FINAL TECHNICAL REPORT

"RADIOLYSIS STUDIES ON FLUOROCARBONS AND ON
REACTIVE INTERMEDIATES"

MASTER

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RADIOLYSIS STUDIES ON FLUOROCARBONS AND ON REACTIVE INTERMEDIATES

During the four year period of this contract the general areas of investigation have included fluorocarbon radiolysis, energy transfer by rare gas sensitization, charge transfer mass spectrometry of fluorocarbons, ionization cross sections, radiolysis of frozen aqueous solutions, spatial distribution of trapped electrons and radicals studied by paramagnetic relaxation, and models for trapped and solvated electrons in polar matrices.

The results of this research have been presented in 33 research publications, which have been published or are in press, 27 scientific papers at national and international meetings, and about 35 research lectures at university, government, and industrial laboratories. During the contract period five students completed their Ph.D. research and received their Ph.D. degree, five other graduate students began their Ph.D. research and are continuing their study, five students completed postdoctoral training in radiation chemistry, and six undergraduates participated in the research program.

The following sections describe (1) research publications, (2) papers presented at meetings, (3) research lectures and, (4) Ph.D. student information.

Research Publications

The titles and references citations of each publication are listed in reverse chronological order. Abstracts are included only for those publications not cited in previous technical progress reports, COO-1528-5, -14, and -26. Where the page number of the reference citation is not indicated the publication is in press.

COO-1528-39   Total Cross Sections In Molecular Charge Transfer

Reactions with Diatomic Neutrals, D. Smith and L. Kevan, Proceedings of International Conf. on Mass Spectrometry, Kyoto, Japan, September, 1969.

Abstract: Total charge transfer cross sections for both atomic and molecular systems have been investigated to assess the importance of internal energy resonance effects and Franck-Condon effects on the cross sections. A new ion source for studying charge transfer reactions in a single stage mass spectrometer was constructed. It allows the primary ion current to be monitored simultaneously with the secondary ion current; the product ions are collected perpendicular to the primary ion direction. The primary ion energy has a broad distribution with a typical average of 58 eV. At this energy the electron jump mechanism dominates. When total cross sections of various projectile ions with the same neutral target are compared, the cross sections exhibit a maximum when the ionization potential between the two colliding species is minimized. This energy resonant behavior holds for both atomic and molecular ions. Cross section maxima are found which correspond to excited electronic states of the product ion. The resonant behavior suggests that high vibrational levels of the product ion are not as easily excited as are lower ones. This is attributed to small Franck-Condon

factors to the vibrationally excited states in the ion. At thermal ion energies, energy resonance effects are not usually observed.

COO-1528-38 A Semicontinuum Model for the Hydrated Electron, K. Fueki, D. Feng, and L. Kevan, J. Chem. Phys. (1970).

Abstract: A semicontinuum model is developed for the hydrated electron. Long range interactions are represented by a polarization potential and short range attractive interactions are represented by a point dipole approximation. Energy levels as a function of cavity radius are calculated within a self-consistent-field approximation. The optical transition energy is rather insensitive to different configurations of the water molecules in the first solvation shell around the electron. The observed optical absorption of the hydrated electron in both water with $D_s = 80$ and in ice at 77°K with $D_s = 3$ can be satisfactorily explained with this model for cavity radii near $1 \text{ \AA}$. The calculated heat of solution and charge distribution of the hydrated electron with this cavity radius are also in good agreement with the experimental values.

COO-1528-37 EPR Studies of Trapped Species Produced by Tritium β -Particles in Alkaline and Acid Ices at 77°K , H. Hase and L. Kevan, J. Chem. Phys., 52, 0000 (1970).

Abstract: EPR Studies were performed on Co^{60} γ -irradiated 6M and 10M NaOH and 11M H_2SO_4 frozen solutions at 77°K and on similar frozen solutions which were tritiated with T_2O . The yield of trapped species was always larger in the γ -irradiated systems than the corresponding yield in

β -irradiated systems. The γ/β yield ratios were in semiquantitative agreement with similar ratios in liquid solutions. This is discussed in terms of different mean linear energy transfer for tritium- β - and Co^{60} - γ radiation. Paramagnetic relaxation studies versus radiation dose were carried out on the tritiated systems and compared with previous results on γ -irradiated systems. For trapped H atoms in acid ice a spatially uniform distribution was found for both β and γ radiolysis. Trapped electrons in alkaline ice show a nonuniform distribution for γ radiolysis characterized by a finite spur radius. The distribution is also nonuniform in β radiolysis but the average spur radius is larger. Surprisingly, the local concentration of trapped electrons appears smaller in β compared to γ radiolysis. A greater fraction of overlapping spurs in β radiolysis can account for these results.

