RADIOLYSIS STUDIES ON REACTIVE INTERMEDIATES

Technical Progress Report

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ABSTRACT

During the past year we have developed a more quantitative characterization of the structure and reaction mechanism of solvated electrons produced by high energy chemistry and have also discovered that neutral-atoms may undergo solvation in polar media to cause significant geometrical rearrangement.

We have shown that the geometrical arrangement of six OH bond oriented water molecules around a localized electron is the preferred geometry in frozen aqueous systems even at low solute ion concentration. The energy level structure of electrons in polar aqueous and alcoholic glasses has been systematized from a comparison of photoconductivity and optical spectra. Experimental and theoretical evidence on electron solvation has been evaluated to suggest the dominance of first solvation shell orientation in the solvation process. A laser photolysis study as a function of temperature suggests that electron solvation in ethanol glass occurs by a hindered molecular reorientation mechanism. In mixed polar and nonpolar glassy matrices we have shown that the electron is first solvated in the nonpolar matrix and is later transformed to a more stable species surrounded by the polar molecules.

We have found that the spin lattice relaxation of solvated electrons is dominated by a new mechanism characteristic of disordered matrices which involves relaxation by tunneling modes in the matrix. The noninteracting spin packet model of electron spin resonance lines has been shown to apply to solvated electrons in deuterated matrices but not in protiated matrices. Thus the magnetic resonance relaxation of solvated electrons is now relatively well understood.

A new type of recombination fluorescence experiment has been devised which allows easy distinction between tunneling and diffusive recombination mechanisms between solvated electrons and cations. Several theoretical studies have helped to delimit the applicability of an electron tunneling mechanism to solvated electron reactions.

We have continued development of electron spin echo spectrometry for studying molecular orientation around trapped radicals and have used this technique to demonstrate that silver atoms undergo dramatic solvation and desolvation changes in frozen aqueous systems.

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RADIOLYSIS STUDIES ON REACTIVE INTERMEDIATES..

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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 quantitatively characterizing the geometrical and electronic structure and the reaction mechanism of solvated electrons in glassy matrices. Solvated electrons are probably the most ubiquitous and important of the reaction intermediates produced by high energy radiation. In addition, we have continued development of electron magnetic resonance methods for obtaining structural data about reactive radical and ionic intermediates in disordered systems such as glasses and polycrystals. This has led to the demonstration that atomic intermediates may undergo solvation interactions to cause substantial geometrical rearrangement of solvent.

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 often poor. Electron spin resonance (ESR) is quite specific for detecting radicals and radical ions and we have shown how advanced ESR methods such as electron spin echo spectroscopy, spin-lattice relaxation time measurement by pulsed ESR and differential saturation of forbidden transitions can lead to specific and definitive information about reactive intermediates.

Fifteen papers have been published or submitted for publication during this report period. In addition, seventeen invited lectures on topics related to the ERDA supported research have been presented. The following sections describe (1) research highlights, (2) research publication list, and (3) scientific talks presented.

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. During part of this report period he was on sabbatical leave, with ERDA's approval, at laboratories in Japan and France where he furthered his knowledge in areas of interest to the Department of Energy.

1. Research Highlights

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

Structure and Reaction Mechanisms of Solvated Electrons

Solvated electrons are probably the most important and ubiquitous of the reactive intermediates produced by high energy radiation of condensed phase systems. Their importance is emphasized by the fact that they appear to be able to undergo electron tunneling reactions with a variety of impurities or deliberately added acceptors as well as with matrix cations. Solvated electrons are generated by ultraviolet photolysis of suitable molecules as well as by X or γ -ray ionizing radiation.

To understand and to control these solvated electron intermediates and their reactivity it is necessary to have both a theoretical and experimental knowledge of their geometrical and electronic structure. Their geometrical structure in aqueous matrices highly doped with an ionic solute like NaOH has previously been deduced in our laboratory by a combination of electron magnetic resonance techniques [J. Chem. Phys., 63, 3008,

3365 (1975); 64, 3153 (1976)]. It is found that six H_2O are arranged octahedrally around the excess electron with one OH bond from each H_2O molecule oriented toward the electron. Although this structure was deduced for 10 M NaOH glassy ice we have suggested that it may also be applicable to the solvated electron in water. To support this suggestion we have studied trapped, solvated electrons produced by codeposition of sodium and water vapor at 77 K.¹ The sodium concentration is less than 0.01 M in this matrix yet the electron yield is sufficient to make detailed ESR studies. By analyzing the difference in second moments of the ESR lineshape at 9 and 35 GHz microwave frequencies, it is possible to deduce the isotropic and anisotropic hyperfine constants for n nearest equivalent interacting protons by our previously developed methodology. The structural results are similar to those obtained earlier for solvated electrons in NaOH glassy ice, so we suggest that this solvation structure is also characteristic of solvated electrons in liquid water.

