a wavelength range of 2000 to 7500 Å using a Perkin-

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Elmer model 137UV spectrophotometer. Only a broad absorption peak was observed in the region 3500 to 4500 Å for the yellow coloured crystals and at 5500 Å for the purple coloured crystals. It appears that the colouration bears no relation to the free radical formation and so, further investigations were considered to be outside the scope of this project.

CHAPTER 7

GENERAL DISCUSSION

7.1 Introduction

One is now in a position to discuss the experimental data and in particular to examine the evidence for the truth or otherwise of the hypothesis of kenon diffusion. It will be recalled that the experimental work was planned on the basis of testing the predictions of the "kenon hypothesis". To what extent is one entitled to believe in the existence of the kenon as a mobile crystal defect? Does it play an important role or indeed any role on the post-irradiation events of irradiated organic crystals?

7.2 Reproducibility of Free Radical Reactions

It can be stated broadly that the accurate reproducibility of free radical reactions by destruction and conversion is consistent with the kenon hypothesis. One does not expect the mobility of the kenon to be much affected by small proportions of impurities in the crystal; certainly not in the case of a conversion reaction as it is "unimolecular". The reduction in reaction rates in irradiated and annealed crystals seem to be clearly connected with the physical damage the crystal suffers, mainly "microscopic cracking". It is natural to expect this to affect the mobility of any entity. In short these results are interesting in themselves but seem to be of little help one way or the other in establishing the kenon hypothesis.

7.3 Reaction Kinetics and Activation Energies

In the first instance the experiments on reaction kinetics have added to the originally meagre knowledge of the kinetics of free radical reactions in irradiated organic crystals. In general, second-order kinetics was found to be associated with free radical destruction which implies that two radicals are involved in free radical recombination. However, this does not, in itself, establish free radical state mobility by hydrogen atom jumping. It has established that some transport mechanism is involved in the destruction as two radicals have to arrive at adjacent lattice sites before they can react. It could hardly be claimed that these results, namely second-order kinetics, are in any way unexpected since it seems perfectly clear, a priori, that the free radicals have to react at least in pairs if the unpaired spins are to be removed.

A point worthy of remark is the accurate second-order kinetics observed for free radical destruction reactions. This would seem to be clear evidence against any hypothesis that free radicals are produced in "spurs" in the crystal. It would seem that the reaction behaviour in polymers is attributed to the inhomogenuity of the material rather than being essentially due to any inhomogenuity in the distribution of the free radicals.

The reaction kinetics observed for conversion reactions were all first-order as predicted. This was more or less expected as a conversion reaction would essentially involve only one radical.

It will be observed that an anomaly was seen in one case of reaction kinetics of radical destruction, namely the third-order kinetics in N - acetylglycine. One does not expect to see third-order kinetics associated with free radical destruction but one can find a reasonable interpretation within the bounds of the hypothesis. Before radicals are able to recombine in N - acetylglycine three radicals must arrive on adjacent sites. The third radical acts as a catylst in lowering the energy barrier for recombination of the other two radicals as a result of the associated distortion of the lattice which accompanies it. As only one radical species is produced in N-acetylglycine (with a simple ESR spectrum) and the kinetics are accurately third-order at a particular temperature this appears to be the essence of any explanation however the radicals may arrive together.

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One will also recall that no free radical destruction was observed in glycylglycine up to the point where the crystal begins to decompose. This may come about because the radical must migrate, either as a whole or by kenon migration, and the temperature cannot be raised sufficiently before the crystal begins to decompose.

Finally, a brief comment can be made about the activation energies that were determined. This list of energies will be useful for comparison with solid state chemical reactions when they come to hand, and in particular, with activation energies of self-diffusion in these hydrogen bonded crystals, which one hopes may eventually be obtained by C_{14} tracer techniques or NMR observations. If the rate determining step for free radical destruction is the migration of the radicals to adjacent sites then the activation energy for kenon diffusion would be expected to be less than for self-diffusion.

7.4 Deuterium Isotope Effect

The kinetic isotope effect was observed in two free radical reactions in this work. This was in the free radical destruction of β-kenoxycarbonyl propionic acid in deuterated succinic acid and the conversion of deuterated kenoacetic acid in glycine. The kinetic isotope effect is consistent with the hypothesis but in itself does not say that radical state migration by hydrogen atom jumping is the migration mechanism involved. The possibility is always open that the rate limiting step in the whole process occurs at the point where the free radicals have reached close proximity to each other whether they got there by kenon diffusion or by diffusion of the whole radical through the crystal lattice. Even in the latter case the deuterium isotope effect may show itself by influencing the rate of combination of the adjacent radicals. Kurita and Kushiwagi (1966) have reported that the deuterium isotope effect was involved in the movement of "radical pairs", as the radicals moved apart. In this case one can say that the deuterium atom is involved in the transfer.

In succinic acid it will be recalled that only one radical species exhibited the kinetic isotope effect while the other radical did not. This may have arisen because of the selectively deuterated crystal used. Destruction of β-kenoxycarbonyl propionic acid may only involve the deuterium atoms attached to the carbonyl group whereas the destruction of kenosuccinic acid may involve the hydrogen atoms attached to the carbon atoms. It is reasonable to anticipate that more of these reactions will show the kinetic isotope effect if the experiments are done with completely, or other partially, deuterated crystals. If an experiment on a completely deuterated crystal were to show no kinetic isotope effect then this could be taken as strong evidence against kenon migration in that particular system. Even such a result, however, could still be open to the interpretation that kenon migration occurred with hydrogen atom jumping without the actual transfer of the deuterium being the rate controlling step.

7.5 I- and H- radical reactions

The behaviour of two distinct radicals when both are present in a crystal was studied in four different compounds. In three cases the predictions of the hypothesis agree with the experimental observations while in the fourth case the observations to not necessarily agree. All four cases will now be discussed.

The results for glycine are in complete agreement with the hypothesis. Both kenoglycine and the unknown radical disappear at the same time apparently with second-order kinetics because of the near equality of the concentrations. If kenoglycine (an H-radical) is reacting with an I-radical, kenoglycine is free to migrate so that it arrives at sites adjacent to the unknown radicals which are able to react with it. If the unknown radical is an H-radical then either both radical species or only one are free to migrate and react.

In methymalonamide the H- and I- radicals behave according to the

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predictions. The H- radical disappears first without affecting the I- radical which is not expected to be mobile unless it converts to an H- radical first.

The results for succinic acid where two different H- radicals are observed initially and which do not show the expected situation of involving a metastable equilibrium can be given an adequate explanation under the terms of the model. A mechanism can be considered where β- kenoxycarbonyl propionic acid can migrate through the lattice by hydrogen atom jumping and only react if it arrives adjacent to a site where a radical of its own type resides. Presumably no reaction can occur when it arrives adjacent to kenosuccinic acid because of the stereospecificity of the two different radicals. When all β- kenoxycarbonyl propionic acid has reacted, kenosuccinic acid can react at a higher temperature when they are able to begin to migrate by kenon diffusion. It should be noted, however, that the particular annealing of the two radical species in succinic acid could take place by the diffusion of the radicals as a whole and so, this must be considered as an alternative mechanism in this situation.

In the case of malonic acid where the I- radical is removed first by thermal annealing, one may consider the release of I- radical kenons into (mobile) H- radical kenons which would then allow the annealing to proceed. However, one has also to consider the alternative hypothesis that the I-radicals migrate until adjacent to sites on which radicals of the same type reside. These radicals could migrate, as was mentioned in Chapter 2.2, either as a whole or by the migration of the I- radical state as a result of the movement of a molecular group from molecule to molecule.