COO-1528-36 On The Dielectric Continuum Model for the Hydrated Electron,
K. Fueki, D. Feng, and L. Kevan, Chem. Phys. Letters, 3, 0000 (1969).

Abstract: A three parameter wavefunction for the ground state of the hydrated electron has been used to calculate the optical transition energy for zero cavity radius within the SCF approximation to the dielectric continuum model. The results indicate that the electron is in a cavity with finite radius.

COO-1528-35 EPR Studies of Silver Atom Formation and Enhancement by Fluoride Ions in Gamma-Irradiated Frozen AgNO_3 Solutions, B. Bales and L. Kevan, J. Phys. Chem., 74, 0000 (1970).

Abstract: The γ -radiolysis of AgNO_3 ices at 77°K produces trapped Ag^0 , OH and NO_2 . Addition of fluoride ion increases Ag^0 , prevents NO_2 formation,

increases the total number of observable spins and increases the linear range of the dose-yield curve for Ag° . The initial Ag° yields are $G(\text{Ag}^\circ) = 1.2$ in 1 M AgNO_3 and $G(\text{Ag}^\circ) = 3.2$ in 1 M $\text{AgNO}_3 - 0.5$ M KF. These effects indicate that fluoride ion acts as an efficient hole trap for H_2O^+ and prevents electron-hole recombination. Low fluoride concentrations are effective, thus some H_2O^+ is mobile.

COO-1528-34 Temperature Dependence of Photocurrent in Gamma-Irradiated Alkaline Ice: Location of Energy Levels of Trapped Electrons, I. Eisele, R. Lapple, and L. Kevan, J. Am. Chem. Soc., 91, 6504 (1969).

Abstract: Photocurrent was observed from detrapping of electrons in γ -irradiated 10 M NaOH ice. The photocurrent shows that the trapped electrons can be optically excited to a mobile state. The photocurrent shows a slight negative temperature dependence between 4 and 77°K; this indicates that the optical transition is from a bound ground state directly to the conduction band. The temperature dependence above 77°K indicates the presence of shallow traps near the conduction band.

COO-1528-32 EPR of Ag° Site Conversion in Gamma-Irradiated Frozen AgNO_3 Ices, B. Bales and L. Kevan, Chem. Phys. Letters, 3, 484 (1969).

Abstract: Gamma radiolysis of AgNO_3 ice at 77°K forms Ag° in 4 magnetically distinct sites due to different orientations of water dipoles. Site interconversion which occurs by rotation of water dipoles due to removal of the electric field of Ag^+ is studied by EPR.

COO-1528-31 Molecular Electron Ionization Cross Sections At 70 eV, J. A. Beran

and L. Kevan, J. Phys. Chem., 73, 0000 (1969).

Abstract: Electron ionization cross sections at 70 eV have been measured for 62 hydrocarbons, fluorocarbons, and halogen-substituted hydrocarbons and fluorocarbons. These results together with previously measured results on other molecular classes have been tested against proposed correlations of ionization cross sections with polarizability, diamagnetic susceptibility and additivity of atomic ionization cross sections. None of these correlations is generally valid but each is valid within a given molecular class. It is striking, however, that there is a single linear correlation with diamagnetic susceptibility for all nonfluorine-substituted compounds. Two empirical equations are developed, based on polarizability and based on modified additivity correlations, which reproduce the experimental cross sections for 98 molecules in a wide variety of molecular classes within average deviations of 3% and 4.5%.

COO-1528-30 Semi-Empirical Calculations of Molecular Polarizabilities and Diamagnetic Susceptibilities of Fluorocarbons, Substituted Fluorocarbons, Ethers, Esters, Ketones, and Aldehydes, J. A. Beran and L. Kevan, J. Phys. Chem., 73, 0000 (1969).

