RADIOLYSIS STUDIES ON REACTIVE INTERMEDIATES

Technical Progress Report

for Period November 1, 1975 - November 1, 1976

Larry Kevan

Department of Chemistry

Wayne State University

Detroit, Michigan 48202

November, 1976

Prepared For

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

UNDER CONTRACT NO. E(11-1)-2086

NOTES
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration nor any of their employees nor any of their contractors, subcontractors, or their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

leg

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

During the past year we have focused on the development of new experimental electron magnetic resonance methods and new theoretical models to study reactive reaction intermediates and on the application of these and other methods to study radical and ionic intermediates produced by high energy radiation. We have continued development of electron spin echo spectrometry for studying molecular orientation around trapped radicals, have suggested a new electron spin-lattice relaxation mechanism applicable to glasses, have shown a correlation between electron spin-lattice relaxation times and trapped radical decay and have shown how electron-electron double resonance measurements of cross relaxation can be analyzed to give radical-radical correlation distances. A new model of electron localization in alkanes has been developed, electron solvation in alcohol-alkane mixtures has been studied theoretically and an improved model of electron solvation times has been formulated. Radical reaction intermediates have been detected and identified by spin trapping in methanol, cyanoalkyl and fluoroalcohol liquids, and by X and Q band ESR in methyltetrahydrofuran glass. In aqueous glasses the electronic structure of $O^{\cdot -}$ and the first solvation shell geometry of $e_t^{\cdot -}$ have been deduced by ^{17}O substitution. Electron tunneling as a function of the $e_t^{\cdot -}$ energy state and the photoionization mechanism of indole in solution have been investigated.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability

or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately owned rights.

RADIOLYSIS STUDIES ON REACTIVE INTERMEDIATES

Report Period: November 1, 1975 - November 1, 1976

The efficient utilization and storage of energy requires an incisive knowledge of a variety of chemical reactions. In order to optimize and control chemical reactions, mechanisms of reaction must be understood in addition to gaining a thorough knowledge of the physical and chemical characteristics of energetic reaction intermediates. During the present report period our research has focused on the development of new experimental electron magnetic resonance methods and new theoretical models to study reactive reaction intermediates and on the application of these and other methods to study radical and ionic intermediates produced by high energy radiation. High energy radiation offers a convenient method by which radical and ionic intermediates may be generated, and the methodology of radiation chemistry allows one to obtain considerable selectivity of specific energetic reaction intermediates.

One general direct method for examination of short-lived, reactive chemical intermediates is matrix trapping. Matrix trapping is typically most efficient in disordered matrices. Therefore we have sought to develop methods to maximize the chemical information available from trapped species in disordered matrices where spectroscopic resolution is generally poor. Electron spin resonance (ESR) is quite specific for detecting radicals and radical ions and we have concentrated on the application of ESR methods in the past year. In particular we have continued development of advanced ESR methods such as electron spin echo spectrometry, spin-lattice relaxation time measurement by pulsed ESR and electron-electron double resonance (ELDOR).

Nineteen papers have been published or submitted for publication during this report period. In addition, two books on topics related to this ERDA

supported research have been published. The following sections describe (1) research highlights, (2) research publication list, (3) scientific talks presented and (4) Ph. D. theses completed.

The principal investigator has spent an average of 35% of his time during the academic year and 100% of two summer months on this project. Although he is currently on sabbatical leave, with ERDA's approval, he anticipates that this average percentage will remain the same for the rest of this academic year.

1. Research Highlights

Reference numbers will relate to the research publications listed in section 2.

New Electron Magnetic Resonance Methods Applied to Disordered Systems

We are currently using the technique of electron spin echo spectrometry to deduce the matrix molecular structure around trapped radicals. We have previously shown that modulation patterns in electron spin echo decay curves can be analyzed for trapped electrons in disordered polar matrices to give detailed data on the arrangement of matrix molecules around the trapped electron. This is possible because the modulation pattern reflects weak electron-nuclear hyperfine interactions which are sensitive to distance and which do not lead to structure in the ordinary ESR spectrum. We have now extended such studies to trapped electrons in deuterated nonpolar glassy matrices like 3-methylpentane- d_{14} .⁹ By fitting a simulated modulation pattern to the experimental one we have shown that the electron's solvation structure is characterized by 18-21 equivalent nearest neighbor deuterons at a distance of 3.0-3.2 Å with essentially zero isotropic hyperfine coupling.

From the structure of 3-methylpentane we suggest that there must be 6-7 first solvation shell molecules around this solvated electron. This is of particular importance since it is the first geometrical data on solvated electron structure in nonpolar matrices. Furthermore, it has shown that the only previous theoretical model for electron solvation in alkanes, the so-called microdipole model, cannot be correct. This has led us to develop a new model which will be discussed below.