Finally, one can say that all free radical conversion reactions studied in this work or reported in the literature conform with the predictions of the hypothesis. No transformations involving an H- radical to an I- radical have been observed. In the case of glycine, kenoacetic acid transforms to

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an unknown radical without affecting kenoglycine. This is allowable under the hypothesis as a conversion is expected to involve only one radical.

7.6 Isotopic Mixing

By far the strongest evidence for kenon diffusion is the isotopic mixing seen in irradiated deuterated succinic acid. In the present work the infrared spectrum was observed to be significantly altered by proton - deuteron (H-D) exchange taking place for a proton which is bonded to a carbon atom.

The first indication of H-D exchange was shown in the ESR spectrum. Apart from the hyperfine lines due to kenosuccinic acid Pooley and Whiffen (1962) observed additional lines. They attributed these lines to a radical that was electronically identical to kenosuccinic acid but with one specific proton attached to a carbon atom replaced by a deuteron. This observation was confirmed in the present work in which incidentally β - kenoxycarbonyl propionic acid was also seen (see Chapter 4.2). The real point is that a large amount of exchange involving a large fraction of the molecules of the crystal must take place if the infrared spectrum is altered. For an infrared spectrum to be significantly altered the induced impurities in the crystal have to be in sufficient concentrations, viz., greater than several per cent. The infrared spectrum does not provide a sensitive test for impurities as the discussion of H-D exchange in deuterated L-α-alanine will later show. As one has established that the mixing is extensive in the crystal an explanation must be sought. For normal G values (viz., in the range 1-5) one can only expect extensive mixing with a very large dose of radiation, or a radio-chemical reaction with a very large G value; the G value being defined as the number of events produced in the irradiated sample per 100 eV of radiation absorbed. However, as only low doses of radiation (6 Megarads) were used here one can discount this as playing a role. It appears that a free radical chain reaction can provide a suitable explanation and kenon migration fits this

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criterion. This chain reaction must have a high G value if such a large fraction of the molecules are to be involved. A determination of the G value from the alteration seen in the infrared absorption spectrum where it is estimated that roughly 10% of the molecules have been altered, is about 400. The G value observed for the formation of free radicals in organic crystals is typically 1 to 3 (Box and Freund, 1959). The extensive isotopic mixing seen in D_2-succinic acid can be understood in the following general way. It will be recalled that when the hydrogen atom vacancy or kenon is formed on a molecule one can expect the possibility of the deuterium atom being moved about on the molecule by means of the "shuffling" that can go on due to the presence of this "hole". Thus the kenon is expected to promote isotopic mixing on each molecule it visits and if the kenons are transferred from molecule to molecule and able to visit adjacent lattice sites without mutual destruction, they will essentially visit every molecule in the crystal, causing isotopic mixing on each. It may well be that in this case the free radical chain reaction is a non-thermal reaction or nearly so proceeding with zero or near zero activation energy since it proceeds very rapidly at room temperature, a fact already remarked upon by Pooley and Whiffen in connection with the ESR data. Furthermore, in the present work the extent of the isotopic mixing was not increased after the crystal was annealed at 100°C for 6 hours indicating that the mixing may well be complete. As one can see, the above scheme, namely the occurrence of large scale isotopic mixing through the agency of the mobility of the kenon is the simplest and most general way that one can expect extensive isotopic mixing to occur.

To undertake a detailed discussion on isotopic mixing in OO'-dideutero-succinic acid it is convenient first to collect all facts which must either be accounted for or may have some bearing on the problem.

(1) The isotopic mixing is stereospecific.

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(2) The ratio $-CH_2-\dot{C}H-/-CHD-\dot{C}H-$ is observed to be about 1:3.

(3) When irradiated and observed at 90°K the dominant feature of the ESR spectrum is a single line presumably attributable to $DOOC-CH_2-CH_2-CO\dot{O}$ or its O-hydrogen analogue.

(4) Crystals of succinic acid and D_2-succinic acid prepared in this laboratory and irradiated at room temperature showed without exception the above single line superimposed on the other spectrum as reported by other workers.

To account for the stereospecifity one requires two of the backbone H positions to be not visited by the kenon and so be precluded from the isotopic mixing. Predictions of the ratio of $-CH_2-\dot{C}H-/-CHD-\dot{C}H-$ follow according to whether it is assumed that the free radicals observed are made either by D or H bond breaking and subsequent isomeric transformations. However, on closer examination the model must be considered in the light of the peculiar structure of the succinic acid molecule and crystal (Kitaigorodskii, 1961). Figure 7.1 represents the general topology of a single one of the parallel chains which make up the crystal lattice of D_2-succinic acid. Sites which participate in the isotopic mixing are marked by an asterisk and the kenon is shown occupying one of these sites. If one imagines a kenon on one of these positions and confined to one molecule then a simple examination shows that its subsequent motion between available sites on the molecule produces only a modest amount of isotopic mixing. Complete shuffling of the three hydrogens that the kenon mobilises is not achieved because the order in which they appear reading from one end of the molecule to the other cannot be altered. Furthermore, although isotopic mixing can occur in the sense that a D atom can be brought onto the carbon backbone, both of the free radical isomers which have the kenon on the backbone would, in the ESR spectrum show coupling of the electron spin exclusively with protons in

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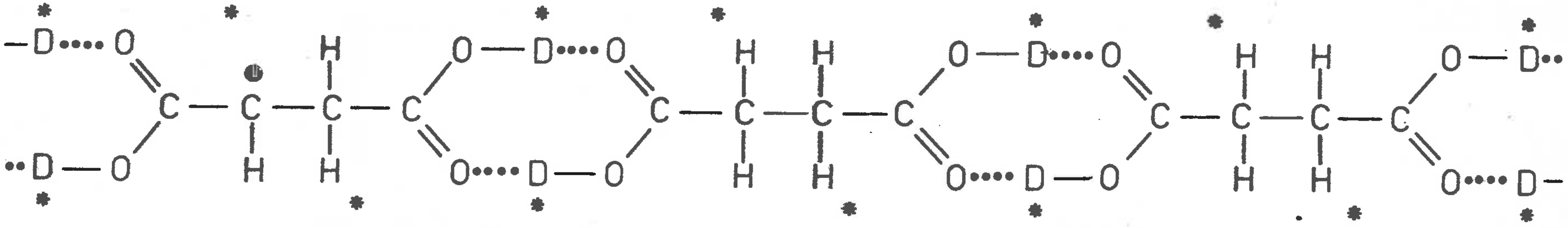

A Schematic Diagram of a Molecular Chain in Deuterated Succinic Acid.

Fig. 7.1

contradiction of the fact that $-\mathrm{CHD}-\dot{\mathrm{C}}\mathrm{H}-$ is prominent in the spectrum. Thus it seems to be necessary to invoke the transfer of kenons from molecule to molecule with the increased scope for isotopic mixing that is entailed. This may take place in the following manner in the solid. The primary act of radiation is regarded as being the production of hydrogen atom vacancies which are immediately mobile and travel a large distance, whether along the length of the chains of molecules or transverse to them being an open question. The evidence above is consistent with the radical $\mathrm{DOOC}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CO}\dot{\mathrm{O}}$ being the major initial product of the radiation, which amounts to saying that the kenons are produced on the deuterated positions. The passage of a single kenon along a path, say, down a chain of molecules results in the movement of all the hydrogens backward by one position. Most of the hydrogen atom vacancies are lost by their mutual destruction and only a few survive by being locked at crystal imperfectionsor in other special sites. One might hope to derive the $-\mathrm{CH_2}-\dot{\mathrm{C}}\mathrm{H}-/-\mathrm{CHD}-\dot{\mathrm{C}}\mathrm{H}-$ ratio theoretically from a consideration of the relative numbers of H and D atoms available for mixing. However, to attempt this at present involves many uncertainties, not the least of which is the question as to whether the free radicals actually observed in the crystal are truly representative of those one imagines to be present in a perfect model crystal.