Abstract: Empirical bond additivity and semi-empirical calculational methods for molecular polarizabilities and diamagnetic susceptibilities have been applied to fluorocarbons, substituted fluorocarbons, ethers, esters, ketones, and aldehydes as well as to a few halogen substituted alkanes and alkyl benzenes. The accuracy of the semi-empirical methods is assessed for the different molecular classes investigated. It is concluded that the calculated values for the fluorocarbon systems, for which little or no experimental data exists, are of sufficient accuracy to be used for evaluation of ion-molecule and electron ionization cross sections.

COO-1528-29 Paramagnetic Relaxation of Radiation-Produced Electrons in Annealed Glassy and Polycrystalline Alkaline Ices, H. Hase and L. Kevan, J. Phys. Chem., 73, 3290 (1969).

Abstract: Paramagnetic relaxation characteristics of e_t^- in γ -irradiated 10M NaOH ices which were annealed at various temperatures prior to irradiation were studied. The spin-spin relaxation time and e_t^- yields depend on the annealing temperature and time, while the spin-lattice relaxation time remains constant. This indicates that electrons are always trapped in similar local environments which are most likely glassy regions in the ice. Variations in total and local electron concentrations and in relaxation times with the temperature are explained by a model of electrons escaping from polycrystalline to glassy regions in the ices.

COO-1528-28 Spatial Distribution of Trapped Electrons in Alkaline Ice Produced by Photoionization, H. Hase and L. Kevan, J. Am. Chem. Soc., 90, 6875 (1968).

Abstract: The paramagnetic relaxation characteristics of trapped electrons in alkaline ice produced by photoionization of ferrocyanide ion was compared with results on electrons produced by gamma radiolysis. Analysis shows that the electron produced by photoionization are trapped with spatial uniformity which contrasts with the nonuniform spatial distribution found for electrons produced by gamma radiolysis.

COO-1528-27 "Radiation Chemistry of Frozen Polar Systems", L. Kevan in The Chemical and Biological Action of Radiations, Vol. 13, M. Haissinsky, Ed., Masson, Paris, 1969, pp. 57-117.

Abstract: A review of the radiolysis of aqueous and alcoholic frozen systems. Frozen systems are considered as those which freeze below room temperature. The focus is on the identification and reactions of trapped intermediates as detected by electron paramagnetic resonance and optical absorption.

COO-1528-25 "Paramagnetic Relaxation of Trapped Electrons in Gamma-Irradiated Organic Glasses," D. H. Chen and L. Kevan in Organic Solid State Chemistry G. Adler, Ed., Gordon and Breach, London, 1969, pp. 183-196.

Abstract: Paramagnetic relaxation characteristics of trapped electrons in γ -irradiated glassy methanol, ethanol and 2-methyltetrahydrofuran (MTHF) at 73°K were studied by power saturation techniques. The spin-spin relaxation time is constant with radiation dose at low doses and decreases at higher doses. Together with data on the total spin concentration the results are interpreted in terms of a "spur" model in which the initial spatial distribution of radiation-produced, trapped electrons and radicals is nonuniform. According to this model the spur radius is about 59 Å in methanol and 72 Å in MTHF. These radii compare with 42 Å for trapped electrons in alkaline ice. The radius within which electrons are trapped appears to increase with decreasing polarity of the matrix. The ratio of local spin concentration to the sample average spin concentration is greater than one at low doses in all matrices.

COO-1528-24 Spatial Distribution of Trapped Electrons in Gamma-Irradiated Organic Glasses, L. Kevan and D. H. Chen, J. Chem. Phys., 49, 1970 (1968).

Abstract: The spatial distribution of trapped electrons in gamma-irradiated methanol, ethanol and methyltetrahydrofuran was investigated by measuring

the spin-spin interaction versus radiation dose. The spatial uniformity of the trapped electrons increases with decreasing matrix polarity.

- COO-1528-23 Spatial Distribution of Trapped Radicals in Gamma-Irradiated Ethyleneglycol Dimethacrylate Polymers, J. Zimbrick, F. Hoecker, and L. Kevan, *J. Phys. Chem.*, 72, 3277 (1968).

Abstract: Trapped radicals are produced in γ -irradiated ethylene glycol dimethacrylate gels. A nine-line EPR spectrum is observed which is identical with the spectrum seen in irradiated methyl methacrylate gels. Paramagnetic-relaxation times as a function of radiation dose from 0.5-2 Mrads were measured by power-saturation methods. The spin-spin relaxation time is constant with dose and indicates that the radicals are trapped inhomogeneously in radiation-produced spurs in which the local radical molarity is several times greater than the average radical molarity.

