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Research Highlights

October 1989 - September 1990

The following survey of the research activities of the Radiation Chemistry and Photochemistry Section is representative of highlights of the past year rather than a comprehensive account. For more detailed accounts of the activities described herein, see the articles listed in *Publications* and *Submissions* at the end of the report, or contact the author(s) indicated.

I. REACTIVE INTERMEDIATES IN THE CONDENSED PHASE: RADIATION CHEMISTRY AND PHOTOCHEMISTRY

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Outside Collaborators: R. Cooper, P. E. Eaton, V. V. Krongauz, R. G. Lawler, R. C. Patel, P. W. Percival, C. Romero, Y. Xiong

The goals of this research are to determine the fundamental chemistry induced by energetic radiation, and to define how energy is transformed when energetic particles or high-energy photons interact with matter. The various short-lived intermediates, radicals, radical cations, electrons, and excited states all play intricate roles in the overall chemical transformations. Our work is directed towards the identification of all the transient species involved and the determination of the chemical transformations that such reactive species can undergo.

Furthermore, the understanding of the chemical transformations of highly energetic species will allow the formulation of a new paradigm for the reactions of highly energetic species. The study of highly reactive species is closely tied to the development of improved experimental tools. State-of-the-art accelerators and lasers are continually being implemented and improved. We have developed several novel tools for studying transient paramagnetic species. Other experimental developments include the exploitation of new matrices and solvent systems such as liquid xenon.

This Survey is presented in two major parts: Part A presents our work on ions, excited states, and other transients in the condensed phase. These include studies of radical cations and ion-molecule reactions by magnetic-resonance methods, picosecond-emission and -absorption studies relevant to the role of ions in condensed-phase chemistry, and studies of photoionization and ion-transformation in low-temperature matrices.

Part B treats the work on the role of solvents in chemical reactivity. $H^\bullet$ and $D^\bullet$ atom reactions provide a probe of e_{aq}^- solvation and are used to study diffusion in ice. Solvent reorganization around molecules in their excited states is probed by fast laser methods, and molecular-dynamics simulations are carried out to establish the role of ions in electron solvation.

The highlights of this past year include:

- (1) Picosecond optical studies of radical cations and excited states produced in hydrocarbon radiolysis provided the first kinetic measurements of ion transformation and production of triplet and singlet excited states by ion recombination.
- (2) Studies of radical cations of alkyl-substituted amines and sulfides provided insights into ion-molecule reactions of radical cations in the condensed phase.
- (3) Studies of the behavior of strained alkane radical cations, such as cubane⁺, revealed new rearrangements and remarkable, medium-dependent differences in their structures.
- (4) $H^\bullet$ atom reactions yielding e_{aq}^- provided the first reliable measurements of hydrated-electron enthalpy and entropy and forced the revision of some previous thinking about the driving force in e_{aq}^- reactions.

A. Chemistry of Ions in the Condensed Phase

A. D. Trifunac, C. D. Jonah, D. W. Werst, M. C. Sauer, Jr., K. H. Schmidt, M. G. Bakker, M. Glezon, A. Liu, X. Qin, R. Cooper, P. E. Eaton, Y. Xiong

1. Condensed-Phase Reactions of Radical Cations D. W. Werst, A. D. Trifunac

In the past year we began a study of radical cations in electron-irradiated hydrocarbon solvents containing alkylamine and alkylsulfide solutes by using time-resolved fluorescence detected magnetic resonance (FDMR). The pulse radiolysis-FDMR method has been very successful for the elucidation of the identity and reactions of radical cations in alkane solutions. Our studies of the observability (and thus, longevity) of alkane radical cations by FDMR provided convincing evidence for the occurrence of ion-molecule reactions between alkane radical cations and neutral alkane molecules. The reactivity of different alkane radical cations varies considerably in a so far unpredictable way.

The purpose of the new studies is to investigate the reactions between solvent radical cations, e.g., alkane radical cations, and neutral solute molecules such as alkylamines and alkylsulfides. In many cases, formation of the solute radical cation allows its reactions to be studied as well. Questions we wish to answer include: 1) Do the solvent radical cations react with solute molecules via electron transfer or proton transfer? 2) Are there predictable trends in radical-cation reactivity? 3) Do the reactivities of the solute radical cations vary in a predictable fashion? 4) How does the solvent influence reactions between solute cations and neutral solute molecules?

The discussion of this work is divided into two parts. Part (a) describes the FDMR results for n-hexane solvent containing various mono-, di- and tri-alkylamine solutes. The expectation that amines should be good proton acceptors is borne out; however, electron-transfer reactions became increasingly competitive as the degree of alkyl substitution of the amine increases. This duality of radical-cation reactivity adds greatly to the complexity of condensed-phase ion chemistry. In part (b) preliminary results are discussed for alkylsulfide solutions in alkane and aromatic hydrocarbon solvents. An interesting solvent

effect on the reactivity of the sulfide radical cations is observed.

a. Alkylaminium Radicals in n-Hexane

The general scheme for generating and observing solute radical cations in alkane solvents by FDMR is depicted in Figure 1 in which n-hexane is used as an example.

Figure 1. Ionic reactions leading to fluorescence in the pulse radiolysis-FDMR experiment.

Electron radiolysis creates geminate ion pairs that consist of alkane radical cations and electrons. The scintillator ($\text{A}=\text{anthracene-d}_{10}$) cation and anion are formed via charge-scavenging reactions. The alkylamine solute (R_2NH), since its ionization potential (IP) is lower than that of the solvent, traps positive charge as well. Time-resolved EPR spectra of radical ions, which recombine on the nanosecond time scale to give ${}^1\text{A}^*$, are detected via the microwave-induced modulation of the yield of ${}^1\text{A}^*$ due to the conversion of initially singlet-phased geminate ion pairs to triplet pairs. A plot of the observed fluorescence intensity vs. magnetic field reveals the superimposed EPR spectra of the ions which recombined geminately to give ${}^1\text{A}^*$ and were present during the microwave pulse.

The purpose of the present study is to use the FDMR signal to probe the occurrence of Reactions *iv* and *vi* (Figure 1) and competing processes. The intensity of the aminium radical FDMR signal depends on the relative rate sequence of the electron-transfer reactions, and on the rates of competitive ion-molecule reactions which result in nonradical-cation products and reduce the FDMR signal. This selectivity makes FDMR an excellent tool for distinguishing between electron transfer and ion-molecule reactions of radical cations.

The ease of observation of aminium radical FDMR signals in alkylamine/n-hexane mixtures increases with increasing alkyl substitution of the amine solute. The radical cations of a variety of tri-alkylamines are observed. Monoalkylamines do not yield aminium radical FDMR signals. Dialkylamines are intermediate in their behavior. The ease of observation of dialkylaminium radicals increases with methylation of the α -C as illustrated, for example, by the series 2,2,6,6-tetramethylpiperidine, 2,6-dimethylpiperidine and piperidine.

The FDMR spectrum observed at 205 K in n-hexane containing 10^{-3} M 2,2,6,6-tetramethylpiperidine and 10^{-4} M anthracene- d_{10} is shown in Figure 1-2. The features which match the simulated stick EPR spectrum are those of the tetramethylpiperidinium radical. The intense feature in the center is due to the unresolved EPR lines of the scintillator radical ions. The spectrum was observed at the earliest time possible by applying a 100-ns microwave pulse immediately after excitation with a 12-ns electron-beam pulse.

Under identical conditions, the piperidinium radical is not observed by FDMR. A plausible explanation for the behavior of the different alkyl amines originates in differences in the rates of their proton-transfer reactions. Inasmuch as all the amines are reactive bases, the transfer of a proton from the n-hexane radical cation to the amine solute, Equation (1), competes with the desired electron-transfer reaction

from the neutral amine to $C_6H_{14}^{\bullet}$. Because neither product of Reaction (1) is a radical cation, neither can be observed by FDMR. Any such destruction of rad

Figure 2. FDMR spectrum observed at 205 K in n-hexane containing 10^{-4} M anthracene- d_{10} and 10^{-3} M 2,2,6,6-tetramethylpiperidine. The stick spectrum was simulated using $a^N \approx 18.6$ G, $a^H = 21.3$ G.

cal cations will decrease the intensity of the total FDMR intensity.

The trends observed in the FDMR results for different amines in n-hexane support the explanation involving the competition between electron transfer and proton transfer. For example, the ease of observation of the aminium radical FDMR signal increases with ΔIP ($IP(n\text{-hexane}) - IP(\text{solute})$), a measure of the relative driving force for electron transfer. In addition, the steric crowding around the nitrogen atom (the proton-acceptor site) also increases with increasing ΔIP /alkyl substitution and may be a significant mitigating factor in the ability of proton transfer to compete with electron transfer.

While $IP(R_2NH)$ decreases with increasing alkyl substitution, $PA(R_2NH)$ increases with the number and size of alkyl substituents. Therefore, the trends in ΔIP and ΔPA oppose one another and cannot act in concert to favor or disfavor proton transfer versus electron transfer. The relative change in ΔPA may be smaller than for ΔIP , or ΔIP may for some reason factor more importantly in the competition between electron and proton transfer. The effect of increasing ΔIP on the competition between electron transfer and proton transfer has been illustrated in gas-phase studies of the reactions between the cyclobutane cation

(IP(C₄H₈) = 9.9 eV) and the amines CH₃NH₂ (IP = 8.97 eV), (CH₃)₂NH (IP = 8.24 eV) and (CH₃)₃N (IP = 7.82 eV). Proton transfer is favored for CH₃NH₂ (~3 to 1), but electron transfer is favored for (CH₃)₂NH (~10 to 1) and (CH₃)₃N (~20 to 1). This trend is observed despite the fact that the PA increases by ~0.5 eV from CH₃NH₂ to (CH₃)₃N.

The failure to observe the aminium radical FDMR signal might mean that the cation is not formed. Alternatively, failure to form the scintillator excited state upon recombination would likewise quench the FDMR signal. Again, we are proposing a competition between electron transfer, Reaction vi (Figure 1), and proton transfer, Equation (2). Reaction (2) should become less facile with decreasing acidity of the aminium radical, i.e., with increasing alkyl substitution, which is consistent with the FDMR results.

(The notation depicts the transfer of H⁺ or H[•]. R₂N[•] in Equation (2) and later equations can denote an aminyl or aminoalkyl radical. Trialkylamines have no α-H; only α-C-H deprotonation is possible.)

The dependence of the FDMR signal intensity on the solute concentration provides additional information about this chemistry. In every case the FDMR signal decreases with increasing amine concentration. This behavior is analogous to that previously observed for solute alkane radical cations. It is indicative of bimolecular, ion-molecule reactions between the aminium radicals and neutral amine solute molecules. Ion-molecule transformation of aminium radicals into neutral radicals has been observed in the gas phase and in freon matrices by EPR spectroscopy. Such transformations require a proton transfer, Equation (3), or H-atom transfer, Equation (4).

We find no evidence from the FDMR experiments for the reaction of aminium radicals with neutral amine molecules to give dimer radical cations, Equation (5).

However, there is evidence that dimer radical cations are intermediates in ion-molecule transformations of radical cations analogous to Reactions (3) and (4), including transformations of the alkylsulfide radical cations to be discussed below. Alkylsulfide dimer cations appear to be relatively long-lived — at least hundreds of nanoseconds. It follows from the FDMR results that the (R₂NH)₂^{•+} dimer cations, if they exist at all, are much shorter lived.

This study illustrates how the selectivity of FDMR can be used to distinguish between electron transfer and ion-molecule reactions of radical cations. The ease of observation of aminium radicals by FDMR varies in a predictable fashion and the trends are consistent with the conclusion that the observation of aminium radicals depends on the balance of competing forces favoring electron transfer vs. proton transfer. The experiments in amine/n-hexane mixtures provide further evidence that alkane radical cations can act as proton donors. Most importantly, experiments such as these emphasize the duality of radical-cation reactivity and offer some rudimentary insights into the reasons for the wide diversity in radical-cation reactivity.

b. Alkylsulfide Radical Cations

The radical cations of alkylsulfides are stabilized by coordination of the unpaired p-electron of the oxidized sulfur atom with free p-electron pairs of other sulfur atoms to form dimer cations possessing S-S three-electron σ bonds. These sulfide dimer radical cations are stable on the FDMR time scale. Pulse radiolysis-FDMR experiments in alkylsulfide/n-hexane mixtures reveal the formation of alkylsulfide dimer radical cations for a variety of sulfide compounds, including dimethylsulfide, trimethylenesulfide, tetrahydrothiophene, and others. Attempts to observe the alkylsulfide monomer radical cations in n-hexane at low-solute concentrations have been inconclusive.

In contrast to experiments in n-hexane solvent, both the monomer and dimer sulfide radical cations can be observed by FDMR in alkylsulfide/toluene mixtures. Figure 3 shows the results for (CH₂)₃S in toluene. The FDMR spectrum observed at 205 K and 3 × 10⁻³ M (CH₂)₃S (Figure 3a) consists of the monomer sulfide radical-cation spectrum and

Figure 3. a) FDMR spectrum observed at 205 K in toluene containing 10^{-3} M anthracene- d_{10} and 3×10^{-3} M trimethylenesulfide. The stick spectrum was simulated by using $a^{4H} = 20.6$ G. b) FDMR spectrum observed at 290 K in toluene containing 10^{-3} M anthracene- d_{10} and 10^{-2} M trimethylenesulfide. The stick spectrum was simulated by using $a^{8H} = 9.8$ G.

scintillator ion resonance. The unpaired electron is localized on the sulfur atom and couples to the four β -protons to give a quintet hyperfine pattern. The dimer radical cation spectrum (Figure 3b) was observed at 290 K at slightly higher solute concentration and is characterized by the hyperfine splitting due to eight β -protons.

The spectroscopy gives a clue as to why the monomer cation is observed in toluene but not in n-hexane. Comparison of the hyperfine-coupling constants for the monomer cations in toluene to those obtained in freon matrices shows the coupling constants obtained in toluene are 30-35% smaller (Table I-1). This difference can be explained by a charge-transfer interaction between the sulfide radical cation and the toluene solvent which results in the sharing of the unpaired electron spin density between the sulfur atom and a toluene molecule. The transfer of spin from sulfur to toluene accounts for the smaller coupling to the β -protons and should lead to a concomitant reduction in the g factor, which is also observed. When m -xylene was used as solvent, coupling constants and g -factors for the sulfide monomer cations were slightly smaller still than in toluene. This indicates that the degree of charge transfer to the solvent is greater in m -xylene than in toluene and is further evidence for the specific solvent interaction with the sulfide cations. We propose that the greater stability of

Table 1. 1H hyperfine parameters for dialkylsulfide radical cations.

Radical cation	Matrix or solvent ^b	T (K)	a (G)
$(CH_3)_2S^+$	CF_3CCl_3	81	20.4 (6H)
	$CF_2ClCFCl_2$	81	20.4 (6H)
	$CFCI_3$	124	20.4 (6H)
	toluene	205	13.1 (6H)
$(CH_2)_3S^+$	$CFCl_3$	90	31.1 (4H)
	$CFCl_3$	ca. 120	31 (4H)
	toluene	205	20.6 (4H)
$(CH_2)_4S^+$	$CF_2ClCFCl_2$	81	28.4 (4H) ^c
	$CFCI_3$	77	30 (4H) ^d
	toluene	205	20.9 (4H)

^aAverage of 20.5, 21.4, and 21.6 G. ^bExperiments carried out in toluene solvent are FDMR results. ^cIsotropic value calculated from $a(2H) = 37.8$, $a(2H) = 18.9$. ^dIsotropic value calculated from $a(2H) = 40$, $a(2H) = 20$.

the monomer sulfide cations in toluene and m-xylene is accounted for on this basis. The EPR parameters of the sulfide dimer cations are not medium dependent.

The observed effects of these solvents on dimer-cation formation illustrate solvent effects on radical-cation behavior and should be manifested for other probe molecules as well. By varying the probe we may learn much about the effects on radical-cation reactions due to solvents which are polar or electron-donating.

2. Picosecond Studies of Ions and Excited States *M. C. Sauer, Jr., C. D. Jonah, M. Glezen, R. Cooper*

a. Picosecond Studies of Excited-State Formation

The kinetics and yields of solute excited states in irradiated hydrocarbon solutions provide information about many different and interesting processes, including insights into high-energy chemistry. For example, the yields and kinetics of solute excited states can be strongly dependent on chemical transformations of the solvent radical cation, so that these studies can also probe the reaction pathways of highly excited states of solvent radical cations. In addition, the yields and kinetics probe the physical separation between the electron and the solvent radical cation. This distance strongly affects the chemistry that results from ionizing radiation.

The amount of energy deposited in a local event and the spatial distribution of the ionization events determine the ratio of singlet-to-triplet excited states that are formed in ion-recombination processes. For isolated pairs, no triplet states are expected because the spin-relaxation processes in the geminate radical-ion pairs cannot compete with the decay of the short-lived ion-pairs, and the initial 100% singlet nature of the ion pairs should be preserved in the isolated ion pairs. Therefore the extent of triplet formation can be used to assess the effects of multiple ion-pair spurs which produce some "random" recombinations among the ions and form triplet states.