Most of our electron spin echo modulation studies have dealt with the analysis of two pulse modulation patterns in which ideally a 90° pulse is followed by a 180° pulse at time τ after the 90° pulse and the echo occurs at time 2τ . Three pulse experiments have also been carried out in which two 90° pulses separated by time τ are followed by a third 90° pulse at time T after the second pulse. The echo occurs at time $2\tau + T$. Since T can be much longer than τ , this method is effective for probing very weak hyperfine interactions in the presence of stronger ones while both weak and strong hyperfine interactions contribute to the two pulse echo modulation. For zero isotropic hyperfine coupling and only dipolar coupling we have found that the three pulse echo modulation changes in phase by 180° at a characteristic time T_p . We have now analyzed this phase reversal in detail⁵ and have derived a simple expression which relates the time of phase reversal to the dipolar distance to weakly interacting magnetic nuclei. This phase reversal is seen experimentally for trapped electrons in 10 M NaOD/D₂O aqueous glass where it corresponds to interaction with next nearest neighbor deuterons. However, for trapped electrons in methyltetrahydrofuran (MTHF) glass no phase reversal is observed even though it is apparently expected on the basis of the geometry deduced from two pulse echo modulation results. We have resolved this anomaly by complete spectral simulation of three pulse electron spin echo signals.⁵ We have found that the magnitude of the isotropic hyperfine coupling is very critical for observation of phase

reversals. In fact, the absence of phase reversal in the three pulse echo modulation from trapped electrons in MTHF glass is consistent with the results obtained from two pulse echo modulation studies and confirms the existence of a small isotropic hyperfine coupling to the nearest neighbor deuterons. This study has extended the utility of three pulse echo modulation patterns for deducing structural information about the molecular surroundings of trapped radicals.

Because deuterons produce a longer modulation cycle than protons, deuterons have proved most convenient experimentally to study radical-matrix molecule interactions by electron spin echo modulation methods. However, deuterons have a significant quadrupole moment which may affect the analysis of the modulation patterns. Thus it is important to understand how the modulation pattern may be affected by the presence of small quadrupole couplings. We have investigated this problem by simulating both two pulse and three pulse modulation patterns for relatively weak dipolar interactions (electron-nuclear distance $\geq 3 \text{ \AA}$) with different values of quadrupole couplings.¹⁷ We have found that a small quadrupole coupling has little effect on three pulse modulation patterns but that a coupling of 0.2 MHz produces a very characteristic modulation pattern that is distinguishable from the dipolar coupling pattern at twice the nuclear modulation frequency. We have not seen such a pattern experimentally for trapped electrons in deuterated organic glasses and deduce that quadrupole interactions are not complicating the analysis of these data. However, it will be interesting to search for the distinctive quadrupolar modulation patterns with other nuclei having quadrupole moments.

In summary, we feel that we have gained a good theoretical understanding of how to analyze electron spin echo modulation patterns and we hope to apply this knowledge to the matrix structures surrounding various types of trapped radicals and in particular to the orientation of molecules adsorbed on catalytic surfaces.

A second technique whose applicability to disordered systems we are investigating is the direct measurement and interpretation of electron spin-lattice relaxation times. During the past year we have completed construction of a pulsed ESR spectrometer which directly measures spin-lattice relaxation times (T_1) by a saturation recovery method (Ph. D. thesis of M. K. Bowman). By measuring T_1 vs temperature it is often possible to deduce the relevant spin-lattice relaxation mechanisms in different temperature ranges. However, we have found for trapped electrons and hydrogen atoms in disordered glassy matrices that the relaxation rate is proportional to temperature over a relatively large temperature range (typically 5-100 K) and that this relaxation rate is several orders of magnitude faster than that measured for similar radicals in single crystals. This has led us to develop a new electron spin-lattice relaxation mechanism which appears to be uniquely applicable to the glassy state and which may be responsible for the low temperature spin-lattice relaxation of many molecular radicals in molecular glasses.¹⁸ The mechanism depends on modulation of the electron nuclear dipolar interaction between a trapped radical and nearby magnetic nuclei by the motion of tunneling nuclei or groups of nuclei in the disordered glass. In glassy systems it appears that modulation by tunneling modes is much more effective than modulation by lattice phonons for electron spin lattice relaxation in low and intermediate temperature ranges, typically to ≈ 100 K. The quantitative mechanism predicts: (a) that the spin-lattice relaxation rate T_1^{-1} is linearly proportional to temperature, (b) that T_1^{-1} is dependent on glass preparation details to the extent that this affects the number and distribution of tunneling groups, (c) that T_1^{-1} is sensitive to the isotopic composition of magnetic nuclei in the glass, (d) that T_1^{-1} for a given radical is larger by several orders of magnitude in a glassy environment compared to a crystalline one, and (e) that $T_1^{-1} \propto \omega^{-2}$ where ω is the ESR frequency. Predictions (a) to (d) have been tested and supported by T_1 measurements vs temperature on trapped electrons in C_2H_5OH , C_2D_5OH and C_2H_5OD glasses.

We expect that the important tunneling nuclei around various types of trapped radicals can be deduced by suitable isotopic substitution. Thus this new spin-lattice relaxation mechanism can lead to dynamic information about the matrix in the vicinity of a trapped radical. This may have important consequences for understanding the limitations on electron tunneling and on radical detrapping in glassy matrices.

