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Technical Progress Report

RADIOLYSIS STUDIES ON REACTIVE INTERMEDIATES

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RADIOLYSIS STUDIES ON REACTIVE INTERMEDIATES

Report Period: April 30, 1971 - April 1, 1972

During this period the general areas of investigation have included paramagnetic relaxation studies of the spatial distribution of trapped species, mechanisms of electron trapping in glassy matrices, application of the semicontinuum model to trapped electrons, discovery of two photon transitions associated with trapped electrons in organic glasses and Hall mobility measurement of photo excited electrons in glassy and crystalline matrices.

Thirteen papers have been published or accepted for publication and have been issued as technical reports; their abstracts are given below. In addition, the reference citations of papers abstracted in the previous report which have since been published are listed.

The following sections describe (1) research publications, (2) scientific talks presented (3) Ph.D. Theses completed and (4) current research summary.

The principal investigator has spent an average of 25% of his time during the academic year and 100% of one summer month on this project.

Three students have completed Ph.D. theses during this report period; their theis titles and present positions are given below.

1. Research Publications

The following publications were abstracted in the previous report (COO-2086-16) and have since been published.

- COO-2086-5 Radiation Chemistry of Frozen Nonpolar and Slightly Polar Systems, L. Kevan, *Actiones Chim. Biolog. Radiations*, 15, 81 (1971).
- COO-2086-10 Total and Dissociative Charge-Transfer of Positive Ions with Perfluoroalkanes Studied by Mass Spectrometry, D. L. Smith and L. Kevan, *J. Chem. Phys.*, 55, 2290 (1971).
- COO-2086-11 Total Charge-Transfer Cross-Sections in Molecular Systems, D. L. Smith and L. Kevan, *J. Amer. Chem. Soc.*, 93, 1102 (1971).
- COO-2086-12 Laser Bleaching of Trapped Electron Optical Bands in γ -Irradiated Alkaline Ice, K. K. Ho and L. Kevan, *Intern. J. Radiation Phys. Chem.* (J. J. Weiss testimonial issue), 3, 193 (1971).
- COO-2086-13 Thermal Decay Effects on Spatial Distributions of Radicals in γ -Irradiated Polymethylmethacrylate, W. Kaul and L. Kevan, *J. Phys. Chem.*, 75, 2443 (1971).
- COO-2086-14 A Semicontinuum Model for the Hydrated Electron II. Configurational Stability of the Ground State, K. Fueki, D. F. Feng, L. Kevan and R. E. Christofferson, *J. Phys. Chem.*, 75, 2297 (1971).

- COO-2086-15 EPR Studies of Multiple Ag^0 Trapping Sites Produced in Gamma-Irradiated Frozen AgNO_3 Ices, B. L. Bales and L. Kevan, J. Chem. Phys., 55, 1327 (1971).

The following publications have been published or accepted for publication during the current report period.

- COO-2086-17 A Semicontinuum Model for the Solvated Electron in Methanol, K. Fueki, D. F. Feng and L. Kevan, Chem. Phys. Letts., 10, 504 (1971).

Abstract: The semicontinuum model for solvated electrons has been applied to methanol at 300°K . The configurational stability of the ground state was established and various physical properties of the solvated electron have been calculated and compared with experiment.

- COO-2086-18 Paramagnetic Relaxation Study of Spatial Distribution of Trapped Electrons in Gamma-Irradiated Organic Glasses, D. P. Lin and L. Kevan, J. Chem. Phys., 55, 2629 (1971).