We have developed our techniques for studying the kinetics and yields of solute-excited states to the

point that a detailed description of the physical and chemical processes is now emerging. We have shown, for example, that liquid cyclohexane is not a good model for the radiolysis of liquid hydrocarbons because its radical-cation chemistry is much different from that of alkane solvents such as n-pentane, n-hexane, and n-decane.

In our experiments, excited-state formation is measured by optical emission and absorption techniques. For emission experiments, the 5-ps linac electron pulse is used for excitation and streak camera detection is used to measure the emission intensity from the fluorescent states of the scintillators. Careful calibration of the equipment and special data-acquisition techniques routinely provide us with accurate kinetic information about the time dependence of the emission for the initial 5 ns. For absorption measurements, the 30-ps linac pulse is used with the "pulse-probe" detection system.

The application of these techniques for the study of 10^{-3} M solutions of scintillators in cyclohexane and the analysis of the results by our stochastic Monte Carlo simulation method suggest that the cyclohexane radical cation undergoes Reaction 6, thereby preventing excited-state formation by recombination with the scintillator anion, Equation (7), after approximately a nanosecond.

The rate constant (k_6) required to bring the simulated results into agreement with experiment is $\sim 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

Work with 10^{-3} M scintillator solutions in n-hexane implies that the analogous reaction for this compound, Equation 6, is about an order of magnitude slower. In this case, significant formation of the excited singlet state, ${}^1\text{A}^*$, occurs after a nanosecond.

Another example of the marked difference between cyclohexane and other alkane liquids was uncovered by the addition of tetramethylethylene (TME). Approximately 1 M TME was added to the solutions in order to scavenge RH^+ , Equation (8). The TME radical cation is known to react with A^- to give ${}^1\text{A}^*$, so the production of ${}^1\text{A}^*$ was expected to be increased.

Figure 4 shows that in n-hexane TME has the expected effect in that the rate of production of $^1\text{A}^*$ in the 2-5-ns region is increased. (However, a decrease in the amount of $^1\text{A}^*$ results from the fact that $\text{TME}^{\cdot+} + \text{e}^-$ recombination apparently does not lead to an excited state capable of transferring energy to the scintillator, whereas $\text{n-C}_6\text{H}_{14}^{\cdot+} + \text{e}^-$ recombination does.) The simulated curve, which is not shown in Figure I-4, accurately portrays the results without corrections for energy transfer from excited n-hexane or for a reaction analogous to Equation 6. Therefore, the addition of TME to n-hexane completely eliminates the proton-transfer reaction.

On the other hand, Figure 5 shows that the production of $^1\text{A}^*$ in cyclohexane was essentially eliminated by TME. Only the small amount of $^1\text{A}^*$ that was formed during the pulse by absorption of Cerenkov radiation remained.

These remarkable observations suggest that proton transfer (Equation 9) takes place in preference to charge transfer (Equation 8).

The cyclohexane radical cation appears to be more acidic than the radical cations of other hydrocarbons.

To better understand radical-cation chemistry in liquid hydrocarbons we have measured, in collaboration with Cooper of the University of Melbourne, the yields (G values) of scintillator (solute) singlet excited states formed during the first 5 ns. The measured yields were compared with the predictions of our model to estimate the efficiency of excited-state formation via ionic pathways. Inefficiency exists if ions are formed, in primary processes or by secondary reactions, which are not capable of leading to the scintillator excited state. In cyclohexane, the creation of $\text{C}_6\text{H}_{13}^{\cdot+}$ by Equation 6 is an example, as is the formation of $\text{C}_6\text{H}_{11}^{\cdot+}$ as an "initial" radiolysis product, which would probably not lead to scintillator excited state. Inefficiency in the formation of the scintillator singlet state also results if the recombination gives triplet state. Therefore, our measurements of the G values of triplet states described below are closely related to the singlet-state measurements.

Figure 4. Reduction of fluorescent-state yield in n-hexane, 10^{-3} M PPO, by TME.

Figure 5. Reduction of fluorescent-state yield in cyclohexane, 10^{-3} M PPO, by TME.

Table 2 presents the experimental $G(^1\text{A}^*)$ values for biphenyl in cyclohexane and n-hexane. (Values for other scintillators are, as expected, about the same.) The simulated G values are also given in Table 2. Concurrence between the calculated and experimental results was judged by fitting the simulated excited-state yield data to the experimental curve. The simulations are based on a "single ion pair model" and assume that the solvent radical cations are initially all the same chemically. These values take into account the occurrence of Reaction (6) (and the analogous reaction for n-hexane) and energy transfer from excited solvent molecules.

In general, the predicted G values are considerably larger than the experimental ones. We recognized that a considerable part of the discrepancy can be explained by the observed formation of the solute

Table 2. G-values at 5 ns for the fluorescent state of biphenyl in cyclohexane and n-hexane.

[biphenyl]	n-hexane		cyclohexane	
	Experimental*	Simulated [‡]	Experimental*	Simulated [‡]
0.05	0.45	2.48	0.50	1.41
0.01	0.19	1.16	0.28	0.62
0.001	0.03	0.062	0.084	0.089

*The contribution from Cerenkov excitation of biphenyl has been subtracted.

[‡]Using an exponential distribution, $\tau_{\text{avg}} = 52 \text{ \AA}$.

triplet state, 3A , and undertook a series of experiments to examine this feature.

Measurement of the rate of formation of the triplet state is more difficult than for the singlet state because other substances have absorptions in the same region of the spectrum. We have nevertheless succeeded in doing this for 0.1 M naphthalene in cyclohexane and n-hexane. The results for the triplet-state formation in cyclohexane are shown in Figure 6.

The results for naphthalene, Figure 6, are qualitatively similar to the results for $^1A^*$ at a similar concentration of A shown in Figure 7.

The $G(^3A)$ determined at $\sim 3 \text{ ns}$ are 0.8 ± 0.2 for 0.1 M naphthalene in cyclohexane or n-hexane. The $G(^1A^*)$ determined for 0.05 M biphenyl solutions in the two solvents are about 0.5 at 5 ns. After making a qualitative extrapolation of the biphenyl results to 0.1 M and taking into account the time difference, it is clear that the triplet yield is at least as large as the singlet yield. The large yield of the triplet state is most likely due to multiple ion-pair spurs, where recombination among ions with different "parentage" will lead to 75% 3A and 25% $^1A^*$. However, the large amount of triplet formed is more than expected on the basis of theoretical estimates of the distribution of spur sizes. The possibility that spin dephasing is more rapid than expected may have to be considered.

The observed G values of 3A are large enough to explain part of the discrepancies between experimental and model values of $G(^1A)$; however, some of the differences between the experimental and model G values of 1A presented in Table 2 are so large that the observed amount of triplet formation is still quite insufficient to explain them.

Figure 6. Triplet formation in the pulse radiolysis of 0.1 M naphthalene in cyclohexane.

Figure 7. Singlet formation in 0.05 M biphenyl in cyclohexane.

At this point, we do not know the source of the remaining discrepancy. Our tentative explanation is that it lies in the initial production of "inefficient" ions and/or in the occurrences of chemical reactions of ions that lead to inefficiencies in 1A production. However, we have not been able to devise a scheme which rationalizes the differences between experiment and model observed in Table 2. The solution to the

problems does not seem to be, at this time, the use of a more sophisticated model allowing multiple ion pair spurs to be considered. Instead, investigations leading to more knowledge about the chemistry of the ions are needed.

b. Experiments with Metal Carbonyl Compounds

Metal carbonyls have been studied in great detail with regard to their catalytic and photochemical properties. The photochemistry of these compounds is fairly well understood and is dominated by neutral reactions. However, very little is known about the ionic chemistry. We have begun an investigation of the ionic species formed by pulse radiolysis of hydrocarbon solutions containing metal carbonyl compounds, such as $\text{W}(\text{CO})_6$ and $\text{Cr}(\text{CO})_6$. The few radiolysis studies that have been done indicate the formation of 17-electron species in solution. These transients are presumed to be key intermediates in both the catalytic and photochemical processes; however, they are difficult to study spectroscopically due to their high reactivity. Electrochemical studies indicate the occurrence of stable 17-electron species such as $\text{Cr}(\text{CO})_6^+$ and $\text{Cr}(\text{CO})_5^-$. However, no time-resolved or spectroscopic studies have been carried out because the strong optical absorptions of the parent $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}$ or W) make it difficult or impossible to study the ion chemistry by conventional photochemistry. Our metal-carbonyl studies have shed light on the formation and reactions of the novel 17-electron metal-carbonyl intermediates.

The primary reactions in radiolysis are ionization, Equation (10), and ion recombination, Equation (11),

where S denotes a solvent molecule. The approximate time scale for each reaction is given in parentheses. Chemical probes such as metal carbonyls intercept the transient species that occur at very early times. Metal carbonyls react quickly with the electron, and the resulting ion is much less mobile. Thus, the geminate ion-recombination reaction is slowed down, and

one can directly observe the geminate recombination kinetics. Similar experiments have been carried out with aromatic molecules, as discussed above; however, both the positive ion and the electron react with the added probe molecule, and one is less able to separate the chemistry. Other probes, such as N_2O , do not lead to ions with convenient absorption spectra. Thus, new and better chemical probes must be developed. The metal-carbonyl compounds react selectively, and the product ions can be conveniently observed by optical absorption spectroscopy.

We have used standard fast kinetic absorption techniques to measure the optical transmission as a function of wavelength. The initial species were formed by using a 30-ps, 20-MeV electron pulse from the Argonne linear accelerator. An E.G.&G. flash lamp was used for the probe light. Wavelength resolution was achieved using a series of approximately 10-nm fwhm interference filters.

Figure 8 shows the absorption spectrum of an n-pentane containing 0.02 M $\text{W}(\text{CO})_6$ immediately after the pulse, 10 ns after the pulse, and 40 ns after the pulse. These data show an absorption with $\lambda_{\text{max}} \approx 415 \text{ nm}$ which we attribute to the final species, $\text{W}(\text{CO})_5\text{S}$, where the S is a solvent molecule. In addition, there is another initial weak absorption in the red which we assign to $\text{W}(\text{CO})_5^-$. The latter species has not been previously observed and is assigned by analogy with other 17-electron species. The data that we obtained for the $\text{Cr}(\text{CO})_5\text{S}$ analog are similar; however, the maximum is near 510 nm. No evidence

Figure 8. Absorption spectra after radiolysis of 0.02 M $\text{W}(\text{CO})_6$ in n-pentane; $\square$ at the pulse; $\triangle$ 10 ns after the pulse; $\blacksquare$ 40 ns after the pulse.

for the $\text{Cr}(\text{CO})_5^-$ species was found in the spectral region that could be scanned in our experiment. This is to be expected for a first-row transition-metal complex where the comparable absorption is expected to be too far into the red. However, experiments that will not be discussed here have revealed a similar species in ethanol for the Cr system where the absorption of the 17-electron transient would be expected to be shifted to the blue compared to that in hydrocarbon solvents.

Figure 9 shows the kinetics of the formation of the 510-nm band as a function of the $\text{Cr}(\text{CO})_6$ concentration. The final absorption increases as a function of the $\text{Cr}(\text{CO})_6$ concentration; however, the kinetics are independent of the concentration of the $\text{Cr}(\text{CO})_6$. The same is true for $\text{W}(\text{CO})_6$.

This unusual behavior is not consistent with the transfer of energy from excited states because the rate of transfer in that case would depend on concentration or the kinetics would be dominated by the decay of the excited states. In the latter case, yields would be described by a Stern-Vollmer equation. Also, the formation curves are not exponential. This behavior may be due to the inhomogeneous deposition of the solvent by ionizing radiation. Let us explore this possibility.

A possible mechanism to explain this unusual behavior is given by the following pair of reactions.

One might predict that the electron-addition reaction in (12) is a dissociative electron capture, similar to the electron reactions with alkyl halides.

The competition between the geminate recombination reaction (11) and Reaction (12) would give a yield of product proportional to the square-root of the metal-carbonyl concentration. This is indeed the case. However, clearly the kinetics that are observed are not those of the competition between the fast geminate electron reaction (11) and Reaction (12) because those kinetics would be on a time scale of 10 ps, and the kinetics seen here are three orders of magnitude slower.

We expect that the kinetics displayed will be due to Reaction (13). Because the charge effects will

Figure 9. Growth curves of $\text{Cr}(\text{CO})_5\text{S}$ monitored at 510 nm for various concentrations of $\text{Cr}(\text{CO})_6$: A) 0.02 M, B) 0.01 M, C) 0.005 M, D) 0.0025 M.

dominate, the reaction rates should not depend on whether the reaction is of the chromium or tungsten carbonyl. Figure 10 clearly shows this is true; the chromium and tungsten results are superimposable. Reaction (13) also explains the results of Figure 9. If an electron reacts with a metal carbonyl to form the anion, the formation of the pentacarbonyl will be determined by the charge-recombination process. Thus, the kinetics would be independent of the initial carbonyl concentration.

Charge-recombination kinetics will determine the kinetics of (13) and the formation of the pentacarbonyl. The theory of such reactions predicts that the concentration of the final product will be linear in $1/t^{1/2}$. Figure 11 shows that this is a good approximation over much of the time region. Only at early times (right-hand side of Figure 11), where it is difficult to separate the solvent absorption, do the data fail to follow the $1/t^{1/2}$ behavior.

We have studied the reactions in both n-pentane and cyclohexane. n-Pentane was selected because we expected minimal overlap of the solvent excited-state absorption. Figure 10 shows the data for n-pentane and $\text{Cr}(\text{CO})_6$ in cyclohexane. The growth rate is slower in cyclohexane than in n-pentane which suggests that the mobility of the positive reactant

Figure 10. Growth curves for $M(CO)_5S$ in *n*-pentane and cyclohexane. All curves have been normalized.

Figure 11. The formation of the $W(CO)_5S$ in *n*-pentane as a function of $1/\sqrt{t}$ to display the geminate character of the reaction (the left tick is 10 ns, the right tick mark is 0.4 ns). The reason for the considerable difference between the two curves at short times is due to inaccuracy in subtraction of the absorbance decay due to the solvent radical cation for the 200-ns full-scale run.

species is lower in cyclohexane than in *n*-pentane. If the positive species with which $Cr(CO)_5^-$ reacts in cyclohexane were the well-known high-mobility species, one would have expected the geminate recombination reaction in cyclohexane to be considerably faster than that in *n*-pentane. This is not

the case. The slower growth in cyclohexane can be explained on the basis of the higher viscosity of cyclohexane.

In summary, these experiments have enabled us to detect a tungsten carbonyl 17-electron anionic species which has not been observed previously. The metal carbonyls seem to react preferentially with the electron and not the solvent radical cation. This behavior gives us a very good probe of the electron and its reactions at early times. Thus, metal carbonyls may enable us to investigate some key early processes in radiation chemistry.

3. Radical Ions in Photoionization

A. D. Trifunac, M. G. Bakker

Photoionization is of interest in many areas of chemistry. Whether charge-pair creation occurs via ionizing or photoionizing radiation, the challenge is to identify the chemistry and dynamics of such reactive and short-lived radical ion pairs. The use of intense UV sources of radiation such as excimer lasers allows easy photoionization of many absorbing species. However, the mechanisms of photoionization, the involvement of the singlet and triplet manifolds of states, and the ability to influence the pathway of photoionization by changing the photon flux must be assessed. We have developed a specialized magnetic-resonance method that provides definitive information on the spin multiplicity of the radical ion pair and thus its precursor state, and quantitatively study laser-power dependence by examining the fluorescence detected magnetic resonance (FDMR) of the geminate radical ions. This technique has been used with considerable success in our laboratory.

The fluorescence signal results from some combination of the following processes. (*A* is an aromatic solute, *S* represents the solvent, and e_s^- is the solvated electron.)

Charge transfer and solvation:

Recombination:

Fluorescence:

The conceivable photoionization pathways include direct one-photon ionization (Equation (14)), simultaneous two-photon absorption (Equation (15)), sequential two-photon absorption through the excited singlet state (Equations (16) and (17)), and sequential two-photon absorption with ionization occurring from a triplet state (Equations (16), (18), and (19)).

The geminate radical ion pairs produced can be singlet or triplet depending upon the spin multiplicity of the state being ionized. The ratio of concentrations of singlet-phased to triplet-phased ion pairs for which no FDMR signal would be observed (due to cancellation of opposite signals) is 1:3. However, as we will discuss, it is unlikely that our experiment is sufficiently sensitive to detect small deviations from this ratio. The observation of an FDMR signal is therefore an indication of a substantial deviation from this ratio, and we will use the term 'predominantly' singlet- or triplet-phased ion pairs to signify this. It is also important to remember that it is only geminate recombination that gives rise to FDMR. Free ions that can recombine to give delayed fluorescence do not give rise to an FDMR signal because the population of all spin levels would be equal.

In our previous work on FDMR using laser photolysis in alcoholic solutions, we observed only singlet FDMR signals; that is, we observed a microwave-induced decrease in fluorescence indicating that the geminate ion pairs which recombine to produce the delayed fluorescence, are predominantly

singlet phased. The excited state leading to photoionization must, therefore, also be predominantly singlet. Accordingly, the combined yield of Equations (16), (18), and (19) must be less than that of Equations (14)-(17). From energy considerations we inferred that ionization resulted from the absorption of two photons. We further concluded that the FDMR signal was produced by the geminate recombination of a solvated electron with a radical cation and that the stabilization of the ion pair caused by solvation of the electron was necessary for observation of an FDMR signal.