- COO-1528-22 Energy Transfer in Radiolysis of Rare Gas-Propane Liquid Mixtures.

R. D. Koob and L. Kevan, *J. Phys. Chem.*, 72, 3808 (1968).

- COO-1528-21 "Free Radical Study by Electron Paramagnetic Resonance", L. Kevan in Methods in Free Radical Chemistry, E. S. Huyser, Ed., M. Dekker, New York, 1969, Vol. 1, pp. 1-33.

- COO-1528-19 Absorption Spectrum of Trapped Dielectrons in Alkaline Ice, L. Kevan,

D. R. Renneke, and R. J. Friauf, *Solid State Commun.*, 6, 469 (1968).

- COO-1528-18 "Radiation Chemistry of Frozen Aqueous Solutions", Larry Kevan, in Radiation Chemistry of Aqueous Systems, G. Stein, Ed., Wiley-Interscience, New York, 1968, pp. 21-72.

- COO-1528-17 Paramagnetic Relaxation of Trapped Hydrogen Atoms in Irradiated Frozen Aqueous Solutions. J. Zimbrick and L. Kevan, *J. Chem. Phys.*, 47, 5000 (1967).
- COO-1528-16 Energy Transfer in Radiolysis of Rare Gas- C_2F_6 Liquid Mixtures. A. Sokolowska and L. Kevan, *J. Phys. Chem.*, 72, 253 (1968).
- COO-1528-15 Comparison of Solvated Electron Rates in Water and in Ice. Larry Kevan, *J. Am. Chem. Soc.*, 89, 4238 (1967).
- COO-1528-13 Paramagnetic Relaxation of Trapped Hydrogen Atoms in Irradiated Frozen Solutions. J. Zimbrick and L. Kevan, *Nature*, 214, 693 (1967).
- COO-1528-12 "The Solvated Electron in Ice", Larry Kevan, in Energetics and Mechanisms in Radiation Biology, G. Phillips, Ed., Academic Press, New York, 1968, pp. 21-33.
- COO-1528-11 Evidence for Trapped Dielectrons in Ice. J. Zimbrick and L. Kevan, *J. Am. Chem. Soc.*, 89, 2483 (1967).
- COO-1528-10 Paramagnetic Relaxation of Trapped Electrons in Irradiated Alkaline Ices. J. Zimbrick and L. Kevan, *J. Chem. Phys.*, 47, (1967).
- COO-1528-9 Radiolysis of Liquid Hexafluoroethane. A. Sokolowska and L. Kevan, *J. Phys. Chem.*, 71, 2220 (1967).
- COO-1528-8 Dissociative Charge-Exchange of Rare Gas Ions with C_2F_6 and C_3F_8 . L. Kevan and D. Smith, *J. Chem. Phys.*, 46, 1586 (1967).
- COO-1528-6 Paramagnetic Relaxation of Trapped Electrons in Irradiated Alkaline Ices. Larry Kevan and John Zimbrick, *J. Am. Chem. Soc.*, 88, 3678 (1966).
- COO-1528-4 Radiolysis of Frozen Solutions. VI. Electron and Excited Water Reactions in Nitrate Ices. Larry Kevan, *J. Phys. Chem.*, 70, 2529 (1966).

COO-1528-3 SO_2 Elimination in the Radiolytic Decomposition of Diaryl Sulfones.

L. Kevan, P. Hall and E. T. Kaiser, J. Phys. Chem., 70, 853 (1966).

COO-1528-2   Trapped Hydrogen Yields and Precursors in Frozen Solution Radio-

lysis. L. Kevan and C. Fine, J. Am. Chem. Soc., 88, 860 (1966).

COO-1528-1   Energy Transfer in Radiolysis of Rare Gas- C_2F_6 Mixtures. Larry

Kevan, J. Chem. Phys., 44, 683 (1966).