Abstract: Paramagnetic relaxation characteristics of trapped electrons in γ -irradiated glassy 3-methylpentane (3MP) at 71°K , and triethylamine (TEA) and methyltetrahydrofuran (MTHF) at 77°K were studied by power saturation techniques. For MTHF and TEA the characteristic relaxation time, $(T_1 T_2)^{1/2}$, is constant with radiation dose at low doses and decreases at higher doses. For 3MP the relaxation time decreases even at low dose. Together with data on the total spin concentration the results are interpreted in terms of a "spur" model in which the radiation-produced

trapped electrons and radicals are trapped in clusters at low dose and constitute a nonuniform spatial distribution. According to this model the spur radius is $> 130\text{\AA}$ in 3MP, $101\text{\AA}$ in TEA and $63\text{\AA}$ in MTHF. These radii compare with $58\text{\AA}$ for trapped electrons in glassy methanol and $41\text{\AA}$ in glassy alkaline ice (10M NaOH). For all of these matrices the radius within which the electrons are trapped appears to increase with decreasing polarity of the matrix, and consequently radiation-produced electrons appear to travel farther before being trapped in less polar matrices.

COO-2086-19 Pulse Radiolysis Study of the Mechanism of Electron Trapping in Alcohol Glasses at 77°K , L. Kevan, Chem. Phys. Letts., 10, 140 (1971).

Abstract: Trapped electron spectra in pulse-irradiated 2-propanol glass at 77°K shift toward the blue on a μsec timescale. Solute effects indicate that molecular reorientation around the electron is responsible for the transient spectral shift rather than a redistribution of electrons among traps.

COO-2086-20 Temperature Dependence of the Hall Mobility of Electrons in Glassy 10M NaOH Ice, I. Eisele and L. Kevan, J. Chem. Phys., 55, 5407 (1971).

Abstract: The electron Hall mobility in γ -irradiated glassy 10M NaOH ice was measured with a new double modulation method for Hall mobility measurements on high impedance photoconductors. At 80°K the electron Hall mobility is $4.7 \pm 1.9 \text{ cm}^2 \text{V}^{-1} \text{ sec}^{-1}$. The temperature dependence between 80°K and 133°K is given by $\mu_{\text{H}} \propto T^{-1.3}$. This temperature dependence is indicative of lattice phonon scattering and suggests that the electron motion can be treated in terms of a band model.

- COO-2086-21 Spatial Distribution of Radicals in Proton-Irradiated and Gamma-Irradiated Polymethylmethacrylate, W. Kaul and L. Kevan, Proceedings of Third Tihany Symposium on Radiation Chemistry, Akademiai Kiado, Budapest, 1972.

Abstract: Synthetically prepared polymethylmethacrylate (PMMA) was irradiated with 2 MeV protons and with Co^{60} γ -rays at 195 and 305°K. The line shape, line width and paramagnetic relaxation characteristics of the radicals produced were examined by electron paramagnetic resonance. The line shape is Gaussian for γ -irradiated samples and Lorentzian for proton-irradiated samples. In proton-irradiated PMMA the local spin concentration is at least 5.9 times greater than in γ -irradiated samples of comparable total spin concentration, and the radicals are less susceptible to microwave power saturation. The spatial distributions of the radicals are discussed in terms of the different linear energy transfer of the radiations.

- COO-2086-22 Pulse Radiolysis of Alcohol Glasses at 77°K:
Mechanism of Electron Trapping, L. Kevan, J. Chem. Phys., 56, 838 (1972).

Abstract: Ethylene glycol/water (50/50), methanol/water (95/5), ethanol, 1-propanol, 2-propanol and 2-propanol/methyltetrahydrofuran (50/50) glasses were studied by pulse radiolysis at 77°K. In each glass a trapped electron spectrum is observed which shifts toward the blue on a micro-second timescale. This suggests a shift from shallow to deeper traps. The spectral shift appears to occur more rapidly in more polar matrices. This is the opposite of the direction expected based on relative matrix

viscosities. When 10^{-2} M biphenyl or benzyl chloride is added to 2-propanol glass about 40% of the electrons are scavenged. The resulting biphenyl anion and benzyl radical spectra show no transient changes in intensity after the pulse while the residual trapped electron spectrum shows the same shift as before. Both the polarity and the solute effects indicate that molecular reorientation around the electron is responsible for the transient spectral shift. A short-range electron-matrix interaction would presumably cause faster reorientation in more polar matrices. An alternative mechanism of a redistribution of electrons among shallow and deep preformed traps seems to be ruled out.