The possible correlation of radical detrapping and electron spin-lattice relaxation times has been investigated indirectly for trapped hydrogen atoms in sulfuric acid glassy matrices.¹³ The relaxation time of an irradiation produced hydrogen atom at a given temperature depends on the irradiation temperature. We have found at a given observation temperature that trapped hydrogen atoms with a shorter T_1 decay more slowly than those with a longer T_1 . The mechanistic details of this correlation are not yet understood but it appears that we have found a sensitive method to probe the structural relaxation around a trapped radical and perhaps to predict the relative rates of radical detrapping and reactions in disordered solids.

We have also explored a different approach to information about spin-lattice relaxation mechanisms of paramagnetic species. In some cases both allowed ESR transitions in which only an electron spin flips and forbidden ESR transitions in which both electron and nuclear spins flip can be observed. A case in point is trapped hydrogen atoms. These two types of transitions saturate differently with microwave power. We have shown experimentally that it is possible to distinguish dominant radial or angular modulation mechanisms of electron nuclear dipolar interaction which lead to spin-lattice relaxation by carrying out differential saturation studies of allowed and forbidden transition (S. Schlick and L. Kevan, *J. Magn. Resonance*, 22, 171 (1976)). The method involves a steady state measurement of ESR intensities that may be done with a conventional ESR spectrometer.

In the current report period we have applied this method to trapped hydrogen atoms in sulfuric acid glass and have shown that the spin-lattice relaxation is dominated by angular relaxation processes.¹⁰ This is the case at both 4 and 77 K and suggests that the tunneling mode relaxation process discussed above can be even more concretely described in terms of an angular tunneling motion. This point needs to be investigated theoretically in more detail, however, before any firm conclusions can be made.

In summary, we feel that we have demonstrated that a new electron spin-lattice relaxation mechanism involving tunneling modes is relevant to trapped radicals in disordered glassy systems and that this mechanism can lead to dynamic information about the matrix and about radical detrapping.

A third technique we have applied to radicals in glassy matrices is electron-electron double resonance (ELDOR). We have shown that this magnetic resonance technique is useful for studying magnetic energy transfer between two different radical systems in the same matrix. In ELDOR two microwave frequencies are used. One microwave frequency pumps a particular ESR line while a second microwave frequency detects the effect of this pumping on a second ESR line. Cross saturation can be observed if the spin-lattice relaxation time of one species is significantly less than that of the other species. Electrons and radicals trapped in γ -irradiated organic glasses meet these criteria and have been studied by ELDOR.^{12, 19} The cross saturation effects in methyltetrahydrofuran and 3-methylhexane glasses have been studied as a function of radiation dose, temperature and frequency difference between the pumping and detecting microwave frequencies. The temperature effects support the interpretation that the cross saturation occurs by dipolar cross relaxation. The dependence on the microwave frequency difference indicates that cross relaxation is dominated by single step rather than multi-step processes. From directly measured electron spin-lattice relaxation times it is possible to obtain cross relaxation times from the ELDOR response as a function of pumping

microwave power. To utilize these cross relaxation times, which have not been measured for disordered systems before, we have developed an analysis of the relationship between cross relaxation times and the dipolar correlation distance between the radicals and electrons that are cross relaxing. This involves knowledge of the cross relaxation lineshape which is not well understood theoretically. We have concluded that this lineshape is Lorentzian in magnetically dilute systems. Then our new analysis indicates that typical electron-radical correlation distances in these organic glasses are $10 \text{ \AA}$.

ELDOR has proved useful for studying both magnetic energy transfer rates and also the spatial correlation between two types of radicals produced in the same disordered matrix.

In summary, we believe that we have significantly advanced the arsenal of experimental techniques available to study trapped radicals in disordered matrices. The electron spin echo technique is the most fully developed and it has already yielded important and unique information on electron solvation in both polar and nonpolar matrices. The relation between direct electron spin-lattice relaxation times and dynamic properties of the matrix and of the radicals looks extremely promising but requires further development and quantification. ELDOR has been developed primarily for studying magnetic energy transfer. ELDOR can also give unique information, but it is currently limited to suitably selected systems in the context studied here. ELDOR is perhaps more widely applicable to purely structural studies on unknown radicals.

Application of ESR Methods to Reactive Radical Intermediates

The general primary goals in the study of reactive radical intermediates

in chemical reactions are detection and identification. Trapping in disordered matrices is extremely useful for detection but all too often the poor resolution makes identification uncertain or impossible. During this report period we have utilized several somewhat special techniques using ordinary ESR spectrometers, in contrast to the previous section, to improve the poor resolution in disordered matrices. We have stressed the utility of combining X- and Q-band ESR investigations, of applying spin trapping methods to radiolytic systems and of using ^{17}O enrichment to increase the information available in disordered systems.

Methyltetrahydrofuran (MTHF) forms a good glassy matrix when rapidly frozen and has been much used as a trapping matrix for electrons and for solute anions produced by radiolysis. However, the radicals produced by the matrix cation have not been definitively identified. We have carried out a study to resolve this question by doping MTHF into adamantane- d_{16} and using both X- and Q-band ESR to enhance the spectral resolution.² Adamantane is a useful matrix for obtaining well-resolved ESR spectra of solute radicals produced by radiolysis. The use of X- and Q-band ESR aids detection of two or more overlapping radicals when present. Variable temperature studies have shown that the following two radicals are formed from MTHF in adamantane.