Here we extend the variety of aromatic solutes studied and consider in detail how the excess energy, extinction coefficients, fluorescence quantum yields, and laser power affect the intensity of the FDMR signal observed. Based on the agreement between the calculated and experimental power dependence of the anthracene FDMR signal, we conclude that photoionization results from sequential absorption of two photons in the singlet manifold.

The distinguishing aspect of the FDMR method is its ability to obtain resolved EPR spectra of the radical ion species which recombine to yield the fluorescent excited state. This is illustrated in Figure 12. The spectrum shown is that from perylene photoionization in 2-propanol and consists of the superimposed EPR spectra of the solvated electron and the perylene radical cation. The FDMR signal is observed as a decrease in the intensity of the delayed fluorescence,

Figure 12. FDMR spectrum from 2.5×10^{-4} M perylene in 2-propanol, excitation at 308 nm. (a) experimental spectrum, (b) simulated spectrum using literature coupling constants (4 H, 4.04 G; 4 H, 3.04 G; 4 H 0.44 G) and 0.6 G line width.

which indicates that the perylene radical cation/solvated electron geminate ion pairs are produced predominantly as singlet-phased ion pairs.

In previous studies we used FDMR to examine many transient radical ion species produced by both ionizing and photoionizing radiation. Here we focus on a different aspect of the FDMR method, and show how to obtain details of the photoionization of aromatic compounds in polar solutions by determining the spin multiplicity of the geminate radical ion pair and by measuring the laser power dependence.

Power Dependence. As discussed above, there are several possible photoionization pathways. Biphotonic photoionization at 353 nm has been reported for pyrene and anthracene in methanol. Monophotonic ionization has been reported for TMPD at ca. 265 nm in tetramethylsilane, at 337 nm in methanol, and at 308 nm in CCl_4 . Biphotonic ionization of TMPD has been reported at 337 nm in 2-butanol. On the other hand, in a study using time-resolved resonance Raman spectroscopy, Isaka et al. concluded that TMPD underwent monophotonic ionization in 2-propanol when irradiated at 308 nm. For the conditions and compounds used in our study, ionization has been found in all cases to occur predominantly through the singlet state. It should be possible on the basis of the dependence of the FDMR signal intensity on the laser power to distinguish between one- and two-photon processes. Accordingly, we have determined the power dependence of the FDMR signals from anthracene and TMPD as shown in Figures 13 and 14, respectively. Data were collected on one sample (flowing solution of total volume 450 ml) by changing laser intensity from low power to high power and then from high power to low power. The differences in the two points at each power indicate the change in FDMR intensity due to decomposition of the starting material and/or product buildup.

The curve drawn through the experimental data for anthracene (Figure 13) represents the singlet population in excess of the 1:3 singlet:triplet ratio which would give a null FDMR signal. This curve was calculated by assuming a sequential two-photon photoionization. Finite-element analysis was used, that is, the sample volume was modeled with a finite

Figure 13. Experimental and simulated power dependence of peak FDMR intensity for 1×10^{-4} M anthracene in 2-propanol at 308 nm. The curve represents the calculated excess singlet concentration as discussed in the text.

Figure 14. Power dependence of peak FDMR intensity for 1×10^{-4} M TMPD in 2-propanol. The symbols are larger than twice the standard error in the peak FDMR intensity.

number of spatial elements and the laser pulse with a finite number of time elements. At the end of each time element, the changes in the concentrations of the species produced by absorption of photons and by decay in each spatial element were calculated from the sum of the first derivatives of the individual processes occurring. The temporal profile of the laser pulse was

explicitly included in this simulation. Because a number of the processes modeled are biphotonic, final yields are dependent upon the peak intensity of the laser pulse and therefore influenced by the shape of the laser pulse. For example, calculations showed an error of 25% in ion pair yields when a square laser pulse was assumed.

The parameters used to simulate the excess spin population of anthracene singlet ion pair were $\epsilon_{S_1 \leftarrow S_0} = 1260 \text{ M}^{-1} \text{ cm}^{-1}$; $\epsilon_{S_n \leftarrow S_1} = 14000 \text{ M}^{-1} \text{ cm}^{-1}$; $\epsilon_{T_n \leftarrow T_1} = 2000 \text{ M}^{-1} \text{ cm}^{-1}$; intersystem crossing rate, $1.27 \times 10^8 \text{ s}^{-1}$; and rate constant for fluorescence, $5.46 \times 10^7 \text{ s}^{-1}$. The quantum yield for ionization (Equation 17) was initially assumed to be 1; however, a value of 0.75 provided a better fit of the data than 1 or 0.5. The only adjustable parameters in this fit, therefore, are the quantum yield for ionization and the scaling factor relating the observed FDMR intensity to the excess singlet population. The plateau observed at high laser energies is produced by bleaching of the ground and first excited-singlet states; essentially all the anthracene has been photoionized under certain conditions.

It is clear from the good agreement between the experimental and calculated laser-energy-dependence curves (Figure 13) that anthracene undergoes sequential two-photon ionization predominantly through the first excited-singlet state. Independent support for this conclusion was provided in the study of the mechanism for photoionization of anthracene in 2-propanol under the same experimental conditions.

For TMPD, the extinction coefficients and quantum yields required to accurately simulate this system are not available. However, the shape of the power-dependence curve (Figure 14) at low powers clearly indicates that photoionization in TMPD is also a two-photon process. Experiments on carbazole show a similarly shaped curve at low powers, again implying that photoionization is a two-photon process.

The anthracene power-dependence data in Figure 13 are consistent with the FDMR signal being proportional to the deviation from the 1:3 singlet-to-triplet ratio. The geminate radical ions observed by FDMR are a subset of the total radical-ion population produced by photoionization, but this subset should be

representative of all the geminate ions produced. (The FDMR component of the delayed fluorescence may still sample a substantial fraction of all the geminate ion pairs produced. We find that for TMPD in 2-propanol the FDMR signal is as much as 10% of the delayed fluorescence signal.) The ion-pair recombination kinetics and escape probabilities are determined primarily by electron localization, solvent polarity, and viscosity, and are not expected to be appreciably influenced by the ion-pair spin multiplicity. The spin multiplicity of the radical ion pair determines whether excited singlet or triplet states are formed by ion recombination. Every radical ion pair encounter gives rise to an excited bound state. This is in contrast to the recombination of neutral radicals where only one channel (singlet state) for reaction is open, giving rise to a spin-sorting process observed as CIDEP and CIDNP.

FDMR monitors a subset of radical ion pairs which are relatively long lived; however, even such a limited time-window for sampling the ion-pair spin multiplicity should properly reflect the initial spin phasing (spin multiplicity of the precursor state) of the radical ion pair at ionization.

The calculations for anthracene also provide some insight into the sensitivity of FDMR detection. The calculations show that photoionization occurs almost completely through the singlet state to produce predominantly singlet-phased radical ion pairs. At the laser powers used in our work, about 96% of the anthracene/solvated electron ion pairs should have singlet spin phasing. Nevertheless, the FDMR signal is still only ca. 1% of the total delayed fluorescence. It is unlikely that compounds in which the ratio of singlet-to-triplet-phased radical ion pairs was close to the 1:3 ratio would show an appreciable FDMR signal.

Intensity of the observed FDMR signal for various compounds. Table 3 presents peak FDMR intensities for a range of aromatic scintillators together with a number of relevant photophysical properties. In all cases, a FDMR signal indicative of the singlet ion pair precursor state was observed.

It is clear from Table 3 that FDMR signals can be observed from a wide range of structurally dissimilar aromatic compounds, so that this means of

Table 3. Peak FDMR intensity of various solutes excited at 308 nm in 2-propanol.

Solute	Peak FDMR Intensity ^a (arbitrary units)	Extinction Coefficient (M ⁻¹ cm ⁻¹)	Fluorescence Yield	Fluorescence Lifetime (ns)	Excess Energy ^b (eV)
TMPD	344±5	1900	0.18	4.3	3.71
diphenylamine	125±15	8520 ^c	0.11	3	3.21
acenaphthene	125±8	2800	0.6	46	2.79
perylene	55±10	330 ^b	0.94	6.4	2.68
carbazole	725±15	2800	0.38	15.2	2.55
PPO	285±10	25000 ^b	1	1.4	2.53
pyrene	0±5	11000	0.32	307	2.53
triphenylene	0±10	1200	0.08	36.6	2.52
1-naphthol	190±8	4300	0.21	10.6	2.47
anthracene	33±4	1260 ^c	0.36	4.9	2.29
naphthalene	5±3	100	0.23	96	2.19
azulene	30±5	1200	0.03	1.4	1.71 ^d
2,5-diphenylfuran	7±0.5	29000	1	1.6	n/a

^aSample concentrations ca. 1×10^{-4} M, appropriate cutoff filters used to provide maximum discrimination, MW(0,100) BC(100,150)ns, laser power ca. 40 mJ/pulse, no correction has been made for the photomultiplier response or for the different transmittance of the filters used.

^bThis work in 2-propanol.

^cExcess energy calculated for S₂ excited state.

observing radical ions is quite general. However, the FDMR intensity is not strongly correlated to any single photophysical property.

The intensity of the FDMR signal would be expected to be strongly affected by the geminate ion pair lifetime, because a finite time is required for the microwave pulse to perturb the geminate ion pair spin states. The geminate lifetime in turn depends upon the distance between the cation and the electron, and the polarity and viscosity of the solvent. Photoionization produces a distribution of cation/electron separation distances. Those geminate ion pairs with smaller separations recombine more quickly than those with larger separation distances. For nonpolar hydrocarbon solvents the geminate ion pair lifetime is very short. For example, in cyclohexane at room temperature, half the geminate ions undergo recombination within several picoseconds. In polar solvents, the photoelectron quickly becomes associated with a solvent molecule (time for solvation is typically 10-50 ps in alcohols), thereby increasing the geminate lifetime.

The distribution of electron/cation distances has been the object of several studies. Intuitively, it might be expected that the distribution produced by

monochromatic radiation would produce a narrower distribution of electron/cation distances than that observed in pulse radiolysis, and that the maximum of this distribution would move to larger distances with increasing excess energy (the energy in excess of that required to cause ionization). There is some evidence to support these conjectures. Work on hydrocarbons here and elsewhere indicates a narrower distribution of separation distances and a lower free-ion yield for laser ionization than for pulse radiolysis. Evidence has also been found for increased free-ion yields from a range of aromatic solutes in isooctane as the excess energy was increased. The free-ion yield is an indication of the mean electron/cation separation, with a larger free-ion yield resulting from a larger mean separation.

The information in Table 3 has been ranked in order of excess energy of the photons above the solute ionization potential. From this discussion, it might be expected that as the excess energy increased, the lifetime of the geminate ion pair would lengthen and increase the FDMR intensity. This does appear to be the case, as there is a weak correlation between the excess energy and the FDMR intensity, with those compounds with higher excess energies having higher

FDMR intensities. In parallel work, it was found that excess energies above about 2 eV produced only small changes in the free-ion yield. These observations imply only small changes in the electron/cation distribution distance. Similarly, Brearley and McDonald concluded from their results on geminate ion pair lifetime in hydrocarbons that a leveling off occurred in the electron/cation distribution at 2- or 3-eV excess energy. Our estimated excess energies fall in the region where we would expect only a weak correlation of FDMR intensity with excess energies, and so our findings are compatible with the observations of Schmidt et al. and those of Brearley and McDonald, even though the present work was carried out in a polar solvent.

Diphenylamine. In recently published work, Troe and co-workers concluded that diphenylamine irradiated at 308 nm is photoionized through the triplet state. Their study was carried out using transient absorption spectroscopy. The intermediacy of the triplet state was suggested by the power dependence of the diphenylamine triplet and solvated-electron absorptions, and the intensity of the fluorescence peak. In all our experiments, we have observed a resonant decrease in fluorescence indicating that photoionization occurs predominantly through the singlet state. Accordingly, we were interested in using our technique to study diphenylamine.

To prevent the build-up of the photoproduct, carbazole, in the solution, we undertook experiments in which the sample passed through the sample cell only once. We found that the observed peak FDMR intensity approached a limiting value of 122 ± 15 at low laser repetition rates, and showed predominantly singlet spin phasing. Experiments without diphenylamine present, and at nonresonant magnetic fields established the absence of any background FDMR signal. We are confident, therefore, that the FDMR signal is due to diphenylamine.

We have attempted to reconcile the two sets of observations by simulating the photophysics of this system to determine the expected yields of singlet and triplet ion pairs in the same manner as we have described above for anthracene. We considered a number of scenarios involving different extinction coefficients and triplet yields, but have not been able to find

any reasonable set of assumptions that would bring our results into agreement with those of Troe and co-workers.

Our simulations show that at low laser powers photoionization is predominantly from the triplet state, and at high powers it is predominantly from the singlet state. Therefore, in such systems the photoionization pathway can be controlled by the laser power. This clearly has important consequences for comparisons of the results from different laboratories. When there are a number of competing processes, the final concentrations of the various excited states and ions will depend upon the shape, power, and length of the excitation pulse.

It is interesting to note how observations of the FDMR spectrum of diphenylamine illustrate the problem of sample decomposition. In experiments in which the sample was recirculated, the FDMR spectra were narrower than the EPR spectrum reported for diphenylamine cation, but were similar to the FDMR spectrum of carbazole, Figure 15. The photocyclization reactions of diphenylamine and its derivatives are

Figure 15. FDMR spectra from carbazole and diphenylamine. (a) Simulated spectrum of diphenylamine radical cation using the following coupling constants: N 9.03 G; H 10.98 G; 4 H 3.46 G; 4 H 1.31 G; 2 H 4.86 G; 1 G line width (fwhm). (b) FDMR spectrum from recirculated 5×10^{-5} M diphenylamine in 2-propanol. (c) FDMR spectrum from 1×10^{-4} M carbazole in 2-propanol. (d) Simulated spectrum of carbazole radical cation using the following coupling constants: N, 6.89 G; H, 8.09 G; 2 H, 3.84 G; 4 H, 0.80 G; 2 H 3.30 G; 1.0 G linewidth (fwhm).

well known, and, indeed, analysis by gas chromatography/mass spectroscopy (GCMS) showed almost total conversion of the diphenylamine into carbazole after long laser irradiation. This illustrates the utility of FDMR in obtaining structural information about the recombining cation. Diphenylamine was the only compound that underwent decomposition in this study.

4. Geminate Ion Pairs From Photoionization *K. H. Schmidt, M. C. Sauer, Jr., A. Liu*

a. Scavenging Studies

We have investigated geminate ion pair production in alkanes by two-photon ionization to obtain information on the mechanism of ionization, the distribution of initial separation distances between the ejected electron and the parent cation, and the effect of photon energy on these quantities. We have measured the transient conductivity and optical absorption and have carried out scavenging experiments.

In principle, the distribution of initial separation distances can be determined by analyzing the kinetics of geminate decay, or by measuring the number of electrons scavenged by a suitable scavenger as a function of its concentration. The two processes are related by a Laplace transformation, with the result that the asymptotic scavenging limit at high-scavenger concentration corresponds to the initial ion yield, the same limit for low concentration to the free-ion yield (the asymptotic limit of the geminate decay function).

The results of a previous study, in which N_2O was used as a scavenger (Equation 25), did not yield suitable results because the concentrations of the scavenger were inadequate. We therefore undertook new work with CH_3Cl , which is ten times more soluble than N_2O . We irradiated *n*-hexane and cyclohexane, which contained 5×10^{-4} M anthracene (A) as a sensitizer by using multiple 308-nm pulses from an excimer laser and measured the yield of methane. The results were analyzed on the basis of the reaction sequence shown in Equations 26-32:

We calculated, for each scavenger concentration, $\phi {}^1\text{A} \rightarrow \text{CH}_4$, assuming that at the high concentration limit $\phi {}^1\text{A} \rightarrow \text{CH}_4 = \phi {}^1\text{A} \rightarrow \text{ions}$. Figure 16 shows the results for *n*-hexane and cyclohexane. For comparison, the results for N_2O are included. Curves based on other assumptions deviated strongly from the data points in the low-concentration region. Also included are best-fitting model curves for different initial distance distributions. Three different distribution functions were considered as illustrated in Figure 17. For each calculation, the best combination of escape probability (determines curve shape) and initial quantum yield (determines vertical position) was chosen. Data for ion mobilities and scavenging rate constants (both affect the horizontal position) were taken from the literature. No other parameter was adjusted. At low-scavenger concentrations, the curves were corrected for the scavenging of electrons by the anthracene (5×10^{-4} M), with the further assumption that the free A^- ions react with the scavenger (S), producing S^- and hence, N_2 or C.

Curves modeling the N_2O results based on an r^2 -Gaussian distribution are not shown because they do not significantly deviate from those for an exponential distribution within the experimental data range. Curves calculated for r^2 -exponential distributions are also omitted. They lie between those for the two other distributions and close to the ones for an r^2 -Gaussian.

The following observations can be made on Figure 16:

Figure 16. Scavenging yields, expressed as $\Phi^1A^* \rightarrow \text{product}$, vs. scavenger concentration for different solvents and scavengers. Points: experimental values. Dots or dashes: model curves for different initial distance distributions and escape probabilities (see text).