COO-2086-23 Double Modulation Method for Hall Effect Measurements on Photoconducting Materials, I. Eisele and L. Kevan, Rev. Sci. Instr., 43, 189 (1972).

Abstract: A new double modulation method for photo-Hall mobility measurements on high impedance photoconductors is described. The magnetic field is modulated by rotating the sample in the field and the density of charge carriers is modulated by chopping the light beam which induces photoconductivity. The Hall signal is detected at the sum frequency of the two modulations and a clear distinction in phase and frequency between the Hall signal and different error signals is obtained. The method has been tested by measuring the Hall mobility of electrons in γ -irradiated KCl. $\mu_H = 1.0 \exp(646/T) \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ with $\mu_H = 9.0 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ at 300°K .

COO-2086-24 Optical Bleaching Effects on the Paramagnetic Relaxation of Trapped Electrons in Methyltetrahydrofuran at 77°K , D. P. Lin, L. Kevan, J. Phys. Chem., 76, 636 (1971).

Abstract: The effect of optical bleaching on the characteristic relaxation time, $(T_1 T_2)^{1/2}$ of trapped electrons (e_t^-) in methyltetrahydrofuran (MTHF) glass at 77°K has been measured for different doses corresponding to different initial spatial distributions. At low radiation doses $(T_1 T_2)^{1/2}$ increases as e_t^- are bleached. This confirms the spur model of electron trapping in this matrix and indicates that the spurs contain more than one e_t^- on the average. At high radiation doses $(T_1 T_2)^{1/2}$ remains constant as e_t^- are bleached. This is interpreted in terms of spin-spin relaxation of e_t^- with MTHF as well as with other e_t^- . A quantitative treatment of $T_1 T_2$ data versus total spin concentration confirms this latter interpretation.

COO-2086-25 Energy Level Structure of Trapped Electrons in Methyltetrahydrofuran Glass from Photoconductivity and Optical Bleaching Studies, T. Huang, I. Eisele, D. P. Lin and L. Kevan, J. Chem. Phys., (May, 1972).

Abstract: Electrons are trapped in γ -irradiated methyltetrahydrofuran (MTHF) glass at 77°K. Monochromatic photoexcitation produces photoconductivity and optical bleaching with a threshold near 780 nm (1.6 eV) and a peak near 520 nm (2.4 eV). This transition is linear in light intensity and independent of temperature between 77° and 4.2°K, so it is interpreted as a one photon transition directly to the conduction band or to an autoionizing state. Effective double beam photoexcitation discloses a two photon transition which depends on the light intensity squared. The first photon corresponds to the well-known optical absorption of trapped electrons in MTHF at 1.0 eV. This transition is interpreted as a $1s \rightarrow 2p$ type. The $2p$ state then presumably crosses to a $2s$ -type state from which the second photon is absorbed. The wavelength dependence of the second

photon transition shows a peak at 950 nm (1.3 eV) and a threshold near 1150 nm (1.1 eV). The temperature of both optical bleaching and photoconductivity under IR photoexcitation shows that population of the 2s-type state involves an activation energy ~ 0.001 eV. The deduced energy level structure agrees well with theoretical calculations based on a semiconductor model for trapped electrons in glassy matrices. Compared to more polar matrices like ice, both experiment and theory indicate that in less polar matrices like MTHF the short-range charge-dipole interactions are relatively less important compared to the long range polarization interactions and cause the bound excited states to be relatively more stable and the ground state to be relatively less stable.

COO-2086-26 A Semiempirical Estimate of the Scattering Cross Section and Mobility of Excess Electrons in Liquid Hydrocarbons, K. Fueki, D. F. Feng and L. Kevan, Chem. Phys. Letts. (1972).

Abstract: The scattering cross sections and intrinsic mobility of electrons in liquid hydrocarbons have been calculated from measurements of the quasi-free electron energy. By incorporating the mobility temperature dependence the calculated mobilities satisfactorily explain the tenfold difference of mobilities in n-hexane and neopentane.