At this stage, however, it is worth noticing one point of interest, viz., that the radical $\mathrm{DOOC}-\mathrm{CHD}-\dot{\mathrm{C}}\mathrm{H}-\mathrm{COOD}$ (or its O-hydrogen analogues) is the only isotopically mixed species revealed by the ESR. As far as the molecules which suffer isotopic mixing are concerned, it is quite possible that DOOC-CHD-CHD-COOD is present. According to this model the presence of this species could not be revealed by ESR because if it receives a "hole" it can only do so on one of the deuterated positions and coupling of the electron spin with two deuterons cannot be achieved. A close examina-

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tion of the IR data does not allow one to say more than that it could possibly be present.

The essence of the above model is that isotopic mixing is the result of a free radical chain reaction with a large G value which must be the case if the infrared absorption spectra is to be significantly altered.

In contrast to the nature of the isotopic mixing in OO'-dideuterosuccinic acid the mixing in deuterated L-α-alanine is confined to the radicals only when the crystal is annealed. The ESR spectrum of radiation damaged deuterated L-α-alanine shows that the radical initially formed is α-kenopropionic acid (CH_3-$\dot{C}H$-COOD) essentially the same radical formed in undeuterated L-α-alanine (CH_3-$\dot{C}H$-COOH). When the crystal is annealed at 100°C the ESR spectrum alters (Itoh and Miyagawa, 1964) in such a way as to indicate that the unpaired electron is interacting with deuterium nuclei which have replaced some of the hydrogen nuclei bonded to the carbon atoms. This radical is identical, both structurally and electronically, to the initial radical species. Sufficient annealing allows all four protons in the radical to be eventually exchanged for deuterons. One can easily see that this exchange is of a similar nature to that in kenosuccinic acid. For discussing the occurrence of H-D exchange in α-kenopropionic acid the concept of free radical isomers can again be considered. However, the difference in this case from succinic acid is that more deuterium atoms must be involved to allow complete exchange, and radical isomeric transformations alone will not explain the occurrence of complete exchange. It seems necessary to presume that deuterium ions from the amino and carboxyl groups of the molecules in the crystal are "pooled". In other words these deuterium ions move through the crystal at an elevated temperature and replace any hydrogen atoms associated with the carboxyl group of the radicals. Now the initial radical is in thermal equilibrium

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with its isomers at this temperature and as they are continually interchanging this allows the deuterium ion from the carboxyl group to be transferred to one of the carbon atoms. An example of a possible reaction sequence is:

$$CH_3\text{-}\dot{C}H\text{-}COOD \longrightarrow CH_3\text{-}CHD\text{-}CO\dot{O} \longrightarrow CH_3\dot{C}D\text{-}COOH$$

If the hydrogen ion is replaced by a deuterium ion from the "pool" the following sequence is possible:

$$CH_3\text{-}\dot{C}D\text{-}COOD \longrightarrow \dot{C}H_2\text{-}CHD\text{-}COOD$$
$$\longrightarrow CH_2D\text{-}CHD\text{-}CO\dot{O} \longrightarrow CH_2D\text{-}\dot{C}D\text{-}COOH.$$

As annealing proceeds the single polar hydrogen position is kept deuterated by exchange with the "pool" and the deuterons are gradually transferred by isomeric transitions to the carbon backbone. Eventually all protons in α-kenopropionic acid are replaced by deuterons. The concept of deuterium ions being "pooled" in the crystal is the essence of the model put forward by Itoh and Miyagawa (1964) who first observed H-D exchange in L-α-alanine. This leads one to infer that protonic conduction (Hoffman and Smyth, 1949) may be possible in L-α-alanine at least to a limited extent at elevated temperatures.

Turning now to the results from the infrared spectra it was observed that no alteration was seen. The spectra remained the same immediately after irradiation or after complete mixing had taken place in α-kenopropionic acid. These observations confirmed the infrared results of Itoh and Miyagawa. One can say in this case of isotopic mixing that it is confined to the radicals and that no extensive mixing in the molecules of the crystal occurs. Since the infrared spectrum is not very sensitive to changes in the crystal and the mixing in α-kenopropionic acid is not detectable then the alteration of the infrared spectrum from deuterated succinic acid is a result of gross mixing in the molecules as well as in the free radicals.

Regarding the fact that deuterated α-kenopropionic acid (an I-radical) disappears at 160°C without any conversion to an H-radical, the kenon hypothesis does provide an explanation whereby these radicals could be thermally annealed by the steady release of I-radical kenons into (mobile) H-radical kenons. However, in the light of no extensive isotopic mixing taking place during annealing of α-kenopropionic acid, one must consider the migration of these I-radicals which may occur either by the migration of the radical as a whole or by the migration of the I-radical state due to the movement of a molecular group from molecule to molecule.

To sum up, this discussion has revealed two distinct types of isotopic mixing. In succinic acid, the evidence points strongly to gross mixing through the crystal while in L-α-alanine it is confined to the radicals only. The extensiveness of the mixing in irradiated D_2-succinic acid leads one to postulate a free radical chain reaction which is the same in essentials as kenon migration with radical isomeric transformations promoting mixing at each site the radical state resides on. The contrasting situation in L-α-alanine has suggested that the deuterium ions in the crystal form a "pool" which exchange positions with each other presumably by an ionic transfer akin to that involved in protonic conduction.

7.7 <u>Free Radical Pairs</u>

Since 1964 free radical pairs have been observed in at least six organic single crystal systems after being irradiated at LNT. The radical pairs formed are listed in table 7.1 and it will be noted that in all cases except one, the pairs are formed between H-radicals. One will recall from the predictions of the hypothesis that kenon diffusion can account for free radical pair formation. It should be mentioned that no experimental studies were undertaken on free radical pairs in the present work. Chapter 3.2.2 outlined the reason why

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TABLE 7.1

A LIST OF KNOWN FREE RADICAL PAIRS IN SINGLE CRYSTAL SYSTEMS

Compound	Pairs formed between the following Radicals	Type of Radicals Forming the Pair	Temperature at which Pairs Form	Reference
Glyoxime	$CH-NOH-CH-N\dot{O}$	H - H	LNT	Kurita and Kashiwagi (1966)
Methylglyoxime	$CH-NOH-C(CH_3)-N\dot{O}$	H - H	LNT	Kurita and Kashiwagi (1966)
Dimethylglyoxime	$C(CH_3)-NOH-C(CH_3)-N\dot{O}$	H - H	LNT	Kurita, (1964a)
Dimethylglyoxime -O-d_2	$C(CH_3)-NOD-C(CH_3)-N\dot{O}$	H - H	LNT	Kurita and Kashiwagi (1966)
Oxalic Acid	$HOOC-CO\dot{O}$	H - H	LNT	Moulten et al, (1967)
Mono-fluoroacetamide	$\dot{C}H_2-CO-NH_2$ and $\dot{C}HF-CO-NH_2$	I - H	LNT	Iwasaki and Tariyama (1967)

no such low temperature work was done.