Exponential:

$$f(r)dr = \frac{1}{r} \exp\left(-\frac{r}{r_f}\right) dr$$

r^2 -Exponential:

$$f(r)dr = \frac{9}{2r_f} \left(\frac{r}{r_f}\right)^2 \exp\left(-3\left(\frac{r}{r_f}\right)\right) dr$$

r^2 -Gaussian:

$$f(r)dr = \frac{32}{\pi^{3/2} r_f} \left(\frac{r}{r_f}\right)^2 \exp\left\{-\frac{4}{\pi} \left(\frac{r}{r_f}\right)^2\right\} dr$$

Figure 17. Definitions of the three different distributions used in the calculations.

(1) The product quantum yields are much lower in the CH_3Cl system than in the N_2O system. As will be discussed below, this is caused by a reaction between the methyl radical and the anthracene triplet.

(2) There is a large discrepancy between the derived escape probabilities for CH_3Cl and those for N_2O ; for the same distribution function, they differ by a factor of two. However, numerous results obtained with ionizing radiation from the literature show a similar discrepancy between N_2O data and alkyl halide data. This is illustrated in Figure 18. In this figure, the free-ion yield is an experimental value, and the initial ion yields were calculated by using an empirical relationship by Warman-Asmus-Schuler. Possible reasons for the discrepancy will be discussed subsequently.

(3) For photoionization, all escape probabilities are significantly lower than the corresponding

Figure 18. Scavenging results for radiolysis from literature (schematic). Curves are normalized for measured free-ion yield. G_0 : initial-ion yields calculated using the empirical formula by Warman-Asmus-Schuler; " N_2O ": results obtained by different authors using N_2O as scavenger; " CH_3Br ": results obtained by different authors using CH_3Br and other alkyl halides as scavengers; p_{esc} : escape probability = $G_{free\ ions}/G_{initial\ ions}$

escape probabilities from radiolysis. This confirms previous results from conductivity measurements.

(4) The CH_3Cl results clearly favor an exponential distribution.

It is appropriate to discuss the contradictory scavenging data for radiolysis and photolysis. In the case of N_2O , a scavenging mechanism that has been proposed would produce more than one N_2 molecule per electron scavenged, e.g.,

No experimental evidence has been advanced for this mechanism. For the CH_3Cl system, we considered a mechanism in which the hydrocarbon (e.g., C_6H_{12}) and anthracene triplet compete for the methyl radical:

In an independent experiment we determined $k_{36} = 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. A similar reaction with the

anthracene singlet would be negligible because of its much shorter half life (ca. 5 ns). We found no evidence for a reaction of the methyl radical with the anthracene ground state. The value for k_{35} in the liquid phase has not been measured. Kinetic model calculations which include various radical-radical reactions and triplet-triplet annihilation, with k_{35} adjusted to $300 \text{ M}^{-1} \text{ s}^{-1}$, show that this model quantitatively reproduces the much lower yields of scavenging product with CH_3Cl , and that the small calculated deviation from proportionality between electron scavenging and methane production (<6%) is within experimental errors, i.e., the calculated escape probability does not change appreciably.

Because of the discrepancy of the two sets of scavenging data, the G value for ionization in hydrocarbons (G_0 in Figure 18) is still uncertain. Further investigation of the two scavenging mechanisms is therefore needed.

b. Absorption Spectroscopy

We previously reported conductivity studies that established the mechanism of two-photon ionization of anthracene and other sensitizers. In order to investigate other photoionizations, we constructed a new, computerized laser flash photolysis apparatus for the nano- to millisecond time domain. Its high sensitivity is achieved by a pulsed light source, signal averaging, and a flow system for the sample solutions. Additional features are automatic correcting absorption measurements for emission components caused by fluorescence, phosphorescence and scattered laser light, and the possibility to operate it with two lasers for photolyzing free radicals, triplet states, etc.

Solutions of anthracene in alkanes with and without electron scavengers have been studied. So far, we have identified the spectrum of the anthracene radical cation that is produced by two-photon ionization, separate from the spectra of other absorbing species, such as anthracene triplet and singlet. Figure 19 shows a plot of the corrected transient absorption spectra for solutions of $5 \times 10^{-4} \text{ M}$ anthracene in hexane and isooctane and, for comparison, in acetonitrile with SF_6 as an electron scavenger.

Figure 19. Spectra of anthracene radical cations in three solvents obtained by photoionization at 308 nm. x: in cyclohexane, 0.5 mM anthracene, saturated with methyl chloride ($\times 3$); Δ : in isooctane, 0.5 mM anthracene, saturated with SF_6 ; $\square$ in acetonitrile, 0.5 mM anthracene, saturated with SF_6 ($\times 1/3$).

The spectrum of the anthracene radical cation in acetonitrile agrees well with a prior report. In the case of cyclohexane and isooctane, the maximum absorption at 730 nm is ascribed to the anthracene radical cation. The spectrum differs slightly from the spectrum reported for pulse radiolysis in cyclohexane with a maximum absorption at 720 nm. It is interesting to note the second maximum at about 810 nm, which is absent in acetonitrile and was not reported for pulse radiolysis. We are at present attempting to identify the origin of the absorption at 810 nm.

Conclusion: The results obtained so far show that our new experimental arrangement is capable of measuring very small changes in optical absorption, even in the presence of large emission signals. It will be a useful tool in the study of two-photon ionization and related processes in new chemical systems.

5. Radical Cation Structure and Transformations. A. D. Trifunac, X.-Z. Qin

The study of radical cations in solid matrices provides needed knowledge about their structures and transformations. The observation of radical cations in solid matrices is often the necessary first stage in their characterization. Comparative studies of the same species in liquids often provide contrasting information that addresses questions regarding "medium

effects" on their structure and reactivity. So far there has not been any definitive evidence regarding the "medium effect" on the structure of simple radical cations. One of the credos of the matrix technique is that the matrix stabilizes but does not influence the structure of the radical cation. Our recent results for the tetramethylallene radical cation suggest that the matrix can alter the structure of certain radical cations.

The electronic structures and the inter-conversions of the $(\text{CH})_8$ hydrocarbons and their radical cations are of considerable interest. The cubane radical cation is especially interesting because it is a species of high symmetry (Oh) and has the highest strain energy in the $(\text{CH})_8$ family. In collaboration with Eaton and Xiong of the University of Chicago, we have examined cubane radical cations in solid matrices and in liquid hydrocarbons, have discovered a remarkable rearrangement of the cubane radical cation, and have made the first spectroscopic observation of cubane radical cation.

a. Cubane Radical Cation in Solid Matrices

We have studied cubane radical cations in three freon matrices (CFCl_3 , CF_3CCl_3 and $\text{CF}_2\text{ClCFCl}_2$). Similar spectra were obtained by radiolytic (γ -irradiation) oxidation of cubane in all three matrices (Figure 20) at 77 K. We observe a broad signal (ΔHpp , 14 G).

In addition to the broad signal, Figure 20a exhibits some other weak EPR spectral features. On thermal annealing of the sample at 110 K, the broad signal gradually and irreversibly decreases as the new EPR spectral features grow in. Figure 20b shows the EPR spectrum of the new entity at 110 K. The spectrum consists of a triplet ($a(2\text{H}_\beta) = 36.3$ G) of quintets ($a(4\text{H}_\alpha) = 7.7$ G), as indicated by the stick spectrum in Figure 20c. This spectrum exactly matches the spectrum of the radical cation (2) under the same matrix and temperature conditions.

Several possible pathways for the rearrangement of the cubane radical cation (1) to the bridged 1,4-bishomobenzene radical cation (2) are shown by Scheme 1.

Figure 20. (a) First derivative EPR spectrum at 77 K obtained from γ -irradiation (dose, 0.75 Mrad) of a solid solution of cubane (0.5 mol%) in $\text{CF}_2\text{ClCFCl}_2$ at 77 K, (b) first derivative EPR spectrum of **2** formed by thermal annealing of the matrix (a) at 110 K in $\text{CF}_2\text{ClCFCl}_2$, and (c) stick spectrum of (b) constructed by $a(2\text{H}_\alpha) = 36.3$ G and $a(4\text{H}_\beta) = 7.7$ G.

Scheme 1

Pathway (a) involves the cuneane radical cation (**3**) as an intermediate, namely, the reaction follows the path **1** - **3** - **2**. Pathway (b) involves the ring opening of **1** to the intermediate cyclooctatetraene radical cation (**4**), followed by a 1,5-ring-closure of **4** to **2**. Pathway (c) assumes no stable intermediate like the cuneane radical cation in the conversion of the cubane radical cation **1** into **2**.

Apparently pathway (a) is the preferred reaction route. The rearrangement of cubane to cuneane is known to be catalyzed by Ag(I) . Cuneane can be further isomerized to semibullvalene by Rh(I) . The oxidation of semibullvalene yields **2**. These catalytic transformations of cubane to semibullvalene via cuneane suggest pathways for radical cation transformations, even though it is not clear whether comparison of structural features of the carbonium ion intermediate and cubane radical cation are meaningful. The suggestion that cubane radical cation (**1**) isomerizes to **2** via **3** are supported by the study of cuneane. The EPR spectra recorded at 77 K and 110 K after γ -irradiation of cuneane in $\text{CF}_2\text{ClCFCl}_2$ at 77 K possess the same features as **2**. The hyperfine data ($a(2\text{H}_\alpha) = 36.3$ G and $a(4\text{H}_\beta) = 7.7$ G) at 110 K are the same as **2**, indicating that the rearrangement of **3** to **2** occurs at 77 K. This observation is consistent with the fact that no EPR signals from any intermediate such as **3** were detected in the transformation of **1** to **2** between 77 K and 110 K, since, if **3** is formed, it must promptly rearrange to **2**.

Pathway (b) with **4** as intermediate is rejected by a comparison of our results with those of Williams and co-workers. First, the matrix that previously contained **1** is nearly colorless. We have carried out an optical absorption study of **1** in the $\text{CF}_2\text{ClCFCl}_2$ matrix at 77 K and found no absorption band in the region between 400 and 900 nm. However, **4** has a rich-red color absorbing strongly at 507 nm. During the isomerization of **1** to **2**, no red color was observed. Thus, **4** cannot be a principal intermediate. Secondly, and more importantly, Williams et al. demonstrated, and we further confirmed, that **4** does not rearrange to **2** thermally, in contrast to the observed thermal transformation of **1** to **2**. Interestingly, transformation of **1** to **2** is also found to be driven by UV or visible light (at 90 K). This may indicate occurrence of a direct transformation pathway (c).

b. First Observation of Cubane Radical Cation

We have examined the cubane radical cation in liquid cyclopentane by fluorescence detected magnetic

resonance (FDMR). This represents the first observation of cubane radical cation.

Cubane⁺ was produced in cyclopentane solutions with 10⁻³ M cubane and 10⁻⁴ M perdeuterated anthracene (A) between 190 and 240 K by using pulsed electron beam (12-ns width) irradiation, generated by a 3-MeV electron Van de Graaff. The ionizing radiation creates singlet-phased radical ion pairs (c-C₅H₁₀, gas-phase ionization potential (IP) = 10.4 eV) consisting of a cyclopentane radical cation (c-C₅H₁₀⁺), and an electron; most of these ions recombine geminately in a few picoseconds. A small part of c-C₅H₁₀⁺ reacts with cubane (IP = 9.1 eV) to form cubane⁺, while some of the electrons are converted to the scintillator radical anion (A⁻). The resulting radical ion pairs, cubane⁺ and A⁻, are still spin-correlated. Upon recombination, an excited singlet state (¹A*) is generated, resulting in fluorescence. The time-resolved FDMR spectra (Figure 21) was obtained by measuring the fluorescence intensity as a function of applied magnetic field. The resonant decrease in the intensity of fluorescence was induced by the application of a single 100-ns microwave pulse immediately following the electron-beam pulse. The fluorescence signal was integrated by a boxcar detector over a 100-ns time window beginning immediately after the microwave pulse.

An FDMR spectrum provides parameters such as an EPR spectrum. The modulation depth, the linewidth and, thus, the spectral resolution are dependent on the lifetime of the radical ion species, the microwave power, and the sampling time window (microwave pulse width). The most important feature after the FDMR spectrum is the occurrence of a *distinct* hyperfine decrease of fluorescence.

Figure 21a consists of an intense central line (off-scale) due to the unresolved FDMR lines of scintillator radical ions superimposed on the wider, multiplet FDMR spectrum due to cubane⁺. This spectrum was not seen when cubane was absent or when other isomeric C₈H₈ hydrocarbons were used. The multiplet is analyzed as a binomial nine-line pattern with a spacing of 16.1 G resulting from the interaction of the electron with the eight equivalent protons of the cubane molecule (cf. the stick spectrum). The two outermost very weak lines were observed. The first

Figure 21. (a) FDMR spectrum observed at 190 K in cyclopentane containing 10⁻³ M cubane and 10⁻⁴ M perdeuterated anthracene. The asterisks indicate the signals from the cyclopentane solvent. The insertion is the enlargement of the left outermost three peaks. (b) First-derivative FDMR spectrum of (a).

derivative (computer generated) in Figure I-21b shows the nine lines decisively. The eight protons must be equivalent, either by symmetry in a static structure, or by a dynamic Jahn-Teller distortion of cubane⁺. Similar results were obtained for cubane⁺ in cyclopentane in a wide temperature range, 190 to 240 K.

Our results prompted Knight to repeat his investigation of cubane at 4 K in neon matrices. He had originally reported that cubane cation radical exhibited $a_H = 3G$. His very recent work revealed that he was observing cyclooctatetraene radical anion rather than cubane radical cation.

AM1-UHF calculations have been applied to many radical cations, and Dewar et al. have applied them to cubane. We have utilized such calculations to qualitatively account for the observed couplings of cubane⁺.

The heats of formation and the averaged coupling constants for the five distorted cubane radical cation structures (1-5) that were obtained by AM1 optimization are listed in Table 4 and are compared

Table 4. AM1 calculations of cubane radical cations.

Radical Cation	Neutral Cubane Geometry	S1	S2	S3	S4	S5
Heat of formation (kcal/mol)	390	361	374	380	385	566
Average coupling (G)	36	3	16	34	36	7

to cubane⁺ calculated with the geometry of the neutral molecule ($d_{C-C} = 1.55 \text{ \AA}$).

Structure **S1** would give rise to a small averaged coupling constant of 3 G, the result of a distortion of cubane from cubic to C_{2v} symmetry by elongating one of the 12 carbon-carbon bonds (to 2.1 Å). The unpaired electron is localized in this bond, which is averaged dynamically. Most of the other structures, in which the unpaired electron is delocalized, give rise to larger coupling constants. Structure **S2** has an averaged coupling constant of 16 G, in good agreement with our observation in liquid cyclopentane. This structure shows a distortion from cubic to C_{2v} by simultaneous elongation of two parallel carbon-carbon bonds (to 1.7 Å) in one of the four-membered rings; the other carbon-carbon bond lengths are almost unchanged. Structure **S3** is distorted from cubic to rectangular symmetry by simultaneous elongation of four bonds (to 1.64 Å). Structure **S4** is the AM1-optimized cubic arrangement and has bond lengths of 1.58 Å. These structures, unlike the Archimedean antiprism **S5** whose energy is very high, are stabilized by modest distortions of the geometry of the parent compound. Spin-density distributions, and consequently the coupling constants, are strongly dependent upon distortions in the structure. The potential surfaces which describe dynamic Jahn-Teller averaging are not yet known. The averaged coupling constants predicted for **S2** agree fairly well with our observations.

c. Tetramethylallene Radical Cation

Tetramethylallene (TMA), like the parent allene, belongs to the D_{2d} point group. It possesses two degenerate π -orbitals. When one electron is removed from one of the two orbitals, the resulting unpaired electron can be delocalized into the other orbital, leading to a deviation from the orthogonality of these two π -orbitals in the neutral molecule with the symmetry being lowered to the D_2 point group.

The distortions of TMA⁺ are characterized by the twist angle θ . For the parent allene radical cation, *ab initio* calculations predict θ to be 45°, a value that is in accord with the results of EPR studies of this substance in dilute solution.

TMA⁺ can be produced in a cyclopentane solution of 10^{-3} M TMA and 10^{-4} M perdeuterated anthracene (A) over a wide temperature range (195 to 295 K) by electron pulse irradiation, and detected by the time-resolved fluorescence detected magnetic resonance (FDMR).

The coupling constant for liquid solutions of TMA⁺ remains the same at all the temperatures studied although the spectra at low temperatures are less resolved. A typical FDMR spectrum of radical ion pairs of TMA⁺ and A^{•-} at 260 K is shown in Figure 22a. It is composed of an intense central line

Figure 22. (a) FDMR spectrum observed at 260 K in cyclopentane containing 10^{-3} M tetramethylallene and 10^{-4} M perdeuterated anthracene with the simulated stick spectrum, and (b) first-derivative EPR spectrum obtained from a solid solution of tetramethylallene (about 1 mol%) in CFCl_3 after γ -irradiation (dose, 0.5 Mrad) at 77 K with the simulated stick spectrum.