Radical I is formed between ~140 to 240 K. From ~240 to 270 K the second radical II is formed while I also remains. The initial preference for formation of I can be rationalized on steric grounds. The hyperfine parameters of both radicals have been obtained, but it does not yet appear possible to successfully simulate the radical spectrum found in irradiated MTHF glass from these parameters.

We have shown that spin trapping can be usefully applied to the detection and identification of radicals produced in liquid phase radiolytic systems.^{3,8,15} Spin trapping involves the addition of a short lived reactive free radical to a compound to form a stable spin adduct radical that can be observed by ESR to identify the original radical. We have used phenyl-t-butyl nitron as a spin trap; the spin adduct is then a nitroxide radical which is observed. Three studies of this type have been completed during this report period. In liquid methanol the neutral radicals formed by γ -radiolysis were studied to probe the primary neutral radicals formed.³ In the temperature range 157 to 300 K both CH_2OH and CH_3O spin adducts are observed. Their limiting ratio at high nitron concentration is $\text{CH}_2\text{OH}/\text{CH}_3\text{O} = 1.5$ which suggests that both of these radicals are initially formed with about the same ratio as deduced in the gas phase by mass spectrometry. The melting point of methanol is 175 K but there is still considerable molecular motion in the solid phase below the melting point until the temperature is lowered to 157 K where a solid-solid phase transformation occurs. Below ~ 157 K the $\text{CH}_2\text{OH}/\text{CH}_3\text{O}$ spin adduct ratio increases exponentially with decreasing temperature with an apparent activation energy of 1.4 kcal/mole; this is consistent with the observation that only CH_2OH radicals are formed by radiolysis at 77 K. We suggest that the primary radical formation mechanisms in methanol radiolysis occur by similar ion-molecule reactions in the gas and liquid phases and that the relative efficiency of the ion-molecule reactions becomes temperature dependent when molecular motion is arrested in the solid.

A second spin trapping study has dealt with the radicals produced in the γ -radiolysis of alkyl cyanides (nitriles) in the liquid phase.⁸ Previous interpretations have been attempted of the ESR spectra produced in the radiolysis of pure solid phase nitriles, but definite radical identification has proved difficult due to lack of spectral resolution. By spin trapping the CH_2CN radical has been identified in acetonitrile as well as H and probably CH_3CHCN in propionitrile, $\text{CH}(\text{CN})_2$ in malononitrile and H, CN and $\text{CH}_2\text{CH}_2\text{CN}$ in

succinonitrile. The identification of H atoms as intermediates is the first such report in nitriles. Our results have led to clarification of the solid phase radiolysis data and have put constraints on the probable radical formation mechanisms in alkyl cyanides subjected to radiolysis.

In γ -irradiated systems we have successfully detected H-atom spin adducts in liquid alkanes, methanol and nitriles. However in each case the H adduct yield has been quite low in comparison to the yields of other radical adducts. One reason for the low yields of H adducts in these systems may be that the H atom can also react by H abstraction with the solvent molecules so that the net spin trapping efficiency is rather low. We appear to have found support for this hypothesis by measuring H-atom spin adducts in partially fluorinated solvents.¹⁵ We have found that H adduct yields are comparable to the radical adducts yields in γ -irradiated $(\text{CF}_3)_2\text{CHOH}$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{OH}$ liquids. This contrasts strikingly with the non-fluorinated alcohols in which the H adduct yield is only about 10^{-2} of the radical adduct yield. Our results show for the first time that large H-atom yields do occur in the radiolysis of alcohols. We have also found that the H spin adduct nitroxides have larger coupling constants in partially fluorinated alcohols than in nonfluorinated alcohols. This appears to be associated with small solvent induced conformational changes in the nitroxides.

A third technique we have used to improve spectral resolution in disordered matrices is ^{17}O enrichment. The most important result has been to obtain the final information needed to definitively determine the solvation structure of a trapped electron in an aqueous environment.⁴ This is of special import since hydrated electrons are among the most reactive chemical species known and since they are undoubtedly important in many biochemical electron transfer reactions ranging from photosynthesis to radiation damage. The ESR lineshape and width of a trapped electron in 34% ^{17}O enriched

10 M NaOH alkaline ice glass at 77 K have been carefully measured. Analysis of the second moment contributions from ^{17}O coupling to the lineshape together with the constraint from electron spin echo studies that the electron-nearest oxygen distance is greater than $2\text{\AA}$ show that the $e^- - ^{17}\text{O}$ hyperfine coupling is mainly isotropic. Simulation of the trapped electron ESR lineshape under these constraints for various numbers of equivalent water molecules in the first solvation shell of the electron shows clearly that the best fit to the experimental lineshape is found for six first solvation shell water molecules. Four or less first solvation shell waters the fit is quite unacceptable. Thus with previous data from electron spin echo results a rather complete geometrical description of the trapped, hydrated electron is defined. Six water molecules surround the electron with one OH bond of each oriented toward the electron along octahedral directions with the $e^- - \text{H}$ distance being $2.1\text{\AA}$.