Accepting the existence of radical pairs one has either to believe that they are formed in pairs as such or the radicals are formed singly and pair up later on. Just how likely or unlikely is the first mechanism is unknown but considering the easy production of pairs which proceeds with a G value at least as large as for the production of single radicals one is inclined to favour the mechanism involving separate production and later pairing by migration. The most likely migration mechanism associated with the radicals in allowing them to come together is kenon diffusion. This is the most likely possibility especially as the pairs are produced at such low temperatures that gross radical migration seems to be out of the question. Now when a radical arrives on a site adjacent to another radical it can be expected that this radical sees a slightly different environment than when not on this particular site. This arises from the fact that bond angles of those molecules which are changed into radicals alter slightly. When two radicals are in this situation the binding energy may be such that it will allow either the two radicals to dissociate again or to hold them together. The later situation appears to be the more favourable one particularly as the pairs exist at LNT. All radical pairs formed at LNT begin to disappear when the temperature is raised; in one case (Kurita and Kashiwagi, 1966) the pairs existed for a very short time at room temperature. The nature of this reaction allows either one of two possible reactions to take place as the crystals are warmed to room temperature. The radicals comprising the pairs may be able to react to annihilate the two unpaired spins (an intrapair reaction) after they overcome an energy barrier of recombination or they can dissociate again. Kurita and Kashiwagi reported that before the ESR spectrum from radical pairs in dimethylglyoxime disappeared at room temperature the spectrum altered in such a way as to indicate that the radicals comprising the pairs had moved apart by a distance of one molecular spacing. This evidence appears to point to the latter reaction mentioned above, as being the more likely at least in this case. Measurements on the absolute concentration of all radicals as the crystal ages can provide further evidence regarding this reaction; the concentration of isolated radicals is expected to increase with dissociation of the pairs. No such measurements have been reported to date.

Other workers on radical pairs have also shown that the same radicals also exist in isolation. From consideration of the simple model on which pair formation can be based two possibilities exist for radicals occurring in isolation. In the first instance one can look at their existence as resulting from thermodynamic equilibrium existing between the pairs and the isolated radicals formed by the dissociation of the pairs. Alternatively, some radicals after formation are unable to migrate because of impurity defects or dislocations in the crystal inhibiting their movement.

In the case of monofluoracetamide where the radical pairs are composed of H- and I- radicals and the isolated radicals are of the I-type the hypothesis provides a suitable explanation. Here it is reasonable to expect only the H- radicals to migrate, after irradiation, to the neighbourhood of I- radicals. As the temperature is raised to 200°K an intrapair reaction takes place as very few H- radicals are seen at this temperature.

To sum up, this discussion on free radical pair phenomena has pointed out that it is most likely that the pairs are formed as a result of post-irradiation events. The free radicals immediately after formation at LNT migrate by kenon diffusion until they arrive on adjacent sites and are held bound by their mutual distortion of the lattice. When the crystal is warmed then either there is an intrapair reaction or the pairs dissociate to form isolated radicals. The possibility of the radical itself migrating at LNT seems most unlikely.

The alternative hypothesis, viz. that the radical pairs are formed in situ has been put forward by Kurita (1964b). The model proposed in this case states that the second radical of the pair is formed as a result of hydrogen abstraction and not by the primary act of the radiation. At this stage one has to accept this model as competing with the model discussed in this section until some way of distinguishing the two processes can be found. The best way of approaching the investigation of this question would seem to be a search for and study of pairing equilibria. As the free radical pairs are destroyed thermally, the strongly split spectrum will also disappear and the spectrum of the isolated radical will increase. If a pair in equilibrium exists then lowering the temperature again causes the reappearance of the easily recognisable strongly split spectrum of the pairs. If one could observe this then excellent evidence for the reality of kenon mobility would be provided.

7.8 Macroscopic Diffusion

The results of the experiments to observe macroscopic diffusion of the free radicals allowed one to place an upper limit on the diffusion coefficient. This limit, however, does not rule out kenon diffusion as a migration mechanism. It may be that an activation energy of migration prevents the radical state from being mobile below the reacting temperature. Further, at this stage one is unable to distinguish between whether it is the radical state or the radical as a whole that migrates when the free radicals recombine.

7.9 Overall Conclusions and Avenues for Future Work

To sum up, this study on free radical phenomena has given a further insight into the knowledge of the properties and behaviour of free radicals in irradiated organic crystals. The study of irradiated crystals by ESR and spectroscopic techniques provides interesting new ways of acquiring further knowledge of molecular phenomena. The preceding discussions reveal that out of all new experimental evidence obtained in this work on post-irradiation phenomena, the isotopic mixing discovered in OO'-dideuterosuccinic acid stands out as the major fact whose explanation is contingent on the validity of the kenon hypothesis. All other evidence, which although conforms in a general way with the ideas of the hypothesis, can at this stage be given alternative explanations; that is, one must still consider the diffusion of the radical as a whole as a competing hypothesis. Reaction kinetics of radical destruction and

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the kinetic isotope effect have established that free radicals migrate but do not allow one to distinguish the mechanism involved. The thermal annealing of I- radicals, which occurs in several cases studied in this work, could possibly be due to the diffusion of the radical as a whole. However, it could equally be held that the I- radical might migrate by the movement of a molecular group from a neighbouring lattice site to the radical site, but at this stage neither of these two mechanisms can be distinguished. In any case, the kenon hypothesis still provides an adequate explanation whereby the I- radical kenons could steadily be released into the (mobile) H- radical state to allow the annealing to proceed.

To understand more about the free radical migration mechanism, particularly during annealing of the radicals, future work should entail self diffusion experiments in those crystals studied in this work. (A recent communication (Sherwood, 1967) has revealed, in fact, that self diffusion can be detected and studied by tracer techniques in hydrogen bonded organic crystals). The activation energies obtained should then be compared with those listed in this work for free radical destruction. The study of isotopic mixing and deuterium isotope effect should be extended to crystals either partially or completely deuterated which were not available for the present work. This would yield more detailed information on the processes involved.

APPENDIX A

THE ESR SPECTROMETER

The ESR spectrometer used to detect and measure the concentration of free radicals studied in the present work was that described by Cavenett (1964). Briefly this was an X-band superheterodyne type using an intermediate frequency of 45 megahertz and a modulation frequency of 135 hertz. The magnet and its control unit were Newport Instruments type C5.

During the project some time was devoted to improving the sensitivity of the spectrometer. According to Cavenett (1964) and Feher (1957) the main factors affecting the sensitivity of a superheterodyne spectrometer are noise sources arising from the frequency fluctuations in the klystron output and sample cavity and microphonics originating in the detecting bridge and waveguide assembly. Thus it was decided to reduce these noise sources as much as possible and alterations were made. These included a fully transistorized klystron frequency stabiliser (whose circuit was developed at the National Standards Laboratories, C.S.I.R.O., Sydney), a temperature controlled oil bath for the signal klystron, regulated DC voltage supplies for the filaments of the two klystrons and a new low frequency selective amplifier. Circuits for all of these modifications are given in Appendix B. Furthermore, precautions had to be taken to reduce the vibrations of a rotary pump, required to evacuate the variable temperature cavities, from reaching the waveguide assembly.

With all of the above modifications a noticeable improvement was made in the sensitivity of the spectrometer.