In addition to the geometrical structure of solvated electrons in polar matrices we have made new measurements on the electronic structure of these species.² We have pioneered the approach of obtaining information about the electronic structure of localized electrons by a comparison of the photoconductivity spectra and the optical absorption spectra. This comparison leads to information on the nature of the optical transitions involved in the absorption band. We have made measurements in a variety of polar matrices which exhibit a gradation of electronic structure in an attempt to understand the distinction between the occurrence of bound-bound and bound-continuum transitions. The photoconductivity spectra measure the efficiency of bound-continuum transitions although there may be an intermediate localized excited state in the conduction band which autoionizes to produce the mobile electron. The optical absorption spectrum may be predominantly due to either or both bound-bound and bound-continuum transitions.

We have been able to divide systems that we have studied into two types.² Type A systems (aqueous 10 M NaOH, 7 M NaClO₄ and 7.5 M CH₃COOK) show a similar wavelength dependence between the photoconductivity and optical absorption spectra, which implies dominance of bound-continuum transitions. Type B systems (aqueous 2.35 M sucrose, aqueous 10 LiCl, methanol, equivolume ethylene glycol/water, glycerol, and probably aqueous 7.2 M sodium formate) display photoconductivity spectra of the solvated electron which are significantly blue shifted from the optical absorption spectra, indicating dominance of bound-bound transitions in the main part of the optical spectra and a bound-continuum contribution in the high energy tail of the optical spectra. Aqueous 5 M potassium carbonate represents an intermediate case where the solvated electron shows some correspondence of the photoconductivity and optical spectra at long wavelengths while at short wavelengths the photoconductivity spectra are blue shifted. Thus in this case both bound-bound and bound-continuum transitions presumably exist, but closely overlapped. All of these measurements on the polar aqueous and alcoholic matrices were carried out at 85 K where the electrons are believed to have reached an equilibrium state with the solvent molecules so that they may be properly described as solvated.

We further find that there is a correlation between the energy level structure that we deduced for the solvated electron in different aqueous matrices with differences in the laser photobleaching behavior of electrons in these various matrices [Walker and May, Int. J. Radiat. Phys. Chem., 6, 345 (1974)]. Although the laser photobleaching behavior was not completely understood in the original study, the additional information about the energy level structure that we obtained appears to make it more explicable.

In addition, from the value of the photocurrent intensity that we measured we have attempted to make estimates of the quantum efficiency of electron photoexcitation into the conduction band. We have found that this varies from about 10^{-1} to 10^{-3} depending upon the particular matrix studied.² In the more efficient cases it appears that the quantum efficiency of electron photoexcitation to the conduction band approaches unity and that such photoexcitation may indeed occur directly to the conduction band.

Thus far we have described studies on the solvated electron in polar matrices. However when an electron is initially injected into polar media such as water, alcohol, or ethers it is initially localized in what we call a presolvated state in which the first solvation shell molecules have not reached an equilibrium configuration around the electron. Diverse experimental studies have suggested that solvation then occurs by orientation of the polar molecules about the electron. This evidence is primarily based on electron spin resonance and optical absorption changes that are observed during the solvation process. There has been some question about whether the spectral changes observed are primarily due to orientation of the first solvation shell molecules or due to orientation of more distant solvation shell molecules. We have, therefore, reevaluated the experimental and theoretical evidence on the solvation process and have concluded that orientation of first solvation shell molecules can well account for the spectral changes observed.⁷

The solvation data on electrons in glassy alcohols near 77 K indicate that both a molecular reorientation mechanism and perhaps an electron migration mechanism may contribute to the solvation process. We have attempted to try to help clarify this possible ambiguity by new laser photolysis studies of the time dependence of the optical spectral shifts associated with the solvation process in ethanol glass as a function of temperature.¹⁴ These studies have been carried out over the temperature range of 83-123 K.