(off-scale) due to the unresolved EPR lines of anthracene ions superimposed on a well-resolved multiplet spectrum due to the TMA^+ . The spectrum consists of a binomial 13-line pattern from the interaction of 12 equivalent methyl protons of TMA^+ as indicated by the stick spectrum. The observed coupling constant is 11.4 G. The cation is quite long-lived, since it can be observed 2 μs after the electron pulse. Similar results were obtained in *n*-pentane between 195 K and 270 K.

The coupling constant of TMA^+ is much smaller in freon matrices (Table 4). For comparison, Figure 22b shows the EPR spectrum of the TMA^+ in CFCl_3 at 155 K. The well-resolved first derivative spectrum is a binomial 13-line pattern due to the interaction of 12 methyl protons of the cation as clearly indicated by the stick spectrum. The coupling constant is, however, only 8.1 G, about 30% smaller

than that observed in cyclopentane solution. Differences of about 5% to 10% in coupling constants have been observed for radicals and radical cations in different media, but this is the first example in which a 30% difference in coupling constant for a π -radical cation is observed!

This difference can be explained by different distortions of TMA^+ with different twist angles (Θ). AM1-UHF calculations show that the heat of formation and the coupling constant of TMA^+ depend on Θ , as indicated in Figure 23. The TMA^+ with the minimum energy possesses a Θ of 41.8° and the average methyl proton coupling constant of 4.8 G. (AM1 calculations often underestimate the coupling constant.) INDO calculations of the coupling constant of the TMA^+ by using the AM1 optimized geometry of the TMA^+ with $\Theta = 41.8^\circ$ give a larger coupling constant of 11.1 G which is closer to the experimental value. These calculations support the idea that TMA^+ adopts its minimum energy geometry in liquid alkanes. The calculations also suggest that TMA^+ in the freon matrix adopts a less stable conformer with $\Theta = 35^\circ$. The energy difference of these two structures is about 1 kcal mol^{-1} . Although the calculated distortions may not be very accurate, they provide a reasonable interpretation of our experimental observations.

Figure 23. AM1 calculated heat of formation and coupling constant for the tetramethylallene radical cation as a function of twist angles of Θ .

Temperature is not responsible for the different results in these media. The coupling constant does not change over a wide temperature range in freon or in liquid alkanes, and we observe that at the same temperature of 195 K, the coupling constant for $\text{TMA}^{\ddagger}$ is 8.1 G in CCl_4 , while it is 11.4 G in cyclopentane (Table 4).

The medium dependence of the distortion of $\text{TMA}^{\ddagger}$ may be caused by several factors. The matrix interaction between radical cations and freon molecules is well documented. The allene radical cation is believed to possess high positive charge density at the central carbon while the unpaired electron is delocalized into two π -orbitals. The spin density and positive charge density vary with the twist angle Θ . In freon matrices, the interaction between the chlorine or fluorine atom of freon molecules and the positive charge of the TMA cation can influence the spin and positive charge density distribution, resulting in different distortion in freons from that in liquid alkanes where such an interaction is lacking. This explanation is favored. Supporting this view are the observations of $\text{TMA}^{\ddagger}$ in softer matrices such as $\text{CF}_2\text{ClCFCl}_2$ at 110 K (Table 5) where smaller coupling is observed, indicating that distortions of $\text{TMA}^{\ddagger}$ must be due to matrix-radical cation interaction, since softer matrices should not restrict distortions of the TMA molecule.

6. Xenon Matrix and Zeolite Na-Y. New Methods for Study of Radical Cations

A.D. Trifunac, X. Qin

We continue to develop two new methods for the study of radical cations. The commonly used freon matrix method is being augmented by the use of a

xenon matrix with an electron scavenger and by the use of a zeolite matrix.

The "stabilization" of organic radical cations must address several problems. Since a convenient means of organic radical cation generation is by γ , X-ray, or electron radiolysis, the radical cation is created by the loss of one electron from the corresponding neutral compounds (R), yielding a highly reactive pair of charged species, Equation (37).

The ejected electron is often within the Onsager radius of its geminate partner cation and in organic, nonpolar liquids, very fast recombination occurs in a few picoseconds. In a solid, recombination can be somewhat retarded into the nanosecond regime. However, in order to "stabilize" the radical cation for a longer period of time, one must further slow the reverse electron transfer. Since the electron is reactive and mobile, the matrix radical cation can be captured easily. The most popular means of studying stabilized radical cations has been to use a freon matrix, like CFCl_3 where, after irradiation at liquid-nitrogen temperatures, Equation (38), the electron is scavenged and converted to Cl^- by the dissociative electron capture, Equations (39) and (40):

On the other hand, the matrix radical cation is transferred to the substrate solute (S), creating the desired radical cation, Equations (41) and (42).

Table 5. ^1H Hyperfine coupling constants of the tetramethylallene radical cation in freon matrices and liquid alkane solvents.

T(K)	Matrix or Solvent	a(G)
88	CFCl_3	8.1 (12H)
155	CFCl_3	8.1 (12H)
110	$\text{CF}_2\text{ClCFCl}_2$	8.1 (12H)
195	CCl_4	8.1 (12H)
195-295	cyclopentane	11.4 (12H)
195-270	n-pentane	11.4 (12H)

Here, the solute ionization potential must be lower than the matrix ionization potential. Other processes which must be prevented are the ion-molecule reactions between the solute radical cation and the parent neutral, such as proton transfer, Equation (43), or aggregation, Equation (44),

This is usually accomplished by using rigid matrices at low temperatures with low substrate concentration. Unfortunately, the freon matrix may affect stability, rearrangements, photochemistry, and bimolecular reactions of radical cations. Thus, it is very desirable to develop new methods that will allow the study of radical cations under a broader range of conditions.

Obviously, the best way to study the radical cations in real time is to actually observe their reactions and transformation solutions, where we wish to decipher reaction mechanisms. This can be accomplished by FDMR. However, there are many other circumstances in which it would be desirable to study "stabilized" radical cations, and we have developed two new means for stabilizing radical cations. We have found that xenon matrices with electron scavengers can be used to stabilize radical cations. Even more remarkable, zeolites Na-Y can be used to stabilize radical cations.

a. Xenon

As mentioned above, the rigidity of a matrix plays a role in slowing ion-molecule reactions. Obviously, inert rare gases would be excellent matrices. Neon matrices have been extensively employed to study radical cations by EPR since 1982. A few transition-metal carbonyl cations have been studied by EPR in krypton. But no study of xenon has been reported, even though xenon has many excellent prop-

erties. Accordingly, we elected to investigate its use and observed that γ -irradiation of xenon matrices containing several organic substrates and an electron scavenger generate radical cations. A good example is the 1,1,2,2-tetramethylcyclopropane radical cation, which was easily produced by γ -irradiation of a xenon matrix containing the parent compound and CH_2Cl_2 or $\text{CF}_2\text{ClCFCl}_2$ as electron scavengers. This radical cation was stabilized in xenon up to ~ 170 K.

To explain radical cation formation in xenon, we have proposed the following mechanism:

A xenon cation and an electron are created as a pair by radiolytic ionization (45). Geminate recombination of the pair is slow because the electron is captured by the electron scavenger, CH_2Cl_2 , and converted to Cl^- , Equations (46) and (47). Xenon cations that escape the recombination transfer the positive charge, Equation (48), and eventually generate substrate radical cations, Equation (49), if the substrate has a lower ionization potential than xenon. This condition is usually satisfied because the (gas phase) ionization potential of xenon is 12.1 eV while that of organic compounds is less than 11 eV.

To stabilize the radical cation, ion-molecule reactions between the substrate radical cation and the parent molecule must also be prevented. Below 110 K the xenon matrix is rigid. But the rigidity does not stop ion-molecule reactions in xenon between 77 K and 110 K. We have found that in the absence of the electron scavenger the ion-molecule reactions between the tetramethylcyclopropane radical cation and its parent molecule can still proceed to form ring-opened neutral radicals $\text{RCH}_2\dot{\text{C}}(\text{CH}_3)_2$ (Table 5). This led us to conclude that the electron scavenger not only prevents the geminate recombination but also interferes with the ion-molecule reactions.

We have studied other organic radical cations in xenon. For example, γ -irradiation of a xenon matrix containing tetramethylethylene (TME) (0.8 mol%) and CH_2Cl_2 (0.8 mol%) at 77 K gave rise to the EPR spectrum shown in Figure 24a. Except for some impurities marked by asterisks, the spectrum shows nine equally spaced lines with a coupling constant of 16.9 G, which is in agreement with the known coupling constant of $\text{TME}^{\cdot+}$. These lines are part of the 13-line pattern due to the interaction of 12 protons of four methyl groups in $\text{TME}^{\cdot+}$ as indicated by the stick spectrum. The outermost lines are too weak to be clearly seen in the experiment. The spectrum in Figure 24a, therefore, can be unequivocally assigned to $\text{TME}^{\cdot+}$. The TME radical cation was found to be stable up to 100 K.

Different concentrations of TME in xenon were investigated. We found that even when the TME concentration reaches 10 mol%, the monomer TME

radical cation remains isolated. Shown in Figure 1-24b is the EPR spectrum that was recorded after γ -irradiation of a xenon matrix containing TME (10 mol%) in the presence of CH_2Cl_2 at 77 K. The main features of the spectrum are nearly the same as Figure 24a. Only a small amount of dimer TME radical cations were formed, as pointed out by the arrows in Figure 24b; the dimer radical cation has a coupling constant approximately half that of the monomer. In contrast to xenon, a previous study has shown that dimer radical cations were mainly detected after γ -irradiation of a glassy solution containing more than 1 mol% of TME in 3-methylpentane. This shows that the xenon matrix method can provide a means of controlling the condensed phase of ion-molecule reactions of radical cations.

b. Zeolite

Zeolites have been studied extensively as catalysts and molecular sieves, but they have not been studied as hosts for stabilizing organic radical cations. To our knowledge, only one report has described a few alkane radical cations at 4 K in a synthetic zeolite, ZSM-5.

Recently, we successfully generated several radical cations in zeolite Na-Y. Examples include the radical cations of hexamethyl(Dewar benzene) (1,2,3,4,5,6-hexamethylbicyclo[2.2.0]hexa-2,5-diene), tetramethylcyclopropane, trans-2,3-dimethylethylene oxide, and tetramethylethylene. The EPR parameters of these radical cations are listed in Table 6. These radical cations were generated by γ -irradiation of zeolite Na-Y containing parent compounds at 77 K. The cation radicals were stable in zeolite over a wide temperature range.

The generation and stabilization of radical cations are associated with the unique structure of the zeolite. The framework of the zeolite is based on infinitely repeating three-dimensional SiO_4 and AlO_4 tetrahedra that are linked by shared oxygen atoms, which in turn form cylindrical channels and spherical cages. Channels and cages are joined by intersections comprising "windows" or "pores". The structure of zeolite Na-Y and Na-X is depicted below:

Figure 24. EPR spectra observed at 85 K after γ -irradiation of a xenon solution containing tetramethylethylene (0.8 mol%) and CH_2Cl_2 (0.8 mol%) at 77 K (a), and after γ -irradiation of a xenon solution containing tetramethylethylene (10 mol%) in the presence of CH_2Cl_2 (b). The asterisks indicate distortions from impurities or CH_2Cl_2 . The arrows indicate the signals due to the dimer tetramethylethylene radical cation.

Table 6. EPR parameters for the radical cations and radicals.

Radical Cations or Radicals	Matrix or Solvent	T/K	Hyperfine Couplings/G
1,1,2,2-Tetramethylcyclopropane [†]	xenon/CH ₂ Cl ₂	77	18.7(2H β), 14.9(12H β)
	zeolite Y	180	18.7(2H β), 14.9(12H β)
RCH ₂ C(CH ₃) ₂	xenon	77	23.3(7H β)
Tetramethylethylene [†]	xenon/CH ₂ Cl ₂	85	16.9(12H β)
	zeolite Y	80	17.0(12H β)
1,1,2-Trimethylallyl	zeolite X	80	a(3H _{exo})=16.0, a(3H _{endo})=12.7 a(2H)=13.5, a(3H)=3.3
	CF ₂ ClCFCl ₂	125	a(3H _{exo})=16.0, a(3H _{endo})=12.7 a(2H _α)=13.5, a(3H)=3.3
Hexamethyl(Dewar benzene) [†]	zeolite Y	100	9.3(12H β)
Trans-2,3-dimethylethylene oxide [†]	zeolite Y	120	22.5(1H α , 3H β)

Zeolites X and Y

The open, nearly circular 12-membered rings have a diameter of about 0.7 nm, through which organic molecules can diffuse into spherical supercages with a diameter of 1.25 nm. Each aluminum atom of the framework contributes a negative charge, which is balanced by exchangeable cations. In the zeolite Na-Y and Na-X, most (99%) cations are Na⁺, with impurities such as Fe³⁺ and Mn²⁺. These cations are located inside the supercages.

As an example, Figure 25 shows the very clean EPR spectrum of TME radical cation in zeolite Na-Y at 80 K. The spectrum consists of a binomial 13-line pattern with a coupling constant of 17.0 G as expected for TME^{•+}. The TME radical cation persisted in zeolite Na-Y to 120 K. Only monomeric TME^{•+} was observed in zeolite Na-Y.

The retardation of ion-molecule reactions can be attributed to the slow diffusion of organic molecules in the zeolite at low temperature. The size and shape of the structure and the chemical properties of the adsorbed organic molecules influence the diffusional motions of organic molecules.

In contrast to the situation in the xenon matrix where an electron scavenger is a necessity, no electron scavenger was needed in zeolite Na-Y. We have proposed the following mechanism to explain the radical cation formation in zeolite:

Figure 25. An EPR spectrum observed at 80 K after γ -irradiation of a zeolite Na-Y-tetramethylethylene system at 77 K.

A radical cation of zeolite ($\text{zeolite}^{\cdot+}$) and an electron are initially produced by γ -irradiation, Equation (50). Since no electron scavenger was added, the ejected electron is postulated to be captured by the metal cations in zeolite, Equations (51) and (52). It is further assumed that sodium or a sodium cluster is oxidized by Fe^{3+} , Equation (53). While reverse electron transfer is prevented by these processes, the radical cation of zeolite is mobile and can be transferred to the adsorbed organic molecules to form the corresponding radical cation, Equation (54). According to this proposal, it is the metal cations existing inside supercages that act as electron scavengers. As in the xenon case, where the electron scavenger plays some role of preventing ion-molecule reactions, we presume that the electrostatic and steric effects in zeolites also affect the ion-molecule reactions in zeolite.

Figure 26a shows the EPR spectrum of paramagnetic species produced by γ -irradiation of zeolite Na-X containing TME at 77 K. The spectrum is different from the $\text{TME}^{\cdot+}$ spectrum shown in Figure 25. It consists mainly of nine lines spaced about 14 G. Except for the much stronger central line, the spectrum can be simulated very well by the known parameters for the 1,1,2-trimethylallyl radical $\text{CH}_2=\text{C}(\text{Me})\dot{\text{C}}(\text{Me})_2$ that is formed by the ion-molecule reaction (proton loss or hydrogen abstraction) between $\text{TME}^{\cdot+}$ and TME. No $\text{TME}^{\cdot+}$ was detected in zeolite Na-X. This preliminary data suggest that $\text{TME}^{\cdot+}$ and TME can easily diffuse together in zeolite Na-X in contrast to zeolite Na-Y. This difference cannot be attributed to the geometrical structure of the two zeolites because zeolite Na-Y and Na-X have the same structure. Therefore, it is attributed to the different number of sodium cations present in the supercage. The ratio of Si/Al for Na-Y and Na-X is 2.3 and 1.23, respectively. Accordingly,

there are five sodium cations per supercage in Na-Y and nine sodium cations per supercage in Na-X.

The EPR observations of several hydrocarbon radical cations (exemplified by the tetramethylethylene radical cation) using xenon and zeolite Na-Y as matrices illustrates the new means for the study of radical cations. In the present study we have shown that many radical cations may be studied in less polar environments such as a xenon matrix, where new insights into radical cation reactions can be realized. We hope to control condensed-phase ion-molecule reactions by controlling the concentration of reacting species and their relative orientation. Thus, steric factors in ion-molecule reactions such as proton transfer can be examined. We have also shown that the use of a "microreactor" matrix such as zeolite is very promising, since many radical cations can be studied by EPR over a wide temperature range.

Figure 26. (a) An EPR spectrum observed at 80 K after γ -irradiation of a zeolite Na-X-tetramethylethylene system at 77 K; and (b) its computer-simulated spectrum according to the EPR parameters shown in Table 5 and a Lorentzian linewidth of 5.0 G.