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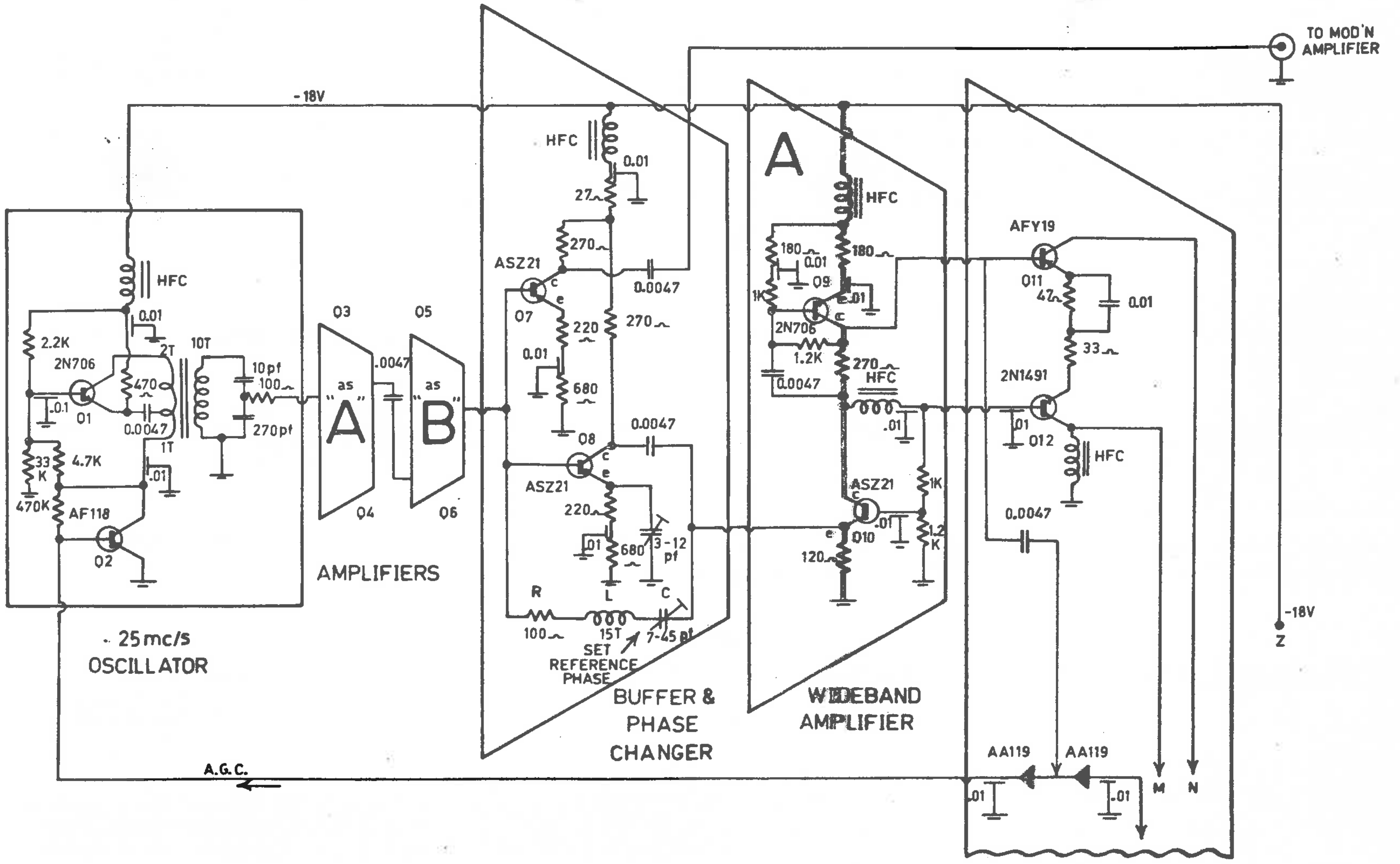
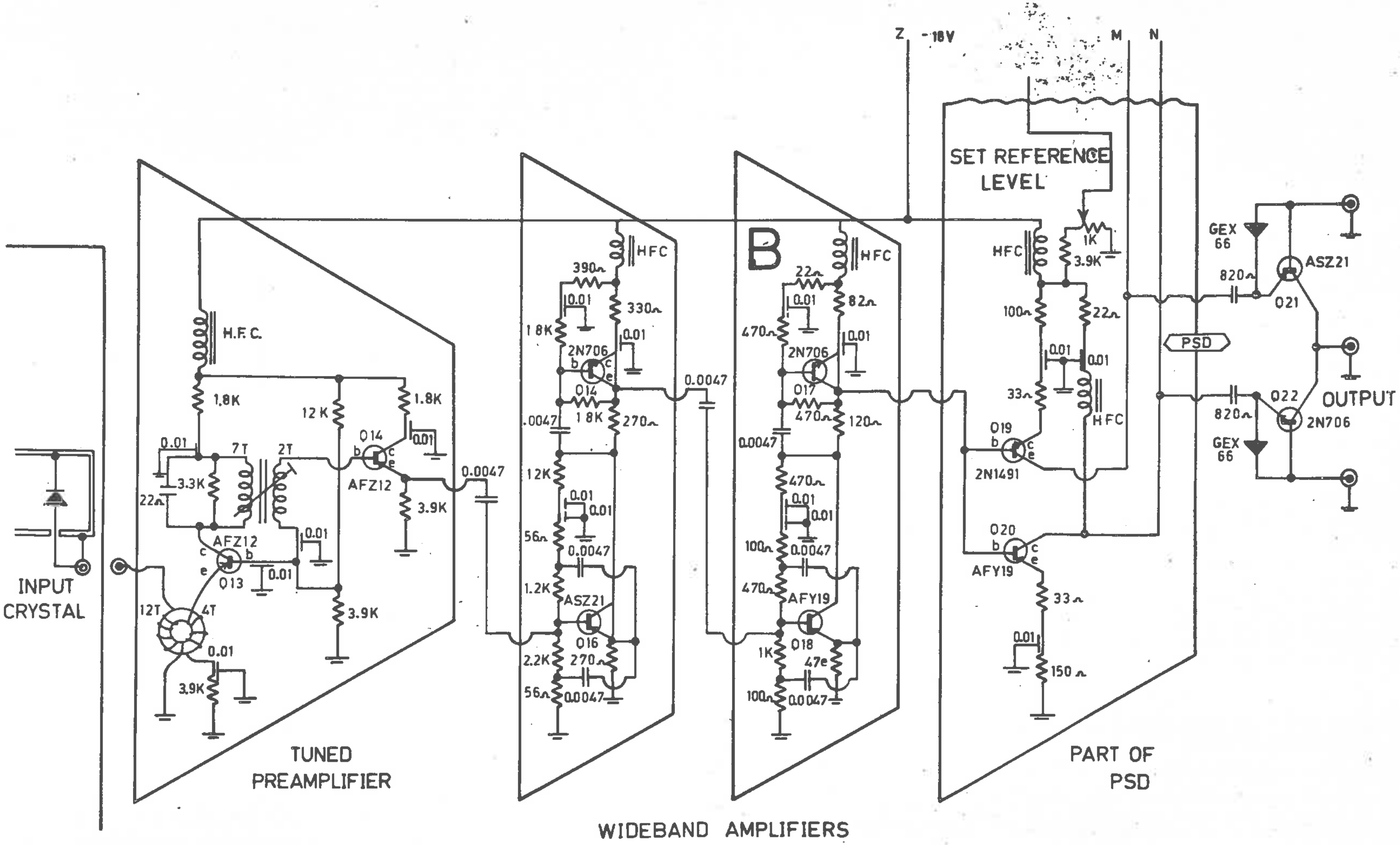
APPENDIX B