The trapped electron in irradiated 10 M NaOH alkaline ice glass is accompanied by a trapped hole in the chemically converted form of O^- . The identification of O^- has been definitively confirmed and its electronic structure revealed by utilizing ^{17}O enrichment together with ESR examination at both X and Q band.¹⁴ The O^- is characterized by $g_{\perp} = 2.070$, $g_{\parallel} = 2.002$ and $A_{\parallel} (^{17}\text{O}) = 99 \pm 3$ gauss. The spin density is largely localized on a $2p$ orbital on O^- (~69%), but a significant percentage of the spin density seems delocalized into the surrounding matrix.

ESR has also been used as a monitor to study the reaction mechanism of electrons with solutes in ethylene glycol/water glass at 77 K. The reactivity of electrons in shallow traps characterized by a non-equilibrium configuration of solvent molecules around the electron has been compared with that of electrons in deep traps characterized by an equilibrium configuration of solvent molecules. For reaction with a series of solute scavengers that

span a range of 250-fold in reactivity for deeply trapped electrons it is found that the range of reactivity is only 60-fold for shallowly trapped electrons. These results appear to be most consistent with a model in which reaction occurs by tunneling of the trapped electrons to the solute. For shallowly trapped electrons the tunneling rate is faster because the barrier is smaller and consequently the differentiation in rates between different solutes is smaller.

In a related study which does not involve ESR the mechanism of photoionization of indole and phenol in aqueous solutions was studied.¹ It is found that photoionization competes with internal conversion from the second excited state to the first excited state. A study of the temperature dependence of this competition supports the involvement in the photoionization process of an intermediate charge-transfer-to-solvent state populated from the second excited state of indole and phenol. In mixed alcohol-water solvents the formation of this charge-transfer-to-solvent state appears to be governed primarily by interaction of the excited solute with the water molecules.

By the use of the various methods indicated, comparison of X and Q band spectra, ¹⁷O isotopic substitution and spin trapping, new information has been obtained about reactive radical intermediates that was not obtainable by conventional ESR methods.

Theoretical Studies on Reaction Intermediates: Excess Electrons

Knowledge of excess electrons in condensed media is a fundamental and important chemical problem. Sudden injection of charge into a dielectric may lead to stable delocalized or localized electron states. The energy states and transport properties of excess electrons in condensed media

determine the insulating properties of dielectrics necessary for electrical energy storage and transmission, the electronic properties of amorphous semiconductors, as well as the limitations on chemical reactions involving electron tunneling and ionic solvation. It is becoming increasingly apparent that localized electrons are also important intermediates in photo or chemically generated charge-transfer reactions, electrochemistry, catalysis, model photosynthetic systems and radiation processing. A detailed knowledge of the physical and chemical characteristics of excess electrons is thus essential to the efficient utilization of such diverse reaction types for energy production, use and storage.

In addition to the experimental studies of localized electrons described in preceeding sections we have carried out several relevant theoretical studies. Only recently has it become possible to experimentally measure the solvation time of electrons suddenly injected into polar liquids by pulse radiolysis or laser photolysis. We have attempted to predict these times theoretically by a simple model of solvent molecular dipole rotation in response to the charge distribution of the excess electron. In liquid alcohols this simple model gave reasonable agreement with experiment (K. Fueki, D. F. Feng and L. Kevan, J. Phys. Chem., 78, 393 (1974)). However, we did not consider any change in the excess electronic charge distribution during solvation. We have now considered this point in detail⁷ since it relates to the degree of involvement of the dielectric relaxation of the medium beyond the first solvation shell of the electron in the solvation process. The rate of dipole rotation in response to the introduction of the excess electron depends upon the charge enclosed within an equilibrium distance from the electron to point dipoles in the first solvation shell. These quantities are calculated within the framework of the successful semicontinuum potential model for the electronic structure of solvated electrons in polar media which we have developed over the last several

years. We have now coupled this formulation with time dependent dielectric polarization in the dielectric continuum beyond the first solvation shell of the electron. This means that the amount of charge enclosed within the electron-point dipole distance changes with time. Electron solvation times have been calculated for methanol, ethanol and 1-propanol at room temperature and for 1-propanol vs temperature. The values are about 25% greater than in the more simplified model. This does improve the agreement with experiment but the improvement does not seem significant enough to warrant the additional calculational complexity of the refined model. Perhaps the most interesting new point is that the electron-point dipole distance increases only slightly and the time dependent dielectric constant remains nearly equal to the high frequency dielectric constant during the solvent dipole orientation. This implies that the orientational relaxation of molecular dipoles in the first solvation shell proceeds first and is followed by the partial orientation of the second and more distant solvation shells (i. e. dielectric relaxation). Thus our theoretical picture is that electron solvation in polar media occurs from inside out.