At 123 K first order kinetics are observed but at lower temperatures the kinetics deviate from first order and can be represented as composite first order or as linear in electron concentration versus log time. From an evaluation of these complex kinetics we conclude that a hindered molecular reorientation mechanism for electron solvation is most probable in low temperature alcohol glasses. Furthermore we show that the temperature dependence and kinetics of this mechanism are not expected to correlate with those of bulk viscosity or dielectric relaxation as is found for electron solvation in liquids. If significant electron loss does indeed occur during solvation, we suggest that this most probably occurs by temperature dependent electron tunneling to a cation or to a solute if present. It is still possible that during the solvation process some electrons transfer from shallow to deeper traps in the matrix but it appears to us that the evidence available does not yet imply that this occurs unambiguously.

We have also begun to attack the interesting question of how electron solvation occurs in mixed matrices involving both polar and nonpolar components. Equilibrium studies in alcohol-alkane liquids show that the electron is preferentially solvated by alcohol since this is the most energetically favorable situation. However, in a mixture containing an excess of the nonpolar component one can ask whether or not the electron is first solvated or at least localized in the nonpolar medium and then is converted by some mechanism to an electron surrounded by the polar molecules in the mixture. We have tried to study this unambiguously by examining a mixture of methanol and methyltetrahydrofuran glass at 109 K by pulse radiolysis.⁶ We chose to study this particular mixture because there is little spectral shift of the electron absorption spectrum in the pure components on a microsecond timescale after electron injection. The experiment shows a very dramatic effect. Initially, at the end of a 40 ns electron pulse we observe a spectrum with a maximum near 1200 nm which is characteristic of the electron localized in a methyltetrahydrofuran environment. After 14 μ s the optical absorption maximum has shifted to < 600 nm which is similar to the maximum for electrons solvated

in methanol itself. The kinetics of this spectral conversion process were analyzed at various wavelengths in order to assess the mechanism by which the electron is converted to the methanol environment. Although the kinetics are quite complex, conversion appears to occur by a diffusive process involving more than one step with methanol clusters. Further work is currently needed in the assessment of the mechanism of electron solvation in mixed matrices but we feel that we have defined some of the kinetic constraints on this process.

In addition to the geometrical and energy level structure of solvated electrons in glassy matrices we have studied the weak magnetic interaction between the localized electron and the surrounding atoms in the matrix containing a nuclear spin. One can carry out such an investigation most sensitively by studying the electron spin lattice relaxation mechanism of the solvated electron. Electron spin lattice relaxation is the process by which a collection of radicals or unpaired electron spins attain thermal equilibrium. In solids, the thermal motions of both the lattice itself and the radical in the lattice are capable of causing a time dependent perturbation of the electron spin of the radical. We have developed a spectrometer to make direct measurements of the electron spin lattice relaxation rate by saturating the spin system with a pulse of resonant microwaves and then following the time dependence of the saturation recovery after this pulse. The temperature dependence of the spin lattice relaxation rate gives information about the dynamics of the modulating interaction and the magnitude of the relaxation rate is determined by the magnitude of the interaction between the radical spin and the lattice atoms. In the previous year we found that a new relaxation mechanism is particularly important for electron spin lattice relaxation in glassy matrices. (J. Phys. Chem., 81, 456 (1976)). This relaxation mechanism is based on the modulation of the electron nuclear dipolar interactions by tunneling of nuclei or molecular groups in the environment of the radical. This tunneling relaxation mechanism is characterized by a linear temperature dependence of the relaxation rate at temperatures less than approximately 100 K. In addition the magnitude of the relaxation rate due to tunneling modes is dependent upon the isotopic nature of the tunneling nuclei. Thus we have been able to identify the tunneling nuclei and characterize

the relaxation rate by suitable isotopic substitution.