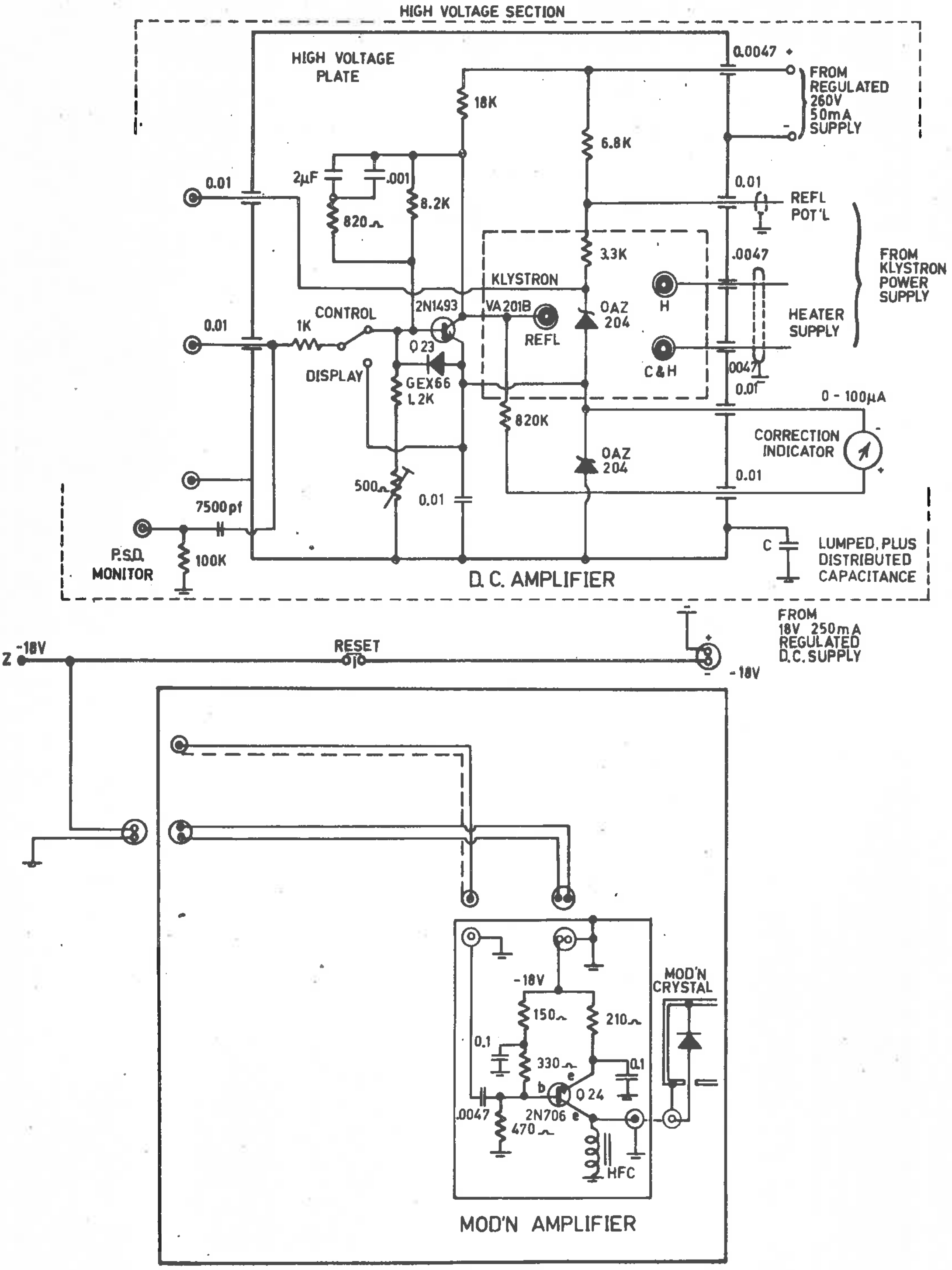
CIRCUITS OF MODIFICATIONS TO ESR SPECTROMETER



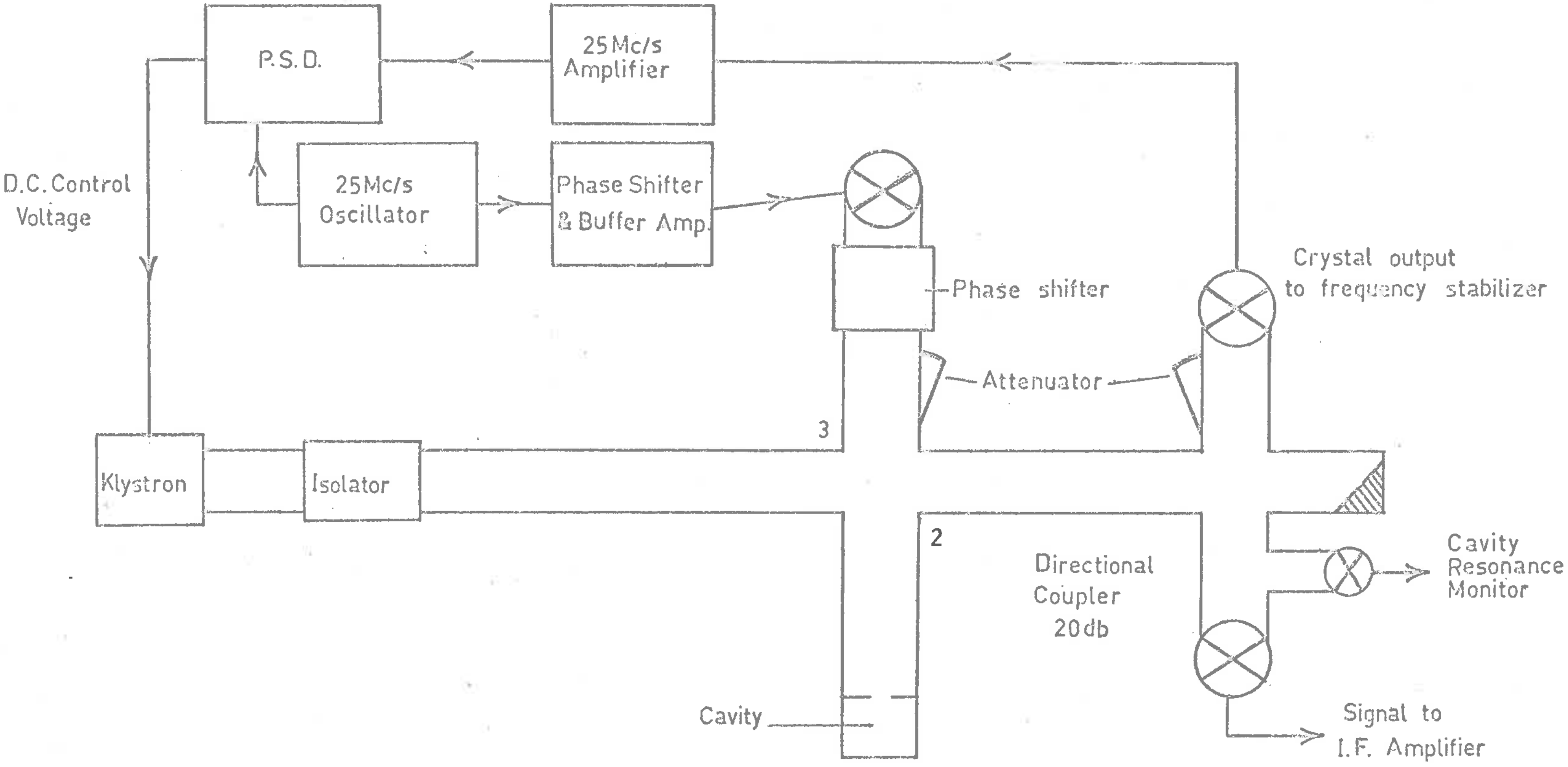
Klystron Frequency Controller (Signal Amplifier)