COO-2086-27 High Temperature Dependence of the Electron Hall Mobility in γ -Irradiated KCl, I. Eisele and L. Kevan, J. Chem. Phys., (1972).

Abstract: The electron Hall mobility in γ -irradiated KCl was measured

with a new double modulation method for Hall mobility measurements on high impedance photoconductors. At 300°K the Hall mobility is $9.0 \text{ cm}^2/\text{V sec}$. The temperature dependence between 150°K and 300°K is $\mu_{\text{H}}(\text{KCl}) = 1.0 \exp(646/T)$. In KCl, $\theta = 300^{\circ}\text{K}$, so weak coupling polaron mobility theories do not apply at high temperatures as they do at temperatures below 100°K . Intermediate coupling polaron theory is required to understand the high temperature mobility data.

COO-2086-28 Application of the Semicontinuum Model to the
Effect of Dipole Re-Orientation on Trapped Electron
Spectra in Glassy Ethanol, K. Fueki, D. F. Feng,
and L. Kevan, J. Chem. Phys. (1972).

Abstract: A semicontinuum model is applied to trapped electrons in glassy ethanol at 77°K . The configurational stability of the ground state has been established. Ground, excited and continuum states are calculated self-consistently for specific orientations from 80° to 0° of the molecular dipoles with respect to the trapped electron. It is shown that the spectral shifts observed for trapped electrons in pulse radiolysis experiments on alcohol glasses and the shifts observed upon warming from 4° to 77°K after γ -irradiation at 4°K can be semiquantitatively accounted for by the molecular dipole orientation mechanism. The cavity radius of the trapped electron also increases somewhat upon dipole orientation but this is a small effect. The effect of dipole orientation upon other physical properties of the trapped electrons in ethanol are also discussed.

- COO-2086-29 Paramagnetic Relaxation Study of Spatial Distribution of Trapped Radicals in Gamma-Irradiated Alkaline Ice and Organic Glasses at 4.2°K , D. P. Lin, P. Hamlet and L. Kevan, J. Phys. Chem. (1972).

Abstract: The spatial distribution of trapped radicals in γ -irradiated 10M NaOH (alkaline ice), 2-methyltetrahydrofuran (MTHF) and triethylamine (TEA) has been studied at 4.2°K by measuring the characteristic paramagnetic relaxation time versus radiation dose. Radical spur radii of $< 36 \text{ \AA}$ in alkaline ice, $< 34 \text{ \AA}$ in MTHF and $< 37 \text{ \AA}$ in TEA are deduced from the data. These radii are smaller than the trapped electron spur radii measured previously in these same matrices.

2. Scientific Talks Presented

- AEC-102 Spatial Distribution of Radicals in Proton-Irradiated and Gamma-Irradiated Polymethylmethacrylate, W. Kaul and L. Kevan, Third Tihany Symposium on Radiation Chemistry, Tihany, Hungary, May 10-15, 1971.
- AEC-103 Thermally Stimulated Conductivity of Gamma-Irradiated Triethylamine Glass, A. K. Munjal and L. Kevan, Regional Amer. Chem. Soc. Meeting, Cincinnati, Ohio, June 6-8, 1971.
- AEC-104 Development of a Semicontinuum Model for Solvated Electrons, D. F. Feng, K. Fueki and L. Kevan, Regional Amer. Chem. Soc. Meeting, Cincinnati, Ohio, June 6-8, 1971.
- AEC-105 Drift Mobility of Photoexcited Electrons in Alkaline Ice, L. Kevan, Gordon Conference on Radiation Chemistry, New Hampton, New Hampshire, July 12-16, 1971.