B. The Role of Solvent in Chemical Reactivity

A. D. Trifunac, D. M. Bartels, C. D. Jonah, Y. Lin, P. Han, R. G. Lawler, P. W. Percival, C. Romero

1. Study of Atomic Hydrogen and Deuterium in Water Radiolysis

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The mechanism(s) of water radiolysis are of undeniable practical importance, and have been the object of study for decades. While the basic question of "what happens?" has been largely settled, the more difficult and fundamental questions of "how and why?" remain in many respects unanswered. H/D isotope effects in the fundamental processes of water radiation chemistry were mostly unexplored, and over the past several years our work has provided some important insights. We have reported on an extensive study of H and D atoms formed in radiolysis spurs, and have identified two major pathways for the dissociation of electronically excited water molecules. This year, we extended our time-resolved EPR measurements to water ice. In addition, we report a high-precision measurement of the activation energy for the unusual reaction $\text{H} + \text{OH}^- \rightarrow (\text{e}^-)_{\text{aq}} + \text{H}_2\text{O}$. Armed with this information, we made the first reliable experimental determination of hydrated electron enthalpy and entropy, which forces revision of some previous thinking about the "driving force" in $(\text{e}^-)_{\text{aq}}$ reactions.

a. Enthalpy and Entropy of Hydrated Electrons

The equilibrium represented by Equation (55)

is of fundamental importance since it determines the lifetime and limiting concentration of solvated electrons — a species of great practical and theoretical significance in aqueous radiation and electrochemistry. Because the free radicals $(\text{H}\cdot)_{\text{aq}}$ and $(\text{e}^-)_{\text{aq}}$ are highly reactive, the equilibrium constant has been determined by separate measurements of the forward- and reverse-reaction rates. Determination of the temperature dependence of these rates allows, via a Born-Haber cycle, the evaluation of solvation enthalpy, entropy, and free energy of the hydrated electron. Using a

newly developed pulsed EPR technique (free induction decay or FID attenuation) we have made new measurements of the rate of Equation 55 vs. temperature. Our result is dramatically different from the only previous report, which was based on a less direct optical measurement. The corresponding revision of solvated-electron enthalpy and entropy has revealed unexpectedly large differences between electrons and classical ions.

H atoms were generated in aqueous solutions in the EPR cavity with short (10-60 ns) pulses of 3-MeV electrons from a Van de Graaff accelerator. Solutions were continuously circulated at a high-flow rate to maintain the sample temperature constant to $\pm 1^\circ\text{C}$, as monitored by thermocouples inserted into the flow before and after the EPR cavity. Immediately after radical formation, a $\pi/2$ microwave pulse was applied, and the subsequent free-induction decay was recorded by signal averaging 10,000 to 50,000 shots in a digital oscilloscope. The time constant for decay of the damped oscillation is linearly related to the pseudo-first-order scavenging rate. An example of raw data and results of the fitting procedure are provided in Figure 27.

Arrhenius plots for the $\text{H} + \text{OH}^-$ reaction are shown in Figure 28. As a check on possible systematic errors, two different radiation doses (55-ns, 39-nC electron pulses and 25-ns, 15-nC pulses) and two different magnetic field offsets (+2.0 G and +3.0 G) from the $\text{H}^\cdot$ low field EPR resonance were analyzed separately. Virtually identical activation energy and pre-exponential factors are obtained, as is readily seen in the four parallel plots of Figure 28. The mean activation energy and pre-exponential factor determined in a weighted least-squares fit of all of the rate data are $E_a = 38.6 \pm 1.7 \text{ kJ/mol}$ and $A = 1.4 \pm 0.4 \times 10^{14} \text{ M}^{-1} \text{ s}^{-1}$ respectively, where the uncertainties listed are the standard errors.

Following the standard activated complex theory of reaction rates, a measured rate constant will be given (in $\text{M}^{-1} \text{ s}^{-1}$) by

$$k_{\text{rxn}} = kT/h \exp(-\Delta G^\ddagger/RT) / (\text{mole/liter}) \quad (56)$$

Figure 27. Examples of raw data (dots) and fitted data (solid line) using a global least-squares fitting procedure. Four data sets, each corresponding to a different scavenger concentration, were collected at +3.0 G field offset from the $H^\bullet$ low field (+1/2) line at $62 \pm 1^\circ\text{C}$.

Figure 28. Arrhenius plot for the reaction $H^\bullet + OH^\bullet \rightarrow (e^-)_{aq} + H_2O$. The same slope and intercept is found using two different radiation doses (55 ns, 39 nC electron pulses and 25 ns, 15 nC pulses) and two different magnetic field offsets (+2.0 G and +3.0 G) relative to the H (+1/2) line.

where h is Planck's constant, k is the Boltzmann constant, and $\Delta G^\ddagger$ is the free energy of formation of the transition state which leads to product. If the temperature dependence of the reaction rate is known, the free energy can be decomposed into the enthalpy of activation and entropy of activation via the definition $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$. A correspondence with the empirical Arrhenius equation is established by the expressions

$$E_a = \Delta H^\ddagger + RT \quad (57)$$

$$A = kT/h \exp(\Delta S^\ddagger/R + 1)/(\text{mole/liter}) \quad (58)$$

From the rate constant of $2.36 \pm 0.30 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for Reaction (55) at 298 K, we obtain the free energy of activation, $\Delta G^\ddagger = 30.9 \pm 0.3 \text{ kJ/mole}$. From the Arrhenius activation energy and Equation 57, we derive the heat of activation $\Delta H^\ddagger = 36.1 \pm 1.7 \text{ kJ/mole}$. The definition of the Gibb's free energy

then gives $\Delta S^\ddagger = 17.3 \pm 6.0$ J/mole.deg as the activation entropy at room temperature.

The pseudo-first-order lifetime of the solvated electron in ultrapure water was measured at Argonne some years ago, and identified with the reverse of Reaction (1). The rate constant k_{-50} is 16 ± 1 M⁻¹s⁻¹ (or rather 890 s⁻¹ in 55.5 M water) at 298 K, and the Arrhenius activation energy was found by Fielden and Hart to be 4.5 ± 1.0 kcal/mole. Following the same prescription as used above, one finds $\Delta G^\ddagger = 56.2 \pm 0.2$ kJ/mole, $\Delta H^\ddagger = 16.3 \pm 4.2$ kJ/mole, and $\Delta S^\ddagger = -134 \pm 14$ J/mole.deg for Reaction (-55). Assuming a common transition state, the overall thermodynamic change for Reaction (55) as written is given in Table 7 by the difference in forward and reverse activation free energy, enthalpy, and entropy: $\Delta G^\circ = -25.3 \pm 0.4$ kJ/mole, $\Delta H^\circ = 19.8 \pm 4.5$ kJ/mole, and $\Delta S^\circ = 151 \pm 15$ J/mole.deg. It is interesting to note that the

equilibrium favors (e⁻)_{aq} formation due to the large positive entropy change.

Given the standard thermodynamic change(s) of Equation (55), we can calculate the molar enthalpy, entropy, and free energy of formation of solvated electrons, provided standard thermodynamic data ($\Delta \bar{X}_f^\circ$, where X = G, H, S) are available for the other reactants and products. Unfortunately, thermodynamic parameters have not been determined for aqueous H atoms, although they are available for H atoms in the gas phase. The problem, therefore, reduces to calculation of the thermodynamics for the solvation process (H)_g → (H)_{aq}. Reasonable estimates for these quantities, with generous error allowances, can be made based on analogy with helium solvation in water. This contribution to the calculation proves to be relatively minor in any case. The result of the calculation is shown in Table 8(a).

Table 7. Thermodynamic changes associated with (H⁺)_{aq} + (OH⁻)_{aq} ⇌ (e⁻)_{aq} + H₂O_{liq}.

	$\Delta G^\ddagger$ (kJ/mole)	$\Delta H^\ddagger$ (kJ/mole)	$\Delta S^\ddagger$ (J/mole deg)
Reaction (55)	30.9±0.3	36.1±1.7	17.3±6.0
Reaction (-55)	56.2±0.2	16.3±4.2	-134±14
Overall standard change $\Delta X_{55}^\ddagger - \Delta X_{-55}^\ddagger$	-25.3±0.4	19.8±4.5	151±15

Table 8. Thermochemical data[†] for Equation 55 and electron solvation.

a)	$\Delta \bar{X}_f^\circ$	$\Delta \bar{G}_f^\circ$ (kJ/mole)	$\Delta \bar{H}_f^\circ$ (kJ/mole)	$\bar{S}_f^\circ$ (J/mole.deg)
H ₂ O _{liq}		-237.2	-285.8	69.9
(H) _{aq} [*]		222±4	217±3	48±10
(H ⁺) _{aq}		0	0	0
(OH ⁻) _{aq}		-157.3	-230	-10.8
(e ⁻) _{aq} [*]		277±4	293±5	118±18
b)	$\Delta \bar{X}_{hyd}^\circ$	$\Delta \bar{G}_{hyd}^\circ$ (kJ/mole)	$\Delta \bar{H}_{hyd}^\circ$ (kJ/mole)	$\Delta \bar{S}_{hyd}^\circ$ (J/mole.deg)
(H ⁺) _{aq}		-1079±13	-1117±10	-130±8
(OH ⁻) _{aq}		-456	-505	-162
(e ⁻) _{aq} [*]		-161±14	-126±11	118±20

^{*}This work. [†]Data taken from standard tables except as noted. Part a) $\Delta \bar{X}_f^\circ$ of ions are based on the $\Delta \bar{X}_f^\circ = 0$ convention for (H⁺)_{aq}. Standard states are 1 atm ideal gas and hypothetical 1 M aqueous solution. Error estimates are indicated only where necessary for the (e⁻)_{aq} calculation.

It is instructive at this point to consider just how much the $\Delta\bar{H}_f^\circ$ and $\Delta\bar{S}_f^\circ$ numbers for $(e^-)_{aq}$ in Table 8(a) differ from earlier estimates. Consider a comparison of the ion recombination equation (59)

ΔG°	ΔH°	ΔS°
-79.9 kJ/mole	-55.8 kJ/mole	+80.75 J/mole.deg

to the corresponding Equation (60) of $(e^-)_{aq}$ with hydronium ion

Noyes estimated (1968):

ΔG°	ΔH°	ΔS°
-55 kJ/mole	-47 kJ/mole	+29 J/mole.deg

this work:

-55 kJ/mole	-76 kJ/mole	-70 J/mole.deg.
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Based on the estimates (e.g., intelligent guesses) of solvated-electron properties published by Noyes in 1968, and accepted as "reliable" at least until the work of Hickel and Sehested in 1985, Equation (60) is thermodynamically similar to the acid-base recombination, Equation (59). Our determination of $\Delta\bar{S}_f^\circ$ and $\Delta\bar{H}_f^\circ$ for the electron completely change this comparison. The entropy change in Equation (60) is negative rather than positive, and a great deal more heat is liberated than originally supposed. The two charge-recombination reactions are therefore quite different. A distinct difference in their rate behavior has been known for many years: Equation (59) is the fastest reaction known in aqueous solution, and is purely diffusion controlled; Equation (60) is fast, but distinctly (five to six times) less than diffusion controlled. A large (negative) activation entropy barrier in Equation (60) is completely consistent with the overall negative ΔS° calculated using our $(e^-)_{aq}$ standard entropy.

Once a single ion such as $(H^+)_{aq}$ has been chosen as standard, $\Delta\bar{X}_f^\circ$ values can be assigned to all other ions in all other media. A large body of high-precision gas-phase data is tabulated using the alternative convention that $\Delta\bar{G}_f^\circ$ and $\Delta\bar{H}_f^\circ$ formation for the gas-phase electron is zero, and absolute entropies are

calculated using the Sackur-Tetrode equation. To convert between the two conventions, we use the $\Delta\bar{H}_{hyd}^\circ$ values for H^+ listed in Table 8(b). The $\Delta\bar{X}_{hyd}^\circ$ values for electrons can then be calculated. Note that the errors quoted for $\Delta\bar{X}_{hyd}^\circ$ of the electron (Table I-8(b)) include both the uncertainty in our experiment and the relatively large uncertainties in proton $\Delta\bar{X}_{hyd}^\circ$.

Comparison of $\Delta\bar{H}_{hyd}^\circ$ and $\Delta\bar{S}_{hyd}^\circ$ for the electron with those of other ions reveals a rather dramatic difference. The electron has the smallest $\Delta\bar{H}_{hyd}^\circ$ of all ions. Much more distinctive is the $\Delta\bar{S}_{hyd}^\circ$, which is large and positive. All other ions are characterized by negative $\Delta\bar{S}_{hyd}^\circ$. Precisely the same unusual solvation thermodynamics have been found for the electron in ammonia. Thus, we have strong evidence in favor of the conventional view that electrons in water and ammonia have a similar solvation "structure."

The $\Delta\bar{G}_{hyd}^\circ$ of common ions is dominated by $\Delta\bar{H}_{hyd}^\circ$, which in turn is dominated by the strong electrostatic bonds formed between the ion and water molecules in the first solvation shell. The $-\Delta\bar{S}_{hyd}^\circ$ contribution is smaller, but much more characteristic of individual ions. A conceptually useful chemical model for the $\Delta\bar{S}_{hyd}^\circ$ of ions was suggested by Friedman and Krishnan in their 1973 review article. They propose that

$$\Delta\bar{S}_{hyd}^\circ = R \ln \left(\frac{V_f}{V_g} \right) + \Delta S_I + \Delta S_{II} + \Delta S_{Born} \quad (61)$$

where V_f/V_g is the ratio of free volumes available to the ion in the liquid and gas phase, ΔS_I is the entropy change of the water molecules in the first solvation sphere, ΔS_{II} the entropy change in the second solvation sphere, and ΔS_{Born} a contribution from the succeeding solvation layers, which is approximated with the classical Born equation. For the standard states used in this work, the first term (representing restriction of translational motion) can be estimated as ca. -50 J/mole.deg. (Note this term is the same sign and magnitude for any solvated species.) The last term is roughly -10 J/mole.deg for all ions. The strong electrostatic bonds in the first solvation layer dictate $\Delta S_I \approx -50$ J/mole.deg for all common ions, both positive and negative. The differences between individual ions are then assigned to the second cosphere water molecules, and the corresponding ΔS_{II} is normally found in the range ± 40 J/mole deg. Friedman and

Krishnan note that the sign of ΔS_{II} correlates very well with the structure-making/structure-breaking characteristics of individual ions.

In terms of this solvation model, it is clear that ΔS_{hyd}° of all common ions will be negative because of the tight binding and negative ΔS_I of the first solvation shell. (One cannot change the first and last terms of Equation 61.) In order to explain the positive ΔS_{hyd}° of the electron, one should look for a dramatic structural difference in this solvation layer. This is precisely what is found in recent quantum molecular dynamics simulations. Both Jonah et al. and Schnitker and Rossky find that the electron solvation structure is similar to that of a halide ion in that, on average, one bond of each water molecule points in toward the ion. However, the radial correlation function $g(r)$ describing the distance distribution between the electron and the water molecules is much more diffuse than for a classical ion. (Compare Figure 33 to 35 below.) Thus, a highly rigid first solvation shell is *not* generated by electron solvation.

The dominant contribution to both the enthalpy and entropy of ion solvation is associated with the inner solvation sphere. The incorporation of an ion replaces a number of water-water hydrogen bonds with new water-solute electrostatic bonds, which might have greater or lesser vibrational/librational frequencies and associated quantum energy levels. From the statistical mechanical definition of entropy, it is clear that creation of strong, tight bonds will result in a decrease of entropy, while replacement of water hydrogen bonds by weaker, looser interactions should increase the total entropy. The contribution ΔS_I for common ions is negative because of the tight binding and high vibrational/librational frequencies of the first solvation shell. The vibrational/librational frequencies associated with the solvated electron-water interaction can reasonably be assumed to be lower than those of the water-water bond it replaces. Qualitatively, when a water molecule "pushes" at a solvated electron, there is relatively little restoring push back — the electron simply moves elsewhere. This gives rise to positive ΔS_I .

The new measurements of the activation energy for reaction of $(H)_{aq}$ with $(OH^-)_{aq}$ force a complete reassessment of the thermodynamic properties of the

hydrated electron. While the Gibbs free energy does not differ from earlier calculations, it can now be seen that the hydrated-electron thermochemistry is often dominated by entropy rather than enthalpy effects. The large positive solvation entropy implies a dramatic modification of the water structure in the vicinity of the electron. There can be little doubt that the electron is the champion "structure-breaker" among aqueous ions.

b. Diffusion and CIDEP of H and D Atoms in Ice

The action of ionizing radiation on ice crystals has taken on major importance in the last few years because this chemistry impacts the "ozone hole" problem in atmospheric chemistry. Radiation chemistry of ice features the same primary products H_3O^+ , e^- , $H\cdot$, and $OH\cdot$, but the timescales of recombination change dramatically from liquid water. Recombination of the ionic products H_3O^+ and e^- occur one-to-two orders of magnitude faster in ice due to the much higher ion mobilities in the crystal. At temperatures near the melting point, H atoms in ice move just as rapidly as in liquid water, but the OH radicals move orders of magnitude slower.

The detrapping of H and OH radicals in ice at temperatures below 100 K has been extensively investigated by CW EPR, but very few studies have been carried out from 100 to 150 K, and none have examined the kinetics above 150 K. As a natural extension of our studies of H and D EPR in liquid water, we undertook in the past year a study of CIDEP and spin relaxation in ice at temperatures above 150 K, the temperature regime of greatest practical importance.

Samples of triply-distilled H_2O and D_2O in 2-mm i.d., 3-mm o.d., Pyrex sample tubes were degassed on a vacuum line and the tubes were sealed. Immediately prior to use, the water was frozen by immersion in liquid nitrogen to yield a random polycrystalline ice. The tube was then transferred to the cold EPR cavity. During irradiation, the samples were maintained at a constant temperature by flowing cold isopentane. The sample temperature, which was measured with a thermocouple embedded in the ice, remained within 1 °C of the coolant for electron-beam

currents of 1 microamp. All of the experiments were performed at approximately this current level. Tests with a solid Pyrex rod in place of the ice revealed no detectable H-atom signal from the Pyrex or isopentane over the -130°C to -5°C temperature range.