Scientific Papers Presented at Meetings

- (AEC-T11) Trapped Hydrogen Atom Yields and Precursors in Frozen Solution Radiolysis, L. Kevan and C. Fine, National ACS Meeting, Atlantic City, New Jersey, September 13-17, 1965.
- (AEC-T18) Paramagnetic Relaxation Characteristics of Trapped Electrons and Hydrogen Atoms in Irradiated Frozen Aqueous Solutions, L. Kevan, Third International Congress of Radiation Research, Cortina, Italy, June 26- July 2, 1966.
- (AEC-T19) Dissociative Charge-Exchange of Rare Gas Ions with C_2F_6 and C_3F_8 , D. Smith and L. Kevan, National ACS Meeting, New York, September 12-16, 1966.
- (AEC-T20) Paramagnetic Relaxation of Trapped Electrons in Irradiated Alkaline Ices, J. Zimbrick and L. Kevan, National ACS Meeting, New York, September 12-16, 1966.
- (AEC-T21) Paramagnetic Relaxation of Trapped Hydrogen Atoms in Irradiated Acid Ices, L. Kevan and J. Zimbrick, Midwest Regional ACS Meeting, Lawrence, Kansas, October 27-28, 1966.
- (AEC-T22) Structure in Ionization Efficiency Curves of CF_2^+ from Perfluoroalkanes, L. Kevan and D. Smith, Midwest Regional ACS Meeting, Lawrence, Kansas, October 27-28, 1966.
- (AEC-T27) The Solvated Electron in Ice, L. Kevan, N.A.T.O. Advanced Study Institute on "Energetics and Mechanisms in Radiation Biology," Portmeirion, Wales, April 1-10, 1967.
- (AEC-T28) The Physical Nature of the Hydrated Electron in Frozen Solutions, J. Zimbrick, F. Hoecker and L. Kevan, Health Physics Society Meeting, Washington D. C., June 18-22, 1967.
- (AEC-T31) Paramagnetic Relaxation of Trapped Radicals in Irradiated Frozen Solutions, L. Kevan, Eighth International Symposium on Free Radicals, Novosibirsk, USSR, July 26-31, 1967.
- (AEC-T34) Thermal Decay of Trapped Electrons in Irradiated Alkaline Ice, L. Kevan

- and C. Elston, National ACS Meeting, Chicago, Illinois, September 13-15, 1967.
- (AEC-T35) Energy Transfer in Radiolysis of Rare Gas- C_2F_6 Liquid Mixtures, A. Sokolowska and L. Kevan, Regional ACS Meeting, Columbia, Missouri, November 2-3, 1967.
- (AEC-T36) A New Ion Source for Studying Charge Exchange Reactions by Mass Spectrometry, D. Smith and L. Kevan, Regional ACS Meeting, Columbia, Missouri, November 2-3, 1967.
- (AEC-T38) Electron Transfer Reactions in Irradiated Ice, L. Kevan, Symposium on Electron Transfer Phenomena, UCLA, December 11-12, 1967.
- (AEC-T39) Radiolysis of Frozen Aqueous Solutions, L. Kevan, Farkas Memorial Symposium on Radiation Chemistry of Aqueous Systems, Hebrew University, Jerusalem, Israel, December 27-30, 1967.
- (AEC-T42) Paramagnetic Relaxation of Trapped Electrons in Gamma-Irradiated Organic Glasses, L. Kevan and D. Chen, Organic Solid State Symposium, Brookhaven National Laboratory, March 25-28, 1968.
- (AEC-T43) Vacuum Ultra-Violet Photolysis of Propane in the Liquid Phase, R. D. Koob, and L. Kevan, National ACS Meeting, San Francisco, April 1-5, 1968.
- (AEC-T44) Quasi-Resonance to Electronic Levels in Charge Exchange Reactions Studied by Mass Spectrometry, D. Smith and L. Kevan, National ACS Meeting, San Francisco, April 1-5, 1968.
- (AEC-T45) Energy Transfer in Radiolysis of Rare Gas - Propane Liquid Mixtures, R. D. Koob and L. Kevan, Symposium on Photochemistry and Radiation Chemistry, U. S. Army Natick Laboratory, Natick, Massachusetts, April 22-24, 1968.
- (AEC-T47) Electron Ionization Cross Sections For Substituted Fluorocarbons, Jo A. Beran and L. Kevan, National ACS Meeting, Atlantic City, New Jersey, September 9-13, 1968.
- (AEC-T48) Paramagnetic Relaxation of Trapped Electrons in γ -Irradiated Triethylamine at 77°K, D. P. Lin and L. Kevan, Regional ACS Meeting, Manhattan, Kansas, October 31 - November 1, 1968.