- AEC-106 Kinetic Transformations of Ag^0 by EPR in Gamma-Irradiated Ice Matrices, B. Bales and L. Kevan, Tenth International Symposium on Free Radicals, Lyon, France August 31-September 3, 1971.
- AEC-107 Drift Mobility of Photoexcited Electrons in Gamma-Irradiated Alkaline Ice, T. Huang, I. Eisele and L. Kevan, National Amer. Chem. Soc. Meeting, Washington, D. C., September 12-17, 1971.
- AEC-108 Mechanism of Electron Trapping in Alcohol Glasses, L. Kevan, Physical Chemistry Seminar, Wayne State University, Detroit, Michigan, October 20, 1971.
- AEC-109 Pulse Radiolysis of Alcohol Glasses at 77°K : Mechanism of Electron Trapping, L. Kevan, CIC Symposium on Pulse Radiolysis, Pinawa, Manitoba, Canada, October 25-27, 1971.
- AEC-110 Photoconductivity and Mobilities of Photoexcited Electrons in Disordered Systems, L. Kevan, Physics Department Seminar, Wayne State University, Detroit, Michigan, January 13, 1972.
- AEC-111 Matrix ENDOR Linewidths of Trapped Electrons in Glassy Matrices at 77°K , L. Kevan, invited lecture, Varian EPR/Double Resonance Workshop, Palo Alto, California, January 26-28, 1972.
- AEC-112 Pulse Radiolysis, L. Kevan, Amer. Chem. Soc. Student Affiliates, Wayne State University, Detroit, Michigan, February 2, 1972.
- AEC-113 Electrons on the Rocks, L. Kevan, Chemistry Seminar, Denver University, Denver, Colorado, February 25, 1972.
- AEC-114 Trapped and Photoexcited Electrons in Amorphous Systems, L. Kevan, Chemistry Seminar, Case Western Reserve University, Cleveland, Ohio, March 2, 1972.

3. Ph. D. Theses Completed

Ding-ping Lin Electron Paramagnetic Resonance Studies on the Spatial Distribution and Structure of Trapped Electrons in Gamma-Irradiated Organic Glasses, Ph.D. Thesis, Wayne State University, June, 1971.

Dr. Lin is currently a postdoctoral research associate with Professor J. E. Willard at the University of Wisconsin.

Timothy C. K. Su Ion-Molecule Reactions in Perfluorocarbons, Ph.D. Thesis, Wayne State University, November, 1971. (Only the early part of Dr. Su's research was supported by the AEC.)

Dr. Su is currently a postdoctoral research associate with Professor M. T. Bowers at the University of California at Santa Barbara.

Ignatz Eisele Photoconductivity and Photo Hall Effect in Gamma Irradiated Alkaline Ice, Ph.D. Thesis, Technical University of Munich, February, 1972. (The research was all carried out at Wayne State University and then the thesis was submitted, by prior arrangement, to the Technical University of Munich.)

Dr. Eisele is currently employed in the basic research lab of Siemens AG in Munich.

For reference, the current positions of the previous Ph.D. 's supported by the AEC on this research program (at the University of Kansas) is as follows.

Robert D. Koob (Ph.D. 1967) Associate Professor, Department of Chemistry, North Dakota State University.

John D. Zimbrick (Ph.D. 1967) Assistant Professor, Department of Radiation Biophysics, University of Kansas.

Jo A. Beran (Ph.D. 1968) Assistant Professor, Department of Chemistry, Texas A and I University.

David L. Smith (Ph.D. 1969) Research Assistant Professor, Department of Chemistry, University of Utah.

4. Current Research Summary

Current areas of research in radiation chemistry supported by the AEC at Wayne State University which are not yet complete are briefly described below.