During the current year we have studied electron spin lattice relaxation mechanisms of solvated electrons in a variety of aqueous and organic glassy matrices.⁸ These matrices include 10 M sodium hydroxide ice, ethanol, methyltetrahydrofuran, and methanol glasses. Below 50 - 100 K, we find that the major spin lattice relaxation mechanism of the solvated electron is indeed this new tunneling relaxation mechanism that we have discovered. However, the interesting point relevant to the structure of solvated electrons in glassy matrices is that the tunneling nuclei around the solvated electron do not seem to be the nearest neighbor nuclei which are oriented by the electron in the process of solvation. Instead the nuclei active in the tunneling relaxation typically appear to be next nearest neighbors to the solvated electron. The identities of the tunneling nuclei have been deduced by isotopic substitution and are attributed to sodium in the sodium hydroxide aqueous glass, to ethyl protons in ethanol glass and, to methyl protons in methanol glass and to methyl protons in methyltetrahydrofuran glass. The picture of the solvated electron that has evolved from this study is that the electron is trapped in a quite stable arrangement in which the nearest nuclei out to several angstroms are constrained from undergoing much motion. The hydroxyl groups in alcohol, the first solvation shell water molecules in aqueous glasses and the methyltetrahydrofuran ring protons which are all oriented to some extent by the potential field of solvated electrons are all fairly well immobilized compared to the more distant methyl or ethyl groups in methyltetrahydrofuran and alcohols and to the sodium ion in the aqueous glass. This suggests that the structure of the first solvation shell around a solvated electron can be regarded as almost crystallike. In that case we would not expect those nuclei to have tunneling modes available to them since the presence of these tunneling modes seems to be characteristic of the disordered glassy or amorphous state. It is certainly quite possible that this diagnostic may turn out to be quite useful in probing the microstructure of disordered materials around trapped radicals.

In contrast to the solvated electron in aqueous glasses we also studied the electron spin lattice relaxation of O^- in aqueous glasses and found that it was not dominated by a tunneling relaxation mechanism but rather by the much more common Raman process with an effective Debye temperature of about 100 K.⁸

We have also been able to study a different aspect of spin relaxation for solvated electrons in aqueous matrices by using the technique of electron-electron double resonance to examine spin diffusion processes that can occur within an inhomogeneously broadened electron spin resonance line.³ By looking at the microwave power saturation of magnetic field swept electron-electron double resonance spectra in comparison with computer simulated spectra based on models involving spin diffusion or not involving spin diffusion between the spin packet substructure of inhomogeneously broadened lines we have been able to deduce the following points. First, in a protiated matrix spin diffusion does produce significant interaction between the spin packets so that the saturation behavior is complex and spin diffusion processes must be considered in trying to evaluate the overall saturation of the electron spin resonance lines. In contrast, the deuterated matrices show that the spin packet substructures can be considered as effectively non-interacting in the inhomogeneously broadened electron spin resonance line. The difference between the protiated and deuterated matrices suggests that nuclear relaxation is the mechanism for spin diffusion in these solvated electron systems.³

Not only are the physical structural properties of solvated electrons of considerable importance, but also one must ultimately relate them to the reactivity and reaction mechanism by which solvated electrons react with other molecules and ions. In solid matrices it now seems clear that a considerable amount of reactivity of localized electrons is due to electron tunneling processes although the range in reactivities by this mechanism is still not very well understood. At sufficiently high temperatures in the liquid

state the electron reaction mechanism with a solute molecule becomes primarily diffusive in nature although some contribution from electron tunneling probably still exists in many cases. What we have tried to do is to develop a simple diagnostic method to distinguish between regimes in which electron tunneling dominates and electron diffusion dominates in the reaction of a localized electron with a cation in organic glassy matrices.⁴ To study this problem we generate electrons and cations by ultraviolet-photoionization of a heterocyclic amine in a glassy matrix. The ejected electrons are initially trapped and localized by potential minima in the disordered glassy matrix and these localized electrons can further deepen their potential well by inducing molecular orientation of the surrounding molecules. Some of these localized electrons may recombine with their parent ion to produce delayed luminescence which consists of both fluorescence and phosphorescence. We have studied the temperature dependence of the recombination fluorescence seen when tetramethyl-p-phenylenediamine is photoionized in methylcyclohexane, 3-methylhexane, and 2-methyltetrahydrofuran glasses and when indole is photoionized in 2-propanol and ethanol glasses. New experiments are performed at each individual temperature. That is, the photoionization process is carried out at different temperatures and the intensity and time dependence of the recombination fluorescence is observed after this photoionization process. We find that the initial intensity and the decay rate of the recombination fluorescence decreases as the ultraviolet irradiation temperature is increased from temperatures below the glass transition temperature of the matrix. This is interpreted in terms of electron tunneling to the cation in which the tunneling barrier height or electron trap depth increases slightly (0.05-0.2 eV) with increasing irradiation temperature. From previous experiments on the electron solvation process in glassy matrices we know how matrix polarity affects the degree of electron trap deepening and from previous measurements of the energy level structure of solvated electrons we know how the electron trap depth relative to the excited singlet level of the photoionizable solutes varies. By using this structural information about the solvated electron we are then able to