In an attempt to better understand electron solvation in polar media several laboratories including our own are studying electron solvation in alcohol-alkane mixtures. It appears that alcohol forms small aggregates in alkane solvents and that the electron is solvated by one or two shells of alcohol molecules in an alkane continuum. We have treated this situation theoretically⁶ by our semicontinuum potential model that has proved quite successful for electrons in pure polar media. An interesting feature of our new treatment is that we can essentially eliminate the electron conduction band energy as a parameter by using recently measured experimental values of this energy for the alkanes. This could not be done in pure polar solvents because the conduction band energy has not been measured in such solvents. We are left with a rather stringent model

containing no adjustable parameters! We have considered two geometrical models. In model I a discrete number (4 or 6) of alcohol molecules forms the first solvation shell for the electron and the alkane forms the continuum. In model II the first solvation shell contains discrete alcohol molecules, the second solvation shell contains a continuum of alcohol molecules, and the alkane forms the continuum beyond the second solvation shell. The calculated optical absorption maxima agree reasonably well with the limited experimental data available. The most interesting prediction is that in the solution at 300 K, but not in the glass at 77 K, a bound-free transition dominates the optical spectrum for model I while a bound-bound transition dominates the optical spectrum for model II. In the glass a bound-bound transition is always predicted. The second alcohol solvation shell appears to play a large role in localizing the excited state wavefunction although it is less essential for localizing the ground state wavefunction. We hope to design suitable experiments to test this interesting prediction.

Finally, we have developed a new model for electron binding in nominally nonpolar alkanes.¹⁶ Not only is this model the first one to account for the variety of experimental data known for localized electrons in 3-methylpentane glass, but it also appears to predict whether the stable electron ground state in liquid alkanes is localized or delocalized as indicated by electron mobility data. The only previous model for electron stability in alkanes was a microdipole model based upon contributions from CH bond dipoles (D. F. Feng, H. Yoshida and L. Kevan, J. Chem. Phys., 61, 4440 (1974)). This model could account for about half of the optical absorption energy for 2 or 4 CH₂ groups surrounding the excess electron. However, the microdipole model is inconsistent with the new electron spin echo data which indicates that there are 18-21 equivalent nearest neighbor CH interactions.⁹ For large numbers of CH dipole interactions the microdipole model leads to no net stability due to large energy cancellation effects from dipole-

dipole repulsions. Our new model is the first to incorporate the explicit molecular structure of the first solvation shell. This new model is based on a semicontinuum potential framework in which the electron-polarizability energy is structured by considering the electron interaction with the polarizability of each C-C bond rather than with a point molecule. In addition we incorporate the effect of hydrogen-hydrogen repulsions because of the large number of equivalent nearest neighbor H-atoms considered. Calculations have been made for electrons in liquid ethane and liquid propane over small temperature ranges and in 3-methylpentane glass at 77 K. A variety of reasonable orientations of the solvent molecules have been considered; different orientations only lead to relatively small changes in the calculated energies which lend confidence to the reliability of the results obtained. The optical transition energy and oscillator strength for a $1s \rightarrow 2p$ bound-bound transition, the photoionization threshold energy and the transition energy at the bound-free transition probability maximum have all been calculated. Comparisons with experiment, where possible, are excellent and it appears that we have constructed the first successful theoretical model for electron binding in alkanes. In liquid alkanes it appears that the optical absorption of the localized electron corresponds to a bound-free transition although more experimental data is needed. In alkane glasses the trapped electron optical band clearly seems associated with a bound-bound transition on both theoretical and experimental grounds. A criterion for electron localization is also established by this model as the difference between the experimental electron conduction state energy and the total ground state energy of the electron being greater than zero. This criterion predicts, for example, that the stable state of the electron in liquid neopentane is delocalized or quasi-free while the electron is predicted to be localized in n-pentane. Both predictions are in qualitative agreement with deductions from the experimental electron mobilities in both liquids. Thus this theoretical model promises to be useful to predict molecular structure effects on electrical breakdown in dielectric liquids.

2. Research Publication List

The following publications were abstracted in the previous progress report, COO-2086-86, but had not yet been published. Their full reference citations are now given here.

P. A. Narayana, M. K. Bowman, L. Kevan, V. F. Yudanov and Yu. D. Tsvetkov, Electron Spin Echo Envelope Modulation of Trapped Radicals in Disordered Glassy Systems: Application to the Molecular Structure Around Excess Electrons in γ -Irradiated 10M Sodium Hydroxide Alkaline Ice Glass, J. Chem. Phys., 63, 3365 (1975).

L. Kevan, Pulse Radiolysis Study of Solvated Electrons in Water-Ethanol Glasses at 76 K: Structure of the First Solvation Shell Around the Electron, J. Phys. Chem., 79, 2846 (1975).

S. Noda, L. Kevan and K. Fueki, Conduction State Energy of Excess Electrons in Condensed Media: Liquid Methane, Ethane and Argon and Glassy Matrices, J. Phys. Chem., 79, 2866 (1975).

S. Schlick and L. Kevan, Hydrogen Spin Flip Satellite Lines Associated with the PO_3^{2-} Radical in a Single Crystal of $\text{Na}_2\text{HPO}_3 \cdot 5 \text{H}_2\text{O}$: Calculated and Experimental Intensities, J. Magn. Resonance, 21, 129 (1976).