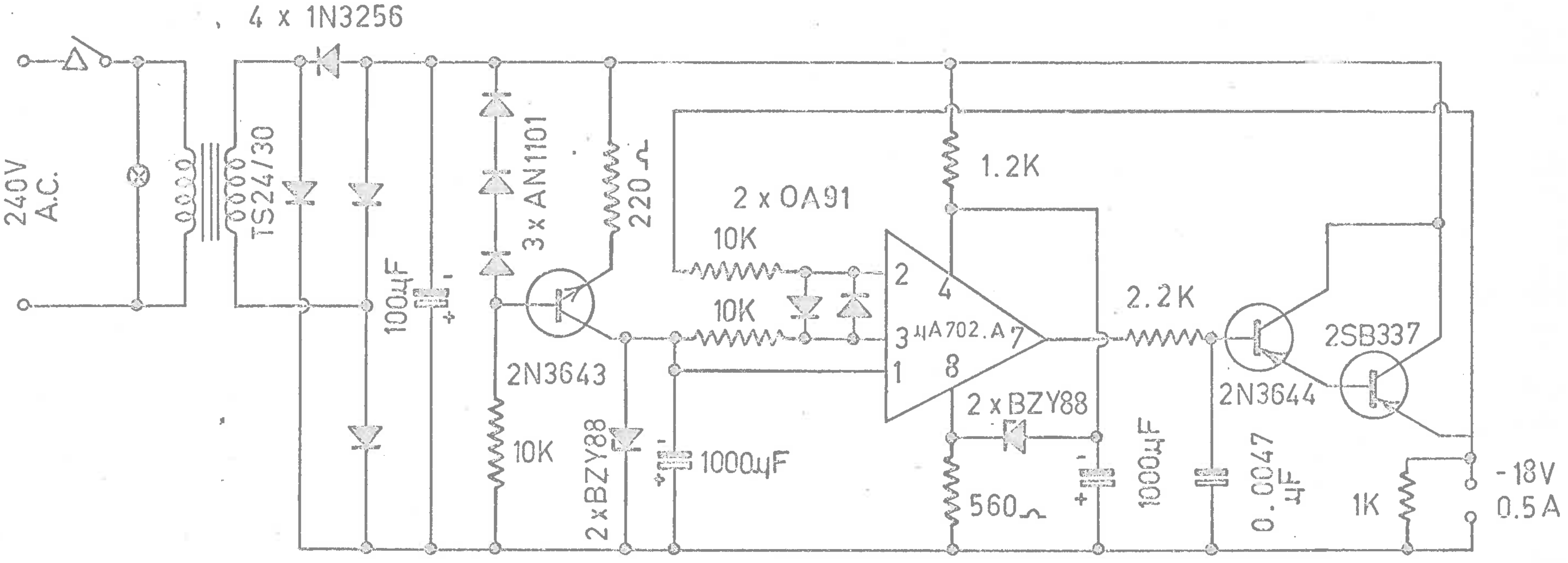
Klystron Frequency Controller (25Mc/s. Oscillator and Reference)



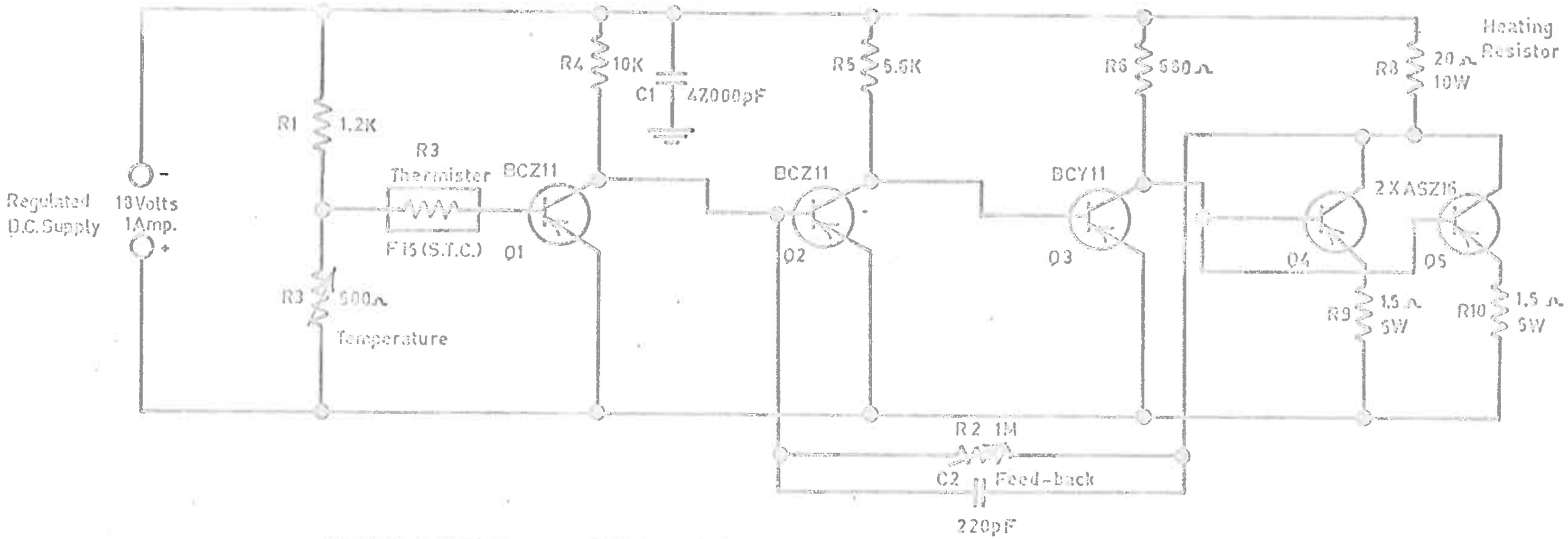
Klystron Frequency Controller (D.C. and Modulation Amplifiers.)