understand the difference in magnitude and changes in magnitude for the initial decay rate and intensity of the recombination fluorescence. When we increase the temperature above the glass transition temperature we find that diffusive recombination dominates tunneling recombination. This is characterized by the observation of a peak in the recombination fluorescence intensity unless the electron trap depth has dropped below the singlet level of the solute in the process of electron solvation. Furthermore, we find that the temperature of this diffusive recombination fluorescence peak varies from 10 - 30 K above the glass transition temperature dependent upon the matrix polarity. Thus, this new type of experiment offers a simple diagnostic for distinguishing tunneling and diffusive recombination of electrons with cations in disordered matrices and shows the importance of a knowledge of the energy level structure of the solvated electron in order to understand its reactivity.

In addition to the experimental work described above, three papers have been completed on theoretical aspects relating to electron tunneling. The experimental evidence that reactions of solvated electrons in solutions occur in part by tunneling mechanisms is that the reaction rate with certain scavengers occur at rates faster than expected for diffusion limited processes. This has been interpreted in terms of mutual diffusion together of the electron scavenger with tunneling of the electron occurring when close enough to the scavenger. The theoretical expression describing this process of combined diffusion and tunneling has not been solved, exactly. However we have found that it is possible to use the Abelian theorem of Laplace transforms to find the probability density function of scavengers around electrons at the limits of time equals zero and time equals infinity.¹²

A uniform theory of electron kinetics in nonpolar liquids has been formulated which applies both to electrons reacting with cations or neutral solutes and to the photoionization of anions or neutral solutes to produce electrons.¹¹ The theory includes solvent screening of the potential between electron and acceptor, spatial variation of electron transport coefficients due to internal electric fields, electron tunneling and chemical activation processes. A general relationship between the electron rate constant and the mean recombination probability is obtained.

Mozumder [J. Chem. Phys., 65, 3798 (1976)] has treated the escape probability of electron-hole pairs in dielectric liquids when the mobility is field independent. We have generalized this problem by including the field dependence of the diffusion coefficient.¹⁰ We find that this may change the escape probability significantly for typical physical parameters.

Atom Solvation and Desolvation

When reaction intermediates are suddenly formed in condensed media by radiolysis or photolysis, the local environment around them does not necessarily correspond to the most energetically stable configuration. However, if enough thermal energy is available the local environment may be rearranged by chemical bonding and electrostatic forces to attain an equilibrium configuration which is energetically more stable. This process is solvation and it has been demonstrated most unambiguously for excess electrons in organic and aqueous matrices as discussed in the previous section. We have begun to extend this type of study of solvation processes to neutral species, initially atoms. Our first studies have dealt with silver atom solvation and desolvation.^{5,15}

Silver salts in ice and organic matrices form silver atoms by reaction with radiation produced electrons. By generating the silver atoms in ice matrices at 4 K we have been able to study the first solvation shell structure by electron spin resonance and electron spin echo spectrometry. Interaction of the silver atom with the surrounding water molecules is indicated crudely by the hyperfine coupling constant of the silver atom. The deviation of the hyperfine coupling constant from that for a free silver atom in the gas phase represents some delocalization of spin density onto the surrounding water molecules. What we have found is that the hyperfine constant drastically changes when silver atoms initially produced at 4 K are warmed to 77 K briefly and then reexamined by electron spin resonance at 4 K. A significant change in the hyperfine coupling of about 300 MHz suggests a

very drastic structural rearrangement of the water molecules surrounding the silver atom. We have used two techniques that we have previously developed for studying the weak hyperfine interaction of paramagnetic species in disordered glassy and polycrystalline systems to develop a detailed structural model of the silver atom environment. First we have studied the differential microwave power saturation of allowed electron spin resonance transitions and forbidden proton spin flip transitions. The analysis of such data enables us to determine an average distance R to N nearest equivalent matrix protons. By this method we find a dramatic difference in the geometry of silver atoms originally produced at 4 K which are characterized by $R=3.25$ Å and $N=8$ and with the silver atoms produced at 4 K warmed to 77 K and reexamined at 4 K which are characterized by at least one proton as close as about 2 Å.