The pulsed EPR kinetics techniques that were used in this study have been reported previously. Briefly, a 3-MeV electron pulse of duration 10-100 ns irradiated the sample, creating the free-radical species of interest. After some programmed time delay t , a

25-ns, $\pi/2$ pulse is applied, and a free induction decay (FID) is observed. After a period τ of some microseconds ($\geq 0.5 \mu\text{sec}$) a second microwave (π) pulse is applied, which generates an electron-spin echo at time 2τ after the initial $\pi/2$ pulse. The initial amplitude of the FID and the amplitude of the spin echo are measured in separate gated integrators.

Typical kinetic results are shown for H in H_2O ice in Figure 29 and for D in D_2O ice in Figure 30. At the high-temperature limit ($\sim -10^{\circ}\text{C}$), the signals

Figure 29. Kinetics of the H-atom magnetization in H_2O ice at several different temperatures, following irradiation with a 55-ns electron pulse. The CIDEP phenomenon is readily observed, and the time-scale indicates fast motion of the H atoms through the lattice.

Figure 30. Kinetics of the D-atom magnetization in D_2O ice at several different temperatures, following irradiation with a 55-ns electron pulse. The CIDEP effect is readily apparent, and the timescale indicates fast motion of the D atoms through the lattice.

are very similar to those found in liquid water. Chemically induced dynamic electron polarization (CIDEP) generated in spin-dependent chemical reactions gives rise to the characteristic low-field emission/high-field absorption (E/A) pattern in the spectra of both H and D. The high-field (-1) and low-field (+1) deuterium lines are antisymmetrically polarized to roughly the same extent, which is typical of dominant ST_0 mixing in the CIDEP mechanism. The hydrogen low-field (+1/2) line becomes polarized much more strongly than the high field (-1/2) line. This indicates that ST_1 mixing is important in the H-atom CIDEP, due to the very large hyperfine coupling of the H proton. The position of the signal maxima at approximately 20 μ sec after the electron pulse indicates that most of the free radicals have already reacted. This single finding demonstrates that H and D diffusion is very facile in the ice matrix. One very important aspect of the kinetics near -10 °C is the presence of an initial signal, which already shows the E/A pattern characteristic of random radical pair CIDEP, immediately after the electron pulse. Just as in liquid water, this prompt signal must arise from radical-radical cross reactions in radiolysis spurs. As the temperature is lowered, the rates decrease; the point of the maximum CIDEP signal moves to longer times; and the maximum signal becomes generally weaker. These effects are all consistent with slower diffusion of the H and D atoms. However, a dramatic change in the initial spectrum is observed, as shown in the insets of Figures 1-29 and 30. By -50 °C, the high- and low-field lines of both H and D are initially in emission. By -70 °C, the high-field line of D is more strongly polarized in emission than the low-field line. In the parlance of chemically induced magnetic resonance, this is an A/E multiplet pattern superimposed upon overall net emissive polarization. The initial A/E multiplet pattern is typical of geminate radical pairs produced with singlet spin phasing. This is, in fact, the polarization pattern that is expected for geminate recombination of singlet (D...OD) radical pairs. Presumably the initial H spectrum is also strongly influenced by this geminate reaction, but the presence of strong ST_1 emissive polarization masks A/E multiplet polarization from the ST_0 mixing. The geminate polarization is presumably absent at higher tempera-

tures because the spin dephasing time of OH (OD) is very short — probably subnanosecond, as in liquid water. When the T_2 of OH becomes longer than one or two nanoseconds, the geminate spin coherence persists long enough for CIDEP effects to become manifest.

A large isotope effect that favors H over D formation was found in experiments on mixed ice of 50/50 and 10/90 H_2O/D_2O composition. In the 50/50 mixture, the H-atom signal was decreased relative to pure H_2O , but only a very small D-atom signal was detected. Signal amplitudes of H and D were comparable in the 10/90 mixture. The results for H and D in the 10 $H_2O/90 D_2O$ system was qualitatively very similar to the isotopically pure ices. A previous study of prompt CIDEP in isotopically mixed alkaline liquid water led to the conclusion that H formation was favored over D, both by the branching ratio of HDO dissociation (on the order of 2.5:1) and in the recombination of electrons with hydronium ion. The CIDEP effect further enhances the H EPR signal relative to D, because of the larger H hyperfine splitting. The similarity of the isotope effects in mixed H_2O/D_2O ice to those in the liquid suggests that the same mechanisms are operative.

The primary aim of the study has been the measurement of spin-relaxation times T_2 and, if possible, T_1 to elucidate the mechanism of H- and D-atom diffusion through the ice- I_h lattice. T_1 measurements proved impossible due to the dominant Heisenberg exchange at the radiation doses needed. T_2 measurements were performed by the standard two-pulse ($\pi/2, \pi$) spin-echo sequence. The results are presented in Figure 31 in the form of an Arrhenius plot for H atoms in H_2O , 50 $H_2O/50 D_2O$, and 10 $H_2O/90 D_2O$ ice, and for D atoms in D_2O and 10 $H_2O/90 D_2O$ ice. For electron-nuclear dipole relaxation modulated by diffusion of the H and D atom through the lattice of ice protons and deuterons, standard theory predicts

$$1/T_2 \equiv \omega_L^2 \tau$$

where ω_L is the second moment of the random magnetic field, and τ is the mean time between jumps from one site to the next. The inverse Arrhenius behavior (negative activation energy) and the relative magnitudes of the relaxation times in the isotopically

Figure 31. Transverse spin relaxation rates of H and D atoms in pure and isotopically mixed ice crystals. The inverse Arrhenius behavior and the dependence of the relaxation rate on the lattice proton/deuteron composition are completely consistent with a dipole-dipole relaxation mechanism modulated by diffusion of the H and D atoms through the lattice.

substituted ices are readily predicted from this simple expression. The activation energies for T_2 relaxation, which may be identified with the activation energies for diffusion, are slightly different for the H and D atoms, but essentially independent of the isotopic composition of the lattice. A surprising and interesting result is that D-atom relaxation/diffusion is faster than H-atom relaxation/diffusion above 200 °K. It appears that this behavior can be explained in terms of a semiclassical model for diffusion through a "bottleneck" between adjacent interstitial sites. Model calculations are in progress.

2. Studies of Solvent Relaxation Dynamics by Ultrafast Laser Spectroscopy Y. Lin

How do solvent molecules react to the sudden creation of a charged species, and what microscopic factors of the charged molecules and the solvent structure control this response? Work in our laboratory in the past year has focused on these questions. We seek to understand the solvent relaxation dynamics after the intra- and intermolecular charge-transfer processes. As

a starting point, we studied the solvation dynamics after an intramolecular charge-transfer process in several polar solvents. The extension of this study to the problem of molecular ion solvation in nonpolar systems will be carried out with our newly developed femtosecond laser system.

The solute molecule used in our study is bis(4-amino-phenyl) sulfane. It possesses an intramolecular charge-transfer state. The short laser pulse excitation raises the solute molecule to its local excited state (LE); subsequent charge redistribution causes the molecule to relax to the lower energy charge-transfer state (CT). The surrounding solvent molecules reorganize to balance the sudden creation of the large dipole. The picosecond time-correlated single-photon counting technique is used to study the Stokes shift in the fluorescence spectrum of these solute molecules, and solvent-relaxation information is obtained.

Rotation of solvent molecules and change in local bonding are recognized as major contributions to solvent relaxation, but these effects have been difficult to separate experimentally. In an attempt to attack this problem directly, we decided to use an isotope-substitution technique. In the past year, we studied the fluorescence Stokes shift of the solute molecules in a series of alcohol and deuterated-alcohol systems. By comparing the fluorescence spectra of the solute molecules in these solutions, we probe the effects of hydrogen bonding and molecular rotation in solute-solvent interactions and solvent reorganization processes. The time scales for these different kinetic processes are also determined.

We have investigated the steady-state and time-dependent fluorescence spectra of bis(4-aminophenyl)sulfone (APS) in CH_3OH , CH_3OD , CD_3OD , etc. The optical excitation is around 290 nm. Time-dependent fluorescence decays are recorded at different wavelengths between 330 nm and 560 nm. A significant shift of the fluorescence band as a function of time is observed in good agreement with the results of Simon and co-workers. This fluorescence band is attributed to the formation of the intramolecular charge-transfer (ICT) excited state. The decay from this ICT state cannot be fit to a single exponential, and the conventional two-state kinetic model, see scheme, also fails to explain the

wavelength-dependent dynamics. In the two-state model, the wavelength-dependent decay would be expected only for the energy region where the LE state and ICT state overlap. Also, in the pure ICT emission band, the fluorescence decay should be wavelength independent. These predictions are inconsistent with our experimental observations. The data suggest that solvent and/or solute molecule relaxation processes are important in the evolution of the ICT state.

SCHEME

We also observed solvent deuterium isotope effects on the fluorescence decay of the APS system. The decay spectrum at 500 nm for methanol, methanol-d, and methanol-d₄ are shown in Figure 32. Under identical experimental conditions, the APS fluorescence decay is significantly slower upon deuterium substitution of the solvent hydroxy proton. Similar results are also observed in ethanol and propanol. However, with increasing carbon-chain length, the differences between the deuterated and protonated solvents become smaller. A summary of these observations is given in Table 9.

Figure 32. The fluorescence decay of the APS in methanol and deuterated-methanol solutions.

Table 9. Summary of average fluorescence-decay times (τ) for APS in different alcohol and deuterated alcohol solutions. Emission wavelength, λ - 520 nm

Solvent	τ
CH ₃ OH	0.98 ns
CH ₃ OD	1.32 ns
CD ₃ OD	1.38 ns
C ₂ H ₅ OH	1.82 ns
C ₂ H ₅ OD	2.08 ns
C ₂ D ₅ OD	2.22 ns
iso-C ₂ H ₇ OH	3.39 ns
iso-C ₂ D ₇ OD	3.38 ns

The solvent isotope effects on the radiative decay of the ICT state can be explained in terms of the following effects. First, hydrogen bonding between the solvent and excited solute molecule induces radiationless decay. Second, hydrogen bond-breaking and bond-making in solvent-solute molecular clusters results in the fluorescence red shift. Third, the rotational motion of the solvent C-OH bond also causes the spectral evolution. These three effects can be separated by measuring the fluorescence quantum yield and the time-dependent fluorescence Stokes shift. Our steady-state fluorescence data indicate that the main contribution to the isotope effect is through the radiationless internal conversion process.

The strong solvent dependence of the internal conversion rate can be understood as follows. For an electronic transition involving a large energy gap, the high-frequency vibrational modes are expected to dominate the Franck-Condon factors. The internal conversion from the ICT state to the ground state results in vibrational excitation of the high-frequency modes involved in hydrogen bonding, i.e., O-H...O and N-H...O, due to the sudden change in bond lengths. The vibrational modes of the intermolecular hydrogen bonds therefore act as acceptor modes in the radiationless transition between the ICT state and the ground state. Deuteration of the solvent O-H group lowers the vibrational frequency and Franck-Condon overlap for the transition. Therefore, a slower internal conversion rate is observed. Detailed quantitative analyses for these systems are currently being carried out.

The study of the solvation dynamics for ion radicals is more interesting and more difficult. It involves the distance distribution of the cations relative to the geminate electron partners. Transient absorption spectroscopy can be used to probe the existence of the ions and the evolution of the ion-energy states. We are currently constructing a femtosecond laser transient-absorption system which will enable us to probe the solute molecules' response to the short pulse excitation. The experiments with this new laser system will provide detailed information about the solvent relaxation around the ion radical pairs.

The optical design of this femtosecond laser system will be similar to that reported by Kafka and co-workers. The system has a mode-locked Nd:YAG laser, an optical fiber pulse compressor which will shorten the excitation pulse from 100 ps to 3 ps, and an ultrafast dye laser system which will deliver 200-fs output pulses. The dye pulses are then amplified by a three-stage dye amplifier, and the final output pulses will be around 250 fs with a pulse energy of 0.5 mJ. This laser system will be completed later this year and will enable us for the first time to study the solvent relaxation dynamics in non-polar systems.

3. Molecular Dynamics Simulations of the Solvated Electron *C. Romero*

The physical properties of the solvated electron as well as the chemical reactions in which it takes part are strongly affected by the presence of other ions in solution. To investigate these effects, we have extended the scope of our previous molecular dynamics simulations on the hydrated electron to include the presence of cations and anions.

In the first part of this project, we have performed comparative studies at 300 K of the hydration shells of Li^+ , Cl^- , and the hydrated electron using the Toukan and Rahman model of liquid water. All the molecular dynamics simulations of the hydrated electron were carried out in the framework of the Feynman path integral formulation of quantum statistical mechanics.

Figures 33, 34 and 35 show the radial pair correlation functions of Li^+ , Cl^- , and e_{aq}^- with the

Figure 33. Radial pair correlation function, Li^+ -water.

Figure 34. Radial pair correlation function, Cl^- -water.

Figure 35. Radial pair correlation function, e_{aq}^- water.

oxygen and hydrogen atoms of the water molecules surrounding them. In each case, the radial distance is measured from the ion (or center of mass (CM) of the electronic density).

Figure 36 shows the orientation of the solvent molecules surrounding the different solutes as a function of distance. There, the variable theta stands for the angle between the dipole moment of a water molecule and the displacement vector joining the oxygen of that molecule with the position of the ion (or CM of the electron). The lack of structure observed in the pair correlation function of the hydrated electron contrasts with the clearly defined first and second peaks characterizing the Li^+ and Cl^- hydration shells. This difference can be traced back to the quantum fluctuations associated with the electron. Notwithstanding, it is found that the water molecules surrounding the electron are not randomly distributed. In fact, they exhibit a high degree of orientation in the electric field of the electron (Figure 36) which is comparable to that observed in the hydration shells surrounding the Cl^- ion. This result suggests that the fluctuations associated with the dimensions of the cavity trapping the electron are mainly radial. This conclusion supports the idea underlying the method we used before to compute the optical absorption spectrum of the hydrated electron on the basis of an ensemble of spherical potential wells of fluctuating dimensions.

Figure 36. Average value of the cosine of the angle θ between the dipoles of molecules at distance r from the charged solute and the displacement vector pointing from the oxygen atom to the position of the solute.

4. Electron Thermalization in H_2O and D_2O C. D. Jonah

To predict the effect of radiation on materials, it is necessary to understand quantitatively the competition between the geminate recombination of an electron with its geminately produced cation, reactions with solutes in the solution, and diffusion into the bulk. This competition will be dominated by the initial separation of the positive and negative ions. Because the ionization event deposits most of the translational energy into the free electron, it is the electron's motion that will determine the initial spatial distribution between the cation and the electron. Thus, the distance the electron travels prior to thermalization must be determined.

Because one needs to be able to predict the spatial distribution between the geminate ions for many different solvent systems such as water, hydrocarbons, mixed media in the nucleus of a cell, and in phosphate esters employed in nuclear-fuel reprocessing without the necessity of measuring the thermalization distance for each system, a fundamental understanding of the physics of the thermalization process is necessary.

Recently there have been attempts to measure the thermalization distance or initial separation in water and in hydrocarbons. The laser experiments for water have been quite discordant, with different measurements giving estimates of 1 and 10 nm. Measurements of the thermalization distance have also been made in hydrocarbons using both photoionization and radiation for the production of the electron-cation pair. However, more information on more diverse systems is needed. For example, measurements have not been made for the mixed media that are present with the nucleus of a cell or in the phosphorus esters that are often used for nuclear fuel reprocessing.

We have begun to examine the processes by which the electrons are thermalized. Clearly, high-energy electrons transfer energy to the electronic modes of the molecules. This process is expected to be very efficient and thus the electron does not travel far. Once the electron has dropped below the excitation threshold, energy must be transferred to rotational (or librational) and vibrational modes. Experiments where the recombination of e_{aq}^- was determined in

H₂O, D₂O, and HDO strongly suggest that the asymmetric stretching mode of the water molecule is important in the thermalization mechanism. These measurements also suggest that the high-energy electrons transfer their energy efficiently and in a short distance to the electronic modes.

Now that experimental data exist, theories need to be developed. These theories first must predict the present experimental data, and eventually they must be able to predict thermalization distances in different solvents. A group at Université of Sherbrooke has recently published a theoretical calculation for the electron-thermalization distance. Unfortunately, those authors did not compare their results critically with present experimental data.

Pulse radiolysis experiments can provide a very sensitive test for predicted thermalization distances. By using data for the decay of the hydrated electron and the OH radical and the long-time yields of the hydrated electron, the OH radical and hydrogen peroxide, we can assess the accuracy of the calculated electron thermalization distances. This is done by using the calculated thermalization distance of the electron to create an initial electron distribution and simulating the chemical consequences of this distribution. This simulation was done using an inhomogeneous diffusion kinetics code. Because we expected (as turned out to be true) that the calculated electron-thermalization distance was too large (which would mean that the reaction would be too slow and diffusion to the bulk of the solution would be too large), we chose a calculational technique that would

overemphasize the amount of reaction. Thus, if the amount of reaction is found to be too small, we know that a more exact simulation would show even less reaction. To quantify approximately the amount that these simulations would overestimate the amount of reaction, we used a second technique, labelled "with depletion" in Table 10. We expected that that technique would possibly slightly underestimate the recombination reaction.