1. Fast Passage Paramagnetic Relaxation Studies.

Radiolysis in solid systems generally produces trapped radicals or electrons. The process by which energy in the spin system is transferred to the solid matrix is called spin-lattice relaxation and is characterized by a time T_1 . Steady state saturation methods in electron paramagnetic resonance under equilibrium or slow passage conditions do not give T_1 directly. However, under fast or nonequilibrium passage conditions T_1 can be determined directly in principle. In practice, this is seldom true because nonadiabatic conditions are generally encountered and the theory for these conditions is not well understood. We have made an experimental analysis of the effect of various experimental parameters such as magnetic field modulation frequency ω_m , magnetic field modulation amplitude H_m , and microwave magnetic field amplitude H_1 on both absorption and dispersion signals under various fast passage conditions. Trapped electrons in polycrystalline KCl, 10M NaOH glassy ice, methyltetrahydrofuran glass, and triethylamine glass have been studied. A new technique for determining T_1 is proposed. This method is associated with the phase change in the dispersion signal due to passage effects. For adiabatic rapid, but not fast, conditions the dispersion signal appears 90° out-of-phase with respect to the modulation field

H_m . For adiabatic fast conditions the dispersion signal appears 180° out-of-phase with respect to H_m . Under generally achievable experimental conditions some signal can be seen at 90° and 180° out-of-phase. These two dispersion signals change in magnitude with H_1 , H_m and ω_m . So dispersion signals in the two regions can be plotted vs H_1 , H_m and ω_m and the intersection is interpreted as $\omega_m T_1 = 1$. Further analysis of the validity and self-consistency of this method is being carried out.

2. ELDOR Studies of Trapped Electrons

Electron-electron double resonance (ELDOR) studies have been initiated on radiation produced trapped electrons in 10M NaOH (alkaline ice) at 77°K . Initial objectives are to test the validity of the spin packet concept for inhomogeneously broadened EPR lines and to see if evidence for spin diffusion between spin packets can be detected. This is possible because in ELDOR one microwave frequency is used to pump or strongly irradiate one part of an EPR line while the second microwave frequency is used to monitor another part of the EPR line. ELDOR responses have been observed for trapped electrons in alkaline ice. An idealized model for the expected ELDOR responses based on a spin packet picture has successfully reproduced the observed ELDOR responses, but the experimental dependence on microwave power is not quantitatively reproduced. Although we are only in the beginning stages of this study it looks very

promising. Only a technique like ELDOR seems capable of answering the questions we have posed. The application of ELDOR is in its infancy, but our current results suggest that it will be practical to obtain rather incisive information about paramagnetic relaxation processes with it.

3. Frozen Solution Radiolysis - Thermal Decay

In the alkaline ice matrix (10M NaOH) only trapped electrons, trapped holes, in the chemically converted form of $O^{\cdot -}$, and a few trapped hydrogen atoms are produced by radiolysis. EPR has been used to follow the thermal decay of all these species simultaneously. Previous studies have focused only on the electron decay and a rather incomplete picture of the kinetics and decay mechanism has resulted. We find that two models can explain the results equally well. One model is a composite first order decay model. In general, more than two concurrent first order decay rates are required to explain the results and the decay of electrons and $O^{\cdot -}$ ions are not completely equivalent. The second model involves an equilibrium between trapped and thermally mobile electrons and a second order loss of the thermally mobile electrons by reaction with $O^{\cdot -}$. Analysis of the total number of electrons that decay in comparison with the total number present at 77°K after irradiation indicates an inequality which can be interpreted in terms of dielectron formation. When both electron and $O^{\cdot -}$ decay are considered simultaneously, homogenous kinetics are not completely satisfactory. However, it has not yet proved possible

to quantitatively apply an inhomogeneous kinetic treatment either. Further analysis is in progress and further experiments are being carried out to attempt to distinguish between the above two models.

4. Hall Mobility Measurements on Photogenerated Charge Carriers.

Using newly developed Hall effect instrumentation for high impedance photoconductors (COO-2086-23) the electron Hall mobility has been measured in 10M NaOH glassy ice from 80° to 133°K (COO-2086-20). This has provided the first definitive information about the charge transport mechanism in glassy aqueous matrices. It is desirable to improve the accuracy of such measurements in aqueous glasses and it is most exciting to be able to extend them to electron mobility in organic glasses. The limiting factor is the high impedance of the glassy matrices. Current research on this project is oriented toward design of a new sample holder and preamplifier to be compatible with the small Hall voltages from the high impedance samples.