More detailed structural information has been possible by our development of an electron spin echo spectrometer in our laboratory. Electron spin echoes are a consequence of classically precessing dipoles. Two microwave pulses separated by a time τ are applied to a spin system located in an external magnetic field and an echo is observed at time 2τ from the first pulse. The amplitude of the echo decays with τ because of the various relaxation processes taking place in the system. In certain cases it is observed that the echo envelope exhibits an intensity modulation, predominantly due to the dipolar coupling between the unpaired electron and the nuclear magnetic moments of the surrounding nuclei. When the decay is divided out one obtains the normalized modulation. We have shown in our work during the past two years how one can analyze this modulation to obtain detailed structural information about the unpaired spin. In fact, one can obtain information about the number of equivalent interacting matrix nuclei, their anisotropic hyperfine interaction which gives a distance, and their isotropic hyperfine interaction which gives a measure of the delocalization of the unpaired electron wave function. In studying the silver atom system we have found that the echo signal is indeed modulated which allows us to distinguish the geometry of the silver atom initially produced after radiolysis at 4 K

and the drastically changed geometry produced after warming the silver sample to 77 K briefly.

The overall picture that we have developed is summarized in Figure 1. The silver atom produced is initially at 4 K in what we call Site I where the arrangement of water molecules around the silver atom is the same as would be expected for a solvated silver ion. In other words no geometry rearrangement has occurred after the silver atom has been formed from the ion. The 2.66 Å distance between the silver nucleus and the oxygen of the first solvation water molecules corresponds quite well to the sum of the silver ion radius and the water molecule radius. The distance of 3.35 Å to the protons in the first solvation shell of 8 protons is consistent with both the electron spin echo results and with the differential saturation of the proton spin flip satellite lines. This structure for site I is a nonequilibrium structure since the water molecules have not had the opportunity to reorient in response to the fact that the silver ion has now been converted into an atom. With a little thermal excitation which is provided by brief heating to 77 K the geometry changes, which we consider to be a solvation process. The geometry change can be envisioned to occur by a rotation of one or two waters around one of their OH bonds. Alternatively it could be considered that the H atom changes its position by a tunneling process in the polycrystalline matrix. The silver to oxygen distance is unchanged but the nearest neighbor proton distance is drastically decreased as is shown in Figure 1 to approximately 1.9 Å. The value of 1.83 Å shown in the figure corresponds to the distance that would be expected if the water molecule rotates around its OH bond without a change in the geometry of the water molecule itself. Thus we may consider the solvation process as corresponding to the development of one or more hydrogen bonds between the silver atom and the first solvation shell water molecules.

Fig. 1. Schematic of geometry changes in silver atom solvation and desolvation.

A remarkable effect that is also observed is what we term desolvation or the conversion of silver in the Site II configuration back to the Site I configuration. This occurs by optical excitation in the absorption band of the silver atom in the ice matrix at 400 nm. This desolvation process is not understood in detail. However, if we consider the optical absorption band for the silver atom to be largely of charge transfer character involving some delocalization of the excited state orbitals over the water molecules we may consider that when the silver atom is excited the silver nucleus again looks like an ion and the water molecules reorient to the configuration that they would have if the silver atom was a silver ion. The detailed information observed demonstrates the power of some of the methods we have developed in the last several years for obtaining structural information about the surroundings of free radicals, even in disordered systems.