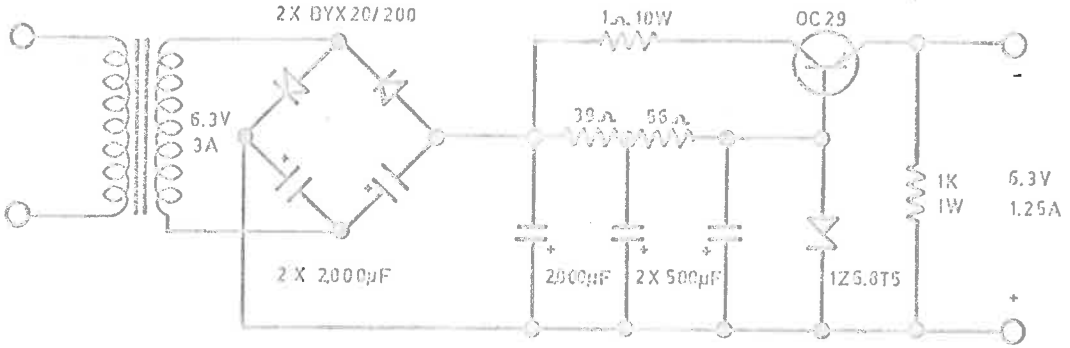
Microwave Frequency Control Circuit



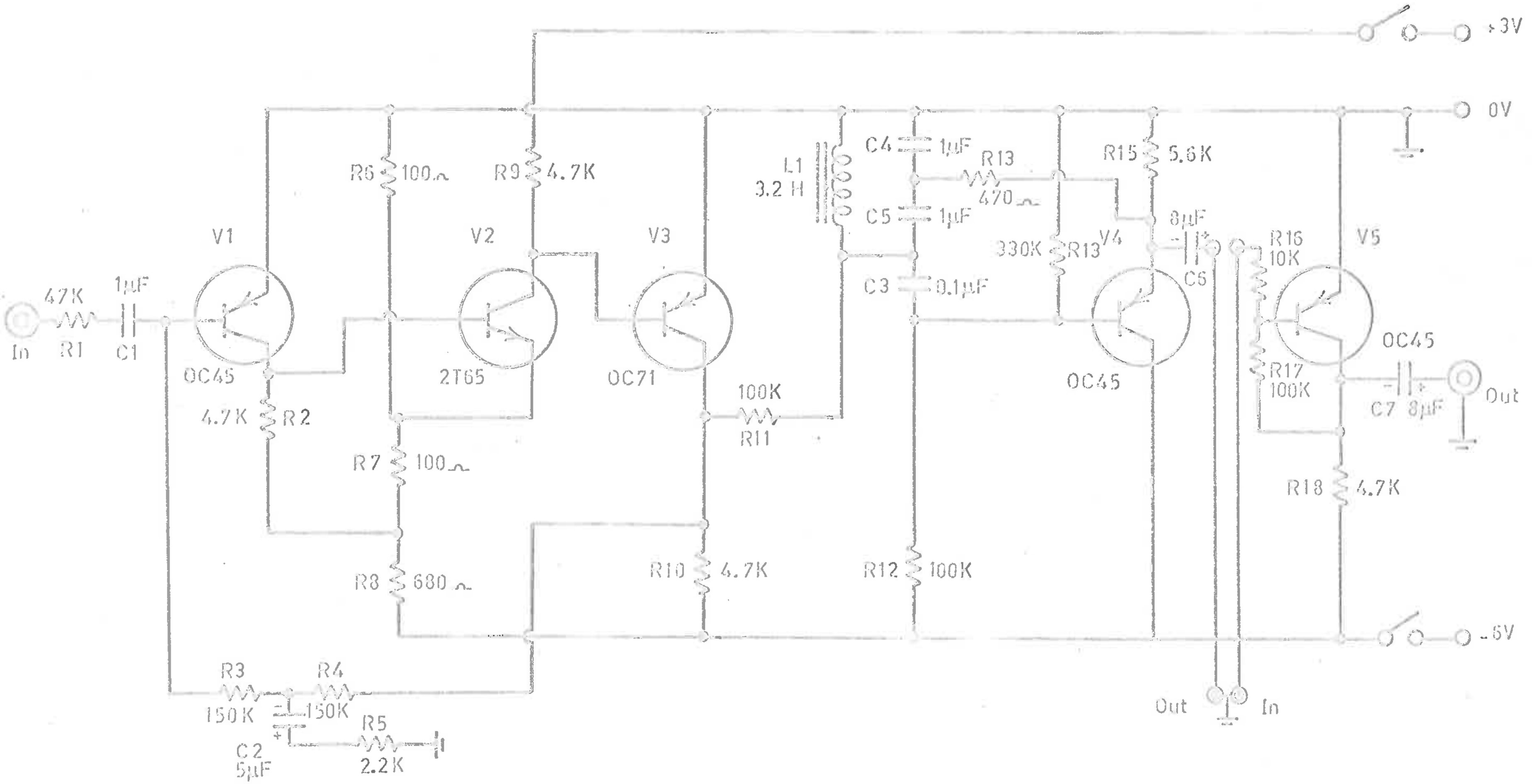
18 V REGULATED POWER SUPPLY FOR KLYSTRON FREQUENCY STABILIZER



KLYSTRON TEMPERATURE CONTROLLER



D.C. FILAMENT SUPPLY



SELECTIVE AMPLIFIER

APPENDIX C

MEASUREMENT OF RADICAL CONCENTRATION FROM THE ESR SPECTRUM

In most experiments undertaken in this work, the concentration of free radicals was needed to be known. Only the relative concentration, viz. the concentration relative to a standard, was in fact needed since the difference between the absolute and relative concentration is a constant factor for a given set of instrumental conditions. The ESR spectrometer used in the project recorded the first derivative of the ESR spectrum and this was the variable related to the concentration that was observed. The following argument will show that the first derivative of an ESR spectrum varies in proportion to the concentration of radicals. It is well known (Ingram, 1958) that the line shape of an ESR spectrum is either a Gaussian or Lorentzian function or a combination of both. The type of function depends on what interaction is the main source of broadening. A Gaussian line shape results from the dipolar spin interaction alone, which is to be expected for free radicals in organic crystals since they are seldom broadened by strong spin-lattice interaction. The spin-orbit coupling is very small for such radicals. In fact Simmons (1962) has shown that the line shape for organic free radicals is Gaussian and it is homogeniously broadened. Assuming the lineshape is Gaussian the parameter observed from the first derivative curve (shown in fig. C1) of a simple Gaussian curve is $h = h_1+h_2$ where h_1 and h_2 are the values of the derivative at the two points of maximum slope, respectively. This parameter can very easily be shown to vary linearly with the area under the total ESR absorption curve, $g(H-H_o)$. The above argument has assumed that saturation broadening is not present. Such broadening is characteristic for organic radicals as they have long spin-lattice relaxation times (Ingram).

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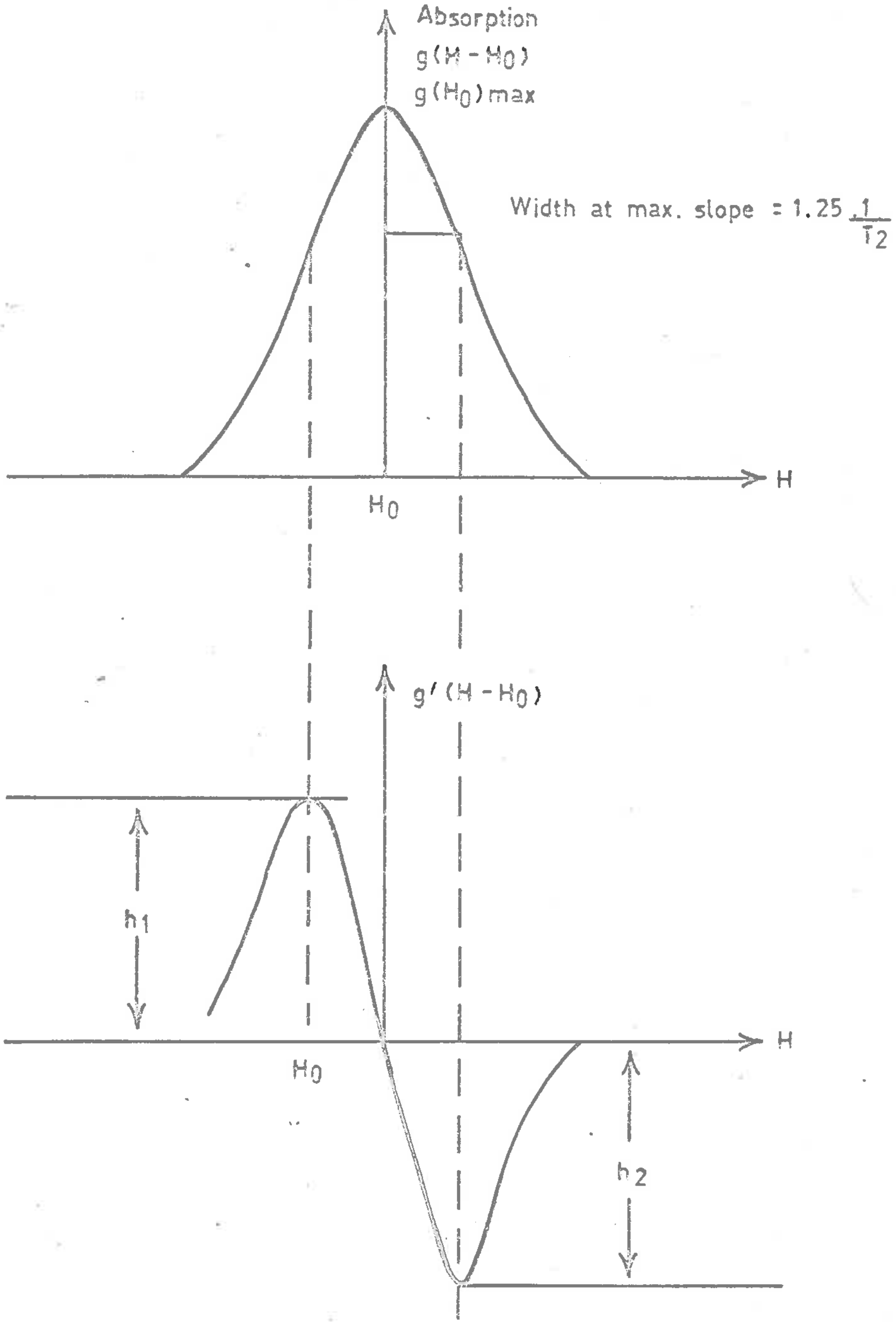

Gaussian line shape and first derivative.

Fig. C1

In all the ESR investigations done in this work, the microwave power was set so that the absorption was not saturated.

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