M. K. Bowman, H. Hase and L. Kevan, Saturation Behavior of Inhomogeneously Broadened EPR Lines Detected with Magnetic Field Modulation, J. Magn. Resonance, 22, 23 (1976).

K. K. Ho, J. Moan and L. Kevan, Effect of Photoionization Energy On the Initial Decay Rate of the Electron-Cation Recombination Fluorescence from Tryptophan and Phenolate Ion in Polar Glasses, Chem. Phys. Lett., 37, 425 (1976).

The following nineteen publications have been published or submitted for publication during the current report period. The numbers correspond to those cited as references under Research Highlights.

1. H. B. Steen, M. K. Bowman and L. Kevan, Temperature Dependence of a Process Competing with $S_2 - S_1$ Internal Conversion in Indole and Phenol in Aqueous Solutions, *J. Phys. Chem.*, 80, 482 (1976).
2. A. C. Ling and L. Kevan, On the Nature of the Radicals Produced by γ -Radiolysis of 2-Methyltetrahydrofuran in Adamantane: A Variable Temperature Comparative Study via X-Band and Q-Band Electron Spin Resonance, *J. Phys. Chem.*, 80, 592 (1976).
3. S. Schlick and L. Kevan, Spin Trapping of Radicals Formed in Gamma-Irradiated Methanol: Effect of the Irradiation Temperature from 77 K to 300 K, *Chem. Phys. Lett.*, 38, 505 (1976).
4. S. Schlick, P. A. Narayana and L. Kevan, ESR Lineshape Studies of Trapped Electrons in γ -Irradiated O^{17} Enriched 10M NaOH Alkaline Ice Glass: Model for the Geometrical Structure of the Trapped Electron, *J. Chem. Phys.*, 64, 3153 (1976).
5. P. A. Narayana and L. Kevan, Analysis of Three Pulse Electron Spin Echo Modulation: Phase Reversal, *J. Magn. Resonance*, 23, 000 (1976).
6. K. Fueki, P. A. Narayana and L. Kevan, A Semicontinuum Model for Solvated Electrons in Alcohol-Alkane Solutions and Glasses, *J. Chem. Phys.*, 64, 4571 (1976).
7. K. Fueki, D. F. Feng and L. Kevan, Relaxation Time of Dipole Orientation Around A Localized Excess Electron in Alcohols, *J. Phys. Chem.* 80, 1381 (1976).

8. S. W. Mao and L. Kevan, Spin Trapping of Cyanoalkyl Radicals in the Liquid Phase γ -Radiolysis of Nitriles, J. Phys. Chem., 80, 800(1976).
9. P. A. Narayana and L. Kevan, Geometrical Structure of Solvated Electrons in γ -Irradiated 3-Methylpentane Glass at 77 K from an Analysis of the Modulation of the Electron Spin Echo Decay Envelope, J. Chem. Phys. 65 3379 (1976).
10. A. Plonka and L. Kevan, Differential Saturation Study of Radial and Angular Modulation Mechanisms of Electron Spin-Lattice Relaxation for Trapped Hydrogen Atoms in Sulfuric Acid Glasses, Chem. Phys. Lett.
11. D. P. Lin and L. Kevan, Electron Scavenging in Ethylene Glycol/Water Glass at 4 K and 77 K: Scavenging of Trapped vs Mobile Electrons, Intl. J. Radiat. Phys. Chem.
12. D. P. Lin, D. F. Feng, F.Q. H. Ngo and L. Kevan, Electron-Electron Double Resonance Study of Magnetic Energy Transfer Between Trapped Electrons and Radicals in Organic Glasses: Relation Between Dipolar Cross Relaxation Times and Dipolar Interaction Distances, J. Chem. Phys., 65, 0000 (1976).
13. L. Kevan and A. Plonka, On the Correlation Between Electron Spin-Lattice Relaxation Times and Hydrogen Atom Decay Kinetics in X-Irradiated Sulfuric Acid Glasses at 4 to 90 K, J. Phys. Chem.
14. S. Schlick and L. Kevan, Confirmation of O^- Formation in γ -Irradiated 10 M NaOH/H₂¹⁷O Alkaline Ice Glass by Electron Paramagnetic Resonance Studies, Mol. Phys.

15. A. C. Ling and L. Kevan, Hydrogen Atom Spin Trapping in γ -Irradiated Fluorinated Alcohols: Solvent Effects on Coupling Constants and Relative Radical Yields, J. Phys. Chem.
16. T. Kimura, K. Fueki, P. A. Narayana and L. Kevan, A Semi-continuum Model with a Structured First Solvation Shell for Excess Electrons in Liquid and Glassy Alkanes, Can. J. Chem.
17. P. A. Narayana and L. Kevan, Effects of Quadrupole Interaction on Electron Spin Echo Modulation Patterns in Disordered Systems, J. Magn. Resonance.
18. M. K. Bowman and L. Kevan, An Electron Spin-Lattice Relaxation Mechanism Dominated by Tunneling Modes for Trapped Radicals in Glassy Matrices: Theoretical Development and Application to Trapped Electrons in γ -Irradiated Ethanol Glasses, J. Phys. Chem.
19. L. Kevan and P. A. Narayana, ENDOR and ELDOR of Disordered Matrices, Chap. VI in Multiple Electron Resonance Spectroscopy, M. Dorio and J. Freed, Eds., Plenum Press, New York.