- (AEC-T49) Spatial Distribution of Trapped Electrons in Alkaline Ice Produced by Photoionization, H. Hase and L. Kevan, Regional ACS Meeting, Manhattan, Kansas, October 31 - November 1, 1968.
- (AEC-T60) Electron Paramagnetic Resonance of Ag° in Gamma-Irradiated Frozen AgNO_3 Solutions, B. L. Bales and L. Kevan, Amer. Phys. Soc. Meeting, Philadelphia, Pennsylvania, March 24-27, 1969.
- (AEC-T61) Photoconduction in Irradiated Alkaline Ice, L. Kevan, Miller Conference in Radiation Chemistry, Portmeirion, Wales, April 14-18, 1969.
- (AEC-T63) Spatial Distribution and Energy Levels of Trapped Electrons in Ices, L. Kevan, Conference on ESR in Radiation Chemistry, Chalk River, Ontario, Canada, May 6-8, 1969.
- (AEC-T72) EPR Studies on Trapped Species Produced by Tritium β -Particles in Ices, H. Hase and L. Kevan, National Amer. Chem. Soc. Meeting, New York, New York, September 8-12, 1969.
- (AEC-T73) Energy Levels of Trapped Electrons in Irradiated Alkaline Ice, P. Hamlet and L. Kevan, National Amer. Chem. Soc. Meeting, New York, New York, September 8-12, 1969.
- (AEC-T74) Total Cross Section in Molecular Charge Transfer Reaction with Diatomic Neutrals, D. Smith and L. Kevan, International Conference on Mass Spectrometry, Kyoto, Japan, September 8-12, 1969.

Research Lectures

About 35 research lectures on work wholly or partially supported by the AEC were given by invitation during the period of this contract. Instead of listing titles, dates, etc., only a selected list of the organizations to which these lectures were presented will be given.

Universities and Colleges: Boston University, USAF Academy, University of Arkansas, Hope College, University of Kansas, Kyoto University - Japan, University of California, Irvine, UCLA, North Dakota State University, University of Paris - Orsay, University of New Hampshire, University of Toledo, Wayne State University, Occidental College, University of Tennessee, University of Florida, University of Colorado, University of Utah, Oklahoma State University, Bratislava Technical University, Comenius University - Czechoslovakia.

Government Laboratories: Aerospace Research Labs. Wright Patterson AFB; Rocket Propulsion Lab, Edwards AFB; Institute of Chemical Kinetics, Novosibirsk; Bhaba Atomic Research Center, Bombay; Institute for Strahlenchemie, Karlsruhe; Nuclear Research Institute and Institute of Physical Chemistry, Prague.

Industrial Laboratories: Bell Telephone Labs, Johnson Labs - Baltimore, Ford Scientific Labs - Detroit.

Ph. D. Students

The following five students received their Ph. D. based on research partially supported by the AEC during the period of this contract. Their names, thesis titles and present positions are given:

Robert D. Koob - Ph. D., January, 1967

Thesis - Direct and Rare Gas Sensitized Radiolysis of Liquid Propane
Present Position - Associate Professor, Department of Chemistry,
North Dakota State University, Fargo, North Dakota

John D. Zimbrick - Ph. D., January, 1967

Thesis - EPR Studies of Trapped Electrons, Hydrogen Atoms and Free
Radicals in Irradiated Solids
Present Position - Assistant Professor, Department of Radiation Biophysics,
University of Kansas, Lawrence, Kansas

James Edward Barnes - Ph. D., July, 1968

Thesis - A Study of Trapped Charge Carriers in Gamma-Irradiated Organic
Polymers
Present Position - Group Leader, Department of Radiobiology, Lovelace
Foundation, Albuquerque, New Mexico

Jo Allen Beran - Ph. D., August, 1968

Thesis - Electron Ionization Cross Sections For Substituted Fluorocarbons
Present Position - Assistant Professor, Department of Chemistry, Texas A
and I University, Kingsville, Texas

David Lee Smith - Ph. D., August, 1969

Thesis - Molecular Charge Transfer Reactions
Present Position - Instructor and Research Associate, Department of
Chemistry, University of Utah, Salt Lake City, Utah