Studies on Other Reactive Intermediates

The laser photolysis apparatus that we have developed to help study the electron solvation process has also been used to study environmental effects on the decay of doublet excited states of the thiocyanate complex of chromium III.¹³ The nature of non-radiative relaxation in chromium (III) complex ions is intimately tied up with the reactive decay of the lowest excited state. To clarify the relationship between the photochemistry and photophysics of these chromium complexes we have studied the room temperature lifetimes and visible absorption spectra of excited doublet states of $\text{Cr}(\text{NCS})_6^{3-}$, $\text{trans-Cr}(\text{NH}_3)_2(\text{NCS})_3^-$ and $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$ in acetonitrile-water mixtures and acetone-water mixtures. The excited doublet transition near 540 nm which is assigned as a charge transfer to metal band shows that the lifetime of the doublet state is strongly dependent upon the composition of the medium. We conclude that many of the photophysical and photochemical properties can be explained with the assumption that the quartet and doublet lowest states are in equilibrium.

An evaluation has been made of the extensive experimental literature on the radiolytic decomposition of carbon dioxide.⁹ By critically evaluating the accuracy, reproducibility and physical self-consistency of the variety of data and decomposition reactions proposed we have tried to use our knowledge of radiation chemical decomposition to develop a comprehensive numerical model of carbon dioxide radiolysis. The model we have developed includes 76 reactions and 19 intermediate reactive species from which we describe the real time concentration of ionic and neutral constituents in the irradiated medium. A computer program has been developed to efficiently handle this complex kinetics system. The significant point is that this model does allow us to predict that the carbon monoxide yield will approximately double when the dose rate is increased from a dose rate regime of approximately 10^{14} eV/g s up to 10^{28} eV/g s at 1 atm pressure. This change in yield is, in fact, observed experimentally. Our model is consistent with the physical reason for this change in yield being a change in the predominant neutralization mechanism of the carbon dioxide ion in the system. We are also able to explain the difference in yields observed for α and proton irradiation as compared to fission fragment irradiation. The overall results give us some confidence that even though radiolytic mechanisms can be extremely complex involving a large variety of ionic, radical and excited state reactions it is possible to model them realistically and to explore the effect of changing various physical parameters on the product yields and reaction mechanism.⁹

2. Research Publication List

The following publications were listed in the previous progress report, C00-2086-87, but had not yet been published. Their full reference citations are now given here.

P. A. Narayana and L. Kevan, Analysis of Three Pulse Electron Spin Echo Modulation: Phase Reversal, J. Magn. Resonance, 23, 385 (1976).

S. W. Mao and L. Kevan, Spin Trapping of Cyanoalkyl Radicals in the Liquid Phase γ -Radiolysis of Nitriles, J. Phys. Chem., 80, 2330 (1976).

A. Plonka and L. Kevan, Differential Saturation Study of Radical and Angular Modulation Mechanisms of Electron Spin-Lattice Relaxation for Trapped Hydrogen Atoms in Sulfuric Acid Glasses, Chem. Phys. Lett., 43, 489 (1976).

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, Int. J. Radiat. Phys. Chem., 8, 713 (1976).

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, 3994 (1976).

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., 81, 913 (1977).

S. Schlick and L. Kevan, Confirmation of O^- Formation in γ -Irradiated 10 M NaOH/ $H_2^{17}O$ Alkaline Ice Glass by Electron Paramagnetic Resonance Studies, J. Phys. Chem., 81, 1093 (1977).

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., 81, 605 (1977).

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., 55, 1940 (1977).

P. A. Narayana and L. Kevan, Effects of Quadrupole Interaction on Electron Spin Echo Modulation Patterns in Disordered Systems, J. Magn. Resonance, 26, 437 (1977).

N. 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., 81, 456 (1977).

The following 15 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. D. P. Lin and L. Kevan, Second Moment Studies of the ESR Lineshape of Trapped Electrons in Sodium-Ice Condensates: Relation to the Molecular Structure Around Trapped Electrons in Aqueous Systems, J. Phys. Chem., 81, 1498 (1977).

2. S. A. Rice and L. Kevan, Comparison of Photoconductivity and Optical Spectra of the Trapped Electron in Polar Aqueous and Alcoholic Glasses, *J. Phys. Chem.*, 81, 847 (1977).
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4. K. K. Ho and L. Kevan, Temperature Dependence of the Recombination Fluorescence of Photoionized Indole and N, N, N', N'-Tetramethyl-p-phenylenediamine (TMPD) in Organic Glasses: Consequences of Electron Tunneling and Diffusion, *J. Phys. Chem.*, 81, 1865 (1977).
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3. Scientific Talks Presented

The following 17 talks were given on ERDA supported research during the current report period at several scientific conferences and by invitation at a number of universities and research institutes.