In addition to the above publications published in refereed scientific journals the following two books were published by the principal investigator during this report period. Both are of direct relevance to the ERDA supported research described herein.

L. Kevan and L. D. Kispert, Electron Spin Double Resonance Spectroscopy, Wiley-Interscience, New York, 1976, 427 pages.

L. Kevan and B. Webster, editors, Electron-Solvent and Anion-Solvent Interactions, Elsevier, Amsterdam, 1976, 360 pages.

3. Scientific Talks Presented

The following 18 talks were given on ERDA supported research during the current report period at several scientific conferences and by invitation at a number of universities.

ERDA-178 Chemical Applications of Electron Spin Echoes, L. Kevan, Chemistry Seminar, University of Rochester, Rochester, New York, November 26, 1975.

ERDA-179 Diffusive and Tunneling Recombination of Electrons with Cations in Aqueous and Organic Glasses, K. Ho and L. Kevan, First Chemical Congress of the North American Continent, Mexico City, Mexico Mexico, November 30 - December 5, 1975.

ERDA-180 Application of Electron Spin Echoes and EPR Second Moment Analysis to the Determination of Matrix Structure Around Trapped Radicals in Disordered Systems, L. Kevan, P. A. Narayana, S. Schlick, M. K. Bowman, B. L. Bales and R. N. Schwartz, Twelfth International Symposium on Free Radicals, Laguna Beach, California, January 4-9, 1976.

ERDA-181 Future Research Trends on Electrons in Condensed Media, L. Kevan, Symposium on Radicals and Electrons in Condensed Media, Caracas, Venezuela, January 26-31, 1976. Invited Lecture.

ERDA-182 Electron Solvation Mechanisms, L. Kevan, Chemistry Seminar, Northern Michigan University, Marquette, Michigan, February 11, 1976.

ERDA-183 Structural Studies of Trapped Electrons by Electron Spin Echo Spectrometry, L. Kevan; Highlands Lecture, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, April 29, 1976.

ERDA-184 Solvated Electron Structure, L. Kevan, Seminar, Technical University, Lodz, Poland, June 7, 1976.

ERDA-185 Solvated Electron Structure, L. Kevan, Invited Lecture, Polish Chemical Society, Warsaw, Poland, June 8, 1976.

ERDA-186 Photoconductive Phenomena and Carrier Transport in Aqueous and Organic Glasses, Invited Lecture, L. Kevan, Gordon Conference On Chemistry and Physics of Photoconductors, Plymouth, New Hampshire, June 21-25, 1976.

ERDA-187 A New Theoretical Model for the Electronic Structure and Localization of Electrons in Alkanes, T. Kimura, K. Fueki, P. A. Narayana and L. Kevan. International Conference on Electrons in Fluids, Banff, Alberta, Canada, September 5-11, 1976.

ERDA-188 Structural Studies of Trapped Electrons by Electron Spin Echo Spectrometry, L. Kevan, Chemistry Seminar, University of British Columbia, Vancouver, B.C., Canada, Sept. 13, 1976.

ERDA-189 Geometrical Structure of Solvated Electrons, L. Kevan, Invited Lecture, Annual Meeting of the Japanese Society of Radiation Chemistry, Kyoto, Japan. Octo. 10-12, 1976.

ERDA-190 The Application of Electron Spin Resonance to Radiation Chemistry I, L. Kevan, Nagoya University, Nagoya, Japan, October 19, 1976.

ERDA-191 The Application of Electron Spin Resonance to Radiation
Chemistry II, L. Kevan, Nagoya University, Nagoya, Japan, October 22, 1976.

ERDA-192 The Application of Electron Spin Resonance To Radiation
Chemistry III, L. Kevan, Nagoya University, Nagoya, Japan, October 26, 1976.

ERDA-193 Localization and Solvation of Electrons in Condensed Media,
L. Kevan, Invited Lecture, Chemical Society of Japan, Nagoya, Japan,
October 26, 1976.

ERDA-194 Localization and Solvation of Electrons in Condensed Media,
L. Kevan, Takasaki Atomic Energy Research Institute, Takasaki, Japan,
October 27, 1976.

ERDA-195 Localization and Solvation of Electrons in Condensed Media,
L. Kevan, Seminar, University of Tokyo, Japan, October 28, 1976.

4. Ph. D. Theses Completed

Michael K. Bowman, The Electron Spin Lattice Relaxation of Radiation Produced Trapped Electrons and Trapped Hydrogen Atoms In Glassy Matrices.

Dr. Bowman is now an NSF Energy-Related Postdoctoral Fellow at Argonne National Laboratory with Dr. J. J. Katz.

Ken K. Ho, Recombination Luminescence from Photoionized Organic and Aqueous Glasses.

Dr. Ho is now a Research Associate with Prof. L. Dorfman at Ohio State University.