- ERDA-T196 Localization and Solvation of Electrons in Condensed Media, L. Kevan, Seminar, University of Tokyo, Japan, October 28, 1976.
- ERDA-T197 Silver Atom Formation and Trapping in Frozen Matrices, L. Kevan, Research Reactor Institute of Kyoto University, Japan, November 15, 1976.
- ERDA-T198 Localization and Solvation of Electrons in Condensed Media, L. Kevan, Radiation Center of Osaka Prefecture, Japan, November 30, 1976.
- ERDA-T199 Electron Spin Echo Modulation from Trapped Radicals in Disordered Systems, L. Kevan, Osaka University, Japan, December 13, 1976.
- ERDA-T200 Application of Electron Spin Resonance to Radiation Chemistry, Lecture Series, L. Kevan, Hokkaido University, Sapporo, Japan, January 20, 1977.
- ERDA-T201 Solvation and Desolvation of Radiation-Produced Silver Atoms in Aqueous Matrices, University Lecture, L. Kevan, Hokkaido University, Sapporo, Japan, January 21, 1977.
- ERDA-T202 Electron-Solvent Interactions, Invited Lecture Series of 12 lectures, L. Kevan, University of Paris-Sud, Orsay, France, March 7 - May 13, 1977.

ERDA-T203

A Numerical Model of CO_2 Radiolysis, R. Kummier, C. Leffert, K. Im, R. Piccirelli, L. Kevan and C. Willis, Nat. Amer. Chem. Soc. Meeting, Symposium on Reaction Mechanism, New Orleans, LA, March 20-25, 1977.

ERDA-T204

Electron Spin-Lattice Relaxation Mechanisms of Radiation Produced Trapped Electrons and Hydrogen Atoms in Aqueous and Organic Glassy Matrices, L. Kevan and M. K. Bowman, Invited Lecture, Faraday Discussion on Radiation Effects in Liquids and Solids, Leicester, England, March 23-25, 1977.

ERDA-T205

Localization and Solvation of Electrons in Condensed Media, L. Kevan, Center for Wave Mechanics, C.N.R.S., Paris, France, March 31, 1977.

ERDA-T206

Laser Photolysis Study of Recombination Luminescence of Trapped Electrons in Low Temperature Glasses, M. Ogasawara, and L. Kevan, Annual Meeting of the Japanese Chemical Society, Osaka, Japan, April 1-5, 1977.

ERDA-T207

Known and Unknown Characteristics of Solvated Electrons, L. Kevan, Seminar, University of Paris-Sud, Orsay, France, May 3, 1977.

ERDA-T208

Solvation of Silver Atoms in Aqueous Matrices, L. Kevan, Seminar, Institute of Chemical Kinetics and Combustion, Novosibirsk, USSR, May 23, 1977.

ERDA-T209

Second Moment Studies of the ESR Lineshape of Trapped Electrons in Sodium-Ice Condensates: Relation to the Molecular Structure Around Trapped Electrons, L. Kevan and D. P. Lin, Nat. Am. Chem. Soc. Meeting, Symposium on Radiation Effects, Chicago, IL, August 29-September 2, 1977.

- ERDA-T210 Ion and Atom Solvation Structure Studied by Electron-Spin Echo Spectrometry, L. Kevan and P. A. Narayana, 26th Int. Congress of Pure and Applied Chemistry, Tokyo, Japan, September 4-10, 1977.
- ERDA-T211 Photoconductivity of Presolvated Electrons in Ethanol Glass, H. Hase, L. Kevan and T. Higashimura, Japan Radiation Chemistry Congress, Hokkaido, Japan, October 6-8, 1977.
- ERDA-T212 Solvation Process of Silver Atoms in Ice, L. Kevan, H. Hase and K. Kawabata, Japan Radiation Chemistry Congress, Hokkaido, Japan, October 6-8, 1977.
- ERDA-T213 Trapped Electrons in MTHF-Methanol Mixtures: Pulse Radiolysis at 77 K and Optical Absorption at 4 K, M. Ogasawara, L. Kevan and H. Yoshida, Japan Radiation Chemistry Congress, Hokkaido, Japan, October 6-8, 1977.