The results for these simulations are given in Table 10 for several different parameter sets. Different distributions for OH, initial OH numbers, and hydrated electron concentrations were used. If one looks at the final electron concentrations, $c_{\infty}(e_{aq}^-)$, we see that these are all too high. This is a characteristic of a distance which is too large — too many electrons escape into the solution. We can get better agreement with $c_{\infty}(e_{aq}^-)$ if we expand the OH distribution (parameter set 2). However this expansion sharply increases the yield of $c_{\infty}(OH)$ to a value above the experimental value and sharply decreases the hydrogen-peroxide yield. Other parameter sets show similar effects. Note that the electron parameters are virtually unaffected by the inclusion of depletion.

From the results of these calculations, it is clear that adjustment of parameters to improve the agreement with a specific experimental result makes the agreement with other experimental results worse. In general, one observes that the yield of the electron is much larger than the experimental data, strongly suggesting that the predicted distance for the electron thermalization must be too large.

Table 10. Spur decay calculations assuming $G(\text{initial})$ of e_{aq}^- is 4.8.

Conditions	$c_{\infty}(e_{aq}^-)$	$t_{1/2}(e_{aq}^-)$, ns	$c_{\infty}(OH)$	$t_{1/2}(OH)$, ns	$c_{\infty}(H_2O_2)$
Experimental	2.8	2	3.3	2	.7-.8
Parameter set 1	3.7	0.85	2.4	0.21	0.67
with depletion	3.7	.81	3.0	0.26	0.38
Parameter set 2	3.3	1.43	3.8	1.68	0.49
with depletion	3.34	1.43	4.06	1.68	0.35
Parameter set 3	3.5	0.81	2.94	0.15	1.01
with depletion	3.5	0.81	3.5	0.15	0.69
Parameter set 4	3.5	1.12	3.9	1.	0.56
with depletion	3.6	0.91	4.32	1.01	0.35

Clearly, new types of calculations must be devised to predict the physical basis for thermalization. Our earlier measurements suggest that the vibrational modes are highly important in the

thermalization process. These suggestions will facilitate the development of new formalisms, including quantum calculations, for the determination of thermalization lengths.

II. ACCELERATOR ACTIVITIES

C. D. Jonah, B. E. Clift, G. L. Cox, D. T. Ficht, R. H. Lowers, A. C. Youngs, D. West

The Chemistry Division maintains and operates three accelerators: a 20-MeV electron linear accelerator (linac), a 3-MeV Van de Graaff accelerator, and a 60-inch cyclotron. Although these accelerators are used primarily by personnel of the Chemistry Division,

A. 20-MeV Linac

C. D. Jonah, B. E. Clift, G. L. Cox, D. T. Ficht

The major development in the last year was the development and implementation of a computer-monitoring system. Because the compressed pulse (described below) is highly sensitive to both phase and power of the RF fed to the waveguides, it is necessary to know and control these parameters accurately. Circuits were designed and built to measure the phase of the 1.3-GHz RF signal from the waveguides, compensate for the ringing of the cavities and hold these 12 signals for digitization in less than 1 μ s. The computer system then checks these signals against previous reference measurements and gives a warning if any have drifted from desired positions or if they have become noisy.

A second monitoring system, which runs concurrently, checks the 64 parameters of the transport system. These modifications have enabled us to eliminate power supplies which drift and to detect failures or oscillations of other power supplies.

The current and pulse length of this machine are ideally suited for radiation-chemical studies because both short pulses and high power are available. Using the subharmonic buncher system, it is possible to obtain a 30-ps, 30-nC pulse or, with the pulse-compression system, a 5-ps pulse with 6-nC. Pulses from 4 to 100 ns are available with about 15-A peak current when the machine is used in the transient mode. In the steady-state mode, pulse widths from 0.5-9 μ s are available with peak currents of 1.2 A. The energy, 20 MeV in the transient mode and 15 MeV in the steady-state mode, is sufficiently high so that the beam will penetrate cell windows or even the walls of

they are also used by other ANL groups and groups from outside the laboratory. Recent improvements of these accelerators are discussed in this section; their use in the scientific programs is detailed in the earlier sections of this Survey.

an oven, but not so high that nuclear activation is a major problem.

The chemical studies that are being conducted with the linac as an excitation source include probing the transfer of kinetic energy from an epithermal electron to chemical potential energy of reactive species. Results in Section I describe the first experiments to make use of the 5-ps pulse. The linac can create unusual short-lived molecules. Electron-transfer reactions can be initiated by using the linac. Unusual oxidation states of many metals can also be created with the linac.

The machine is also used by several groups of high-energy physicists. High-bandwidth detectors can be tested by using the short linac pulses. This allows the study of fast beam monitors. Cavity prototypes for the new Advanced Photon Source have been tested using the linac. These experiments are critical to the success of that machine because the eddy currents induced by the positron beam as it goes through the chambers will lead to the premature loss of ring current and thus light. The Wake-Field design group in the ANL High Energy Physics Division is using the machine to do feasibility tests for a new type of accelerator.

B. 3-MeV Van de Graaff Accelerator

R. H. Lowers, A. C. Youngs, D. Werst

The 3-MeV Van de Graaff accelerator supports the magnetic-resonance studies that have been discussed above. The machine can provide 1-ns to 10- μ sec pulses of electrons or protons. The low

noise of the machine makes it ideal for studying radical processes via magnetic resonance and fluorescence-detected magnetic-resonance techniques.

PUBLICATIONS

UNIFICATION OF ELECTRON SCAVENGING AND FLUORESCENCE QUENCHING RESULTS IN CYCLOHEXANE RADIOLYSIS - EVIDENCE FOR THE IMPORTANCE OF EXCITED IONS

C. D. Jonah and M. C. Sauer, Jr.

Radiat. Phys. Chem. 34, 497-501 (1989)

THE GAS-PHASE REACTIONS OF HYDROXYL RADICALS WITH SEVERAL UNSATURATED HYDROCARBONS AT ATMOSPHERE PRESSURE

A. Liu*, C. D. Jonah, and W. A. Mulac

Int. J. Radiat. Chem. 34, 687-691 (1989)

THE PHOTODECOMPOSITION OF ALKANE RADICAL CATIONS IN FREON MATRICES: AN EPR STUDY

B.-E. Brauer*, X. Li*, and A. D. Trifunac

Radiat. Phys. Chem. 34, 849-852 (1989)

PROTON TRANSFER IN ALKANE RADICAL CATIONS. FDMR PULSE RADIOLYSIS STUDY

A. D. Trifunac, D. W. Werst, and L. T. Percy*

Radiat. Phys. Chem. 34, 547-552 (1989)

QUANTUM YIELDS OF PHOTOIONIZATION IN THE 308-nm TWO-PHOTON IONIZATION OF SOLUTES IN HYDROCARBON SOLUTIONS AND THEIR RELATIONSHIP TO THE OBSERVED CONDUCTIVITY SIGNALS

K. H. Schmidt, M. C. Sauer, Jr., Y. Lu*, and A. Liu*

J. Phys. Chem. 94, 244-251 (1990)

THE FATE OF ALKANE RADICAL CATIONS IN LIQUID AND SOLID HYDROCARBONS. TIME-RESOLVED FLUORESCENCE DETECTED MAGNETIC RESONANCE

D. W. Werst, M. G. Bakker*, and A. D. Trifunac

J. Am. Chem. Soc. 112, 40-50 (1990)

²B₂: THE GROUND STATE OF THE HEXAMETHYL(DEWAR BENZENE) RADICAL CATION. TIME-RESOLVED FLUORESCENCE DETECTED MAGNETIC RESONANCE

X.-Z. Qin*, D. W. Werst, and A. D. Trifunac

J. Am. Chem. Soc. 112, 2026-2027 (1990)

RADIOLYTIC GENERATION OF RADICAL CATIONS IN XENON MATRICES. TETRAMETHYLCYCLOPROPANE RADICAL CATION AND ITS TRANSFORMATIONS

X.-Z. Qin* and A. D. Trifunac

J. Phys. Chem. 94, 3188-3192 (1990)

RADIOLYTIC GENERATION OF ORGANIC RADICAL CATIONS IN ZEOLITE Na-Y

X.-Z. Qin* and A. D. Trifunac

J. Phys. Chem. 94, 4751-4754 (1990)

**ISOMERIZATION OF THE CUBANE RADICAL CATION TO THE BRIDGED 1,4-BISHOMOBENZENE
(BICYCLO[3.3.0]OCTA-2,6-DIENE-4,8-DIYL) RADICAL CATION**

X.-Z. Qin*, A. D. Trifunac, P. E. Eaton*, and Y. Xiong*

J. Am. Chem. Soc. Comm. 112, 4565-4567 (1990)

XENON MATRIX AND ZEOLITE Na-Y. TWO METHODS FOR STUDY OF RADICAL CATIONS

A. D. Trifunac and X.-Z. Qin*

Appl. Mag. Reson. 1, 29-40 (1990)

**H/D ISOTOPE EFFECTS IN WATER RADIOLYSIS II. DISSOCIATION OF ELECTRONICALLY EXCITED
WATER**

P. Han* and D. M. Bartels

J. Phys. Chem. 94, 5824-5833 (1990)

EARLY PROCESSES IN LIQUIDS

M. C. Sauer, Jr. and C. D. Jonah

chapter, Pulse Radiolysis, Editor, Y. Tabata, CRC Press: Boca Raton, FL, 1990

TIME-RESOLVED MAGNETIC RESONANCE STUDY

A. D. Trifunac, D. M. Bartels, D. W. Werst

chapter, Pulse Radiolysis, Editor, Y. Tabata, CRC Press: Boca Raton, FL, 1990

THE MECHANISM OF ELECTRON THERMALIZATION IN H₂O, D₂O AND HDO

C. D. Jonah and A. C. Chernovitz*

Can. J. Chem. 68, 935 (1990)

SUBMISSIONS

STUDY OF RADICAL CATIONS BY TIME-RESOLVED MAGNETIC RESONANCE

A. D. Trifunac and D. W. Werst

Ionic Molecular Systems, Kluwer Academic Publishers (1990)

REEVALUATION OF ARRHENIUS PARAMETERS FOR $H^\bullet$ AND $OH^\bullet \rightarrow (e^-)_{aq} + H_2O$ AND THE ENTHALPY AND ENTROPY OF HYDRATED ELECTRONS

P. Han* and D. M. Bartels

J. Phys. Chem. (1989)

SUBEXCITATION ELECTRON INTERACTIONS IN RARE GASES: PRODUCTION OF ELECTRONIC EXCITED STATES IN HELIUM OR NEON MIXTURES WITH ARGON, KRYPTON OR XENON

R. Cooper* and M. C. Sauer, Jr.

Radiat. Phys. Chem. (1989)

PRIMARY EVENTS IN HYDROCARBON RADIOLYSIS: REAL-TIME STUDIES OF RADICAL-CATION CHEMISTRY

M. C. Sauer, Jr., D. W. Werst, C. D. Jonah, and A. D. Trifunac

Rad. Phys. Chem. (1990)

TIME RESOLVED MEASUREMENT OF G-VALUES OF SOLUTE EXCITED STATES IN CYCLOHEXANE AND n-HEXANE

C. D. Jonah, M. C. Sauer, Jr., and R. Cooper*

J. Phys. Chem. (1990)

STUDY OF THE REACTIONS OF GEMINATE IONS IN IRRADIATED SCINTILLATOR, HYDROCARBON SOLUTIONS USING RECOMBINATION FLUORESCENCE AND STOCHASTIC SIMULATIONS

M. C. Sauer, Jr., C. D. Jonah, and C. A. Naleway*

J. Phys. Chem. (1990)

EFFECT OF ION PAIRING ON ELECTRON SCAVENGING AND SOLVATED ELECTRON YIELD ENHANCEMENT IN METHANOL: A COMPARISON BETWEEN PULSE RADIOLYSIS AND POSITRON LIFETIME SPECTROSCOPY DATA

G. Duplaire* and C. D. Jonah

J. Phys. Chem. (1990)

RADICAL IONS IN CONDENSED PHASE PRODUCED BY TWO PHOTON IONIZATION; A STUDY OF GEMINATE RECOMBINATION BY FLUORESCENCE DETECTED MAGNETIC RESONANCE (FDMR)

M. G. Bakker* and A. D. Trifunac

J. Phys. Chem. (1990)

TRANSIENT ALKYLAMINIUM RADICALS IN n-HEXANE. CONDENSED PHASE ION-MOLECULE REACTIONS

D. W. Werst and A. D. Trifunac
J. Phys. Chem. (1990)

CUBANE RADICAL CATION IN LIQUID HYDROCARBONS: TIME-RESOLVED FLUORESCENCE DETECTED MAGNETIC RESONANCE STUDY

X.-Z. Qin*, A. D. Trifunac, P. E. Eaton*, and Y. Xiong*
J. Am. Chem. Soc. Comm. (1990)

PULSE RADIOLYSIS OF $\text{Cr}(\text{CO})_6$ AND $\text{W}(\text{CO})_6$ IN ALKANE SOLUTION

M. M. Glezen and C. D. Jonah
J. Phys. Chem. (1990)

PHOTODISSOCIATION OF HEXAARYLBIIIMIDAZOLE. 1. TRIPLET STATE FORMATION

X.-Z. Qin, A. Liu, A. D. Trifunac, V. V. Krongauz
J. Phys. Chem. (1990)

OTHER PRESENTATIONS

Picosecond Pulse Radiolysis of Alkane Liquids: Recent Insights into the Chemistry of Cations

Myran C. Sauer, Jr.

Argonne National Laboratory Chemistry Division Monday Morning Seminar

December 11, 1989

Alkane Radical Cations: Observations and Reactions

A. D. Trifunac, invited talk

University of Minnesota, Minneapolis, Minnesota

March 26, 1990

Solvated Electron Thermodynamics

David M. Bartels

Argonne National Laboratory Radiation Research Seminar

March 28, 1990

Early Events in Radiation Chemistry of Hydrocarbons

A. D. Trifunac, invited talk

Faculty of Medicine, Department of Nuclear Medicine, University of Sherbrooke, Sherbrooke, Quebec, Canada

May 16, 1990

Structure and Rearrangement of the Cubane Radical Cation

X.-Z. Qin and A. D. Trifunac

Gordon Conference on Radical Ions, Wolfeboro, New Hampshire

June 25-29, 1990

Radiolytic Generation and Stabilization of Reactive Hydrocarbon Radical Cations in Zeolite Na-Y

X.-Z. Qin and A. D. Trifunac

Poster, Gordon Conference on Radical Ions, Wolfeboro, New Hampshire

June 25-29, 1990

Radical Ions in Condensed Phase Produced by Resonant Two-Photon Ionization: A Study of Geminate Recombination by Fluorescence Detected Magnetic Resonance (FDMR)

M. G. Bakker and A. D. Trifunac

Poster, Gordon Conference on Radiation Chemistry, Providence, Rhode Island

July 8-13, 1990

Studies of Geminate Recombination by Fluorescence Detected Magnetic Resonance (FDMR)

M. G. Bakker and A. D. Trifunac, invited talk

University of Alabama, Tuscaloosa, Alabama

July 2, 1990

H and D Atom Diffusion in Ice

D. M. Bartels, invited talk

Gordon Conference on Radiation Chemistry, Providence, Rhode Island

July 8-13, 1990

Experimental Facts on the Hydrated Electron

C. D. Jonah, invited talk

Gordon Conference on Radiation Chemistry, Providence, Rhode Island

July 8-13, 1990

Radical Cation Transformations in Condensed Phase Radiolysis. The Fate of the Solvent Holes

D. W. Werst, invited talk

Gordon Conference on Radiation Chemistry, Providence, Rhode Island

July 8-13, 1990

Radical Ions in Condensed Phase Produced by 2-Photon Ionization. A Study of Geminate Recombination by Fluorescence Detected Magnetic Resonance (FDMR)

M. G. Bakker and A. D. Trifunac

Poster, Gordon Conference on Radiation Chemistry, Providence, Rhode Island

July 8-13, 1990

Pulse Radiolysis of Cr(CO)₆ and W(CO)₆ in Alkane Solution

M. M. Glezen and C. D. Jonah

Poster, Gordon Conference on Radiation Chemistry, Providence, Rhode Island

July 8-13, 1990

Radiolytic Generation and Stabilization of Reactive Hydrocarbon Radical Cations in Zeolite Na-Y

A. D. Trifunac and X.-Z. Qin

Poster, Gordon Conference on Radiation Chemistry, Providence, Rhode Island

July 8-13, 1990

Reevaluation of Arrhenius Parameters for $H + OH^{\cdot-} \rightarrow e_{aq}^{\cdot-} + H_2O$ and the Enthalpy and Entropy of Hydrated Electrons

Ping Han and D. M. Bartels

Poster, Gordon Conference on Radiation Chemistry, Providence, Rhode Island

July 8-13, 1990

Structure and Rearrangement of the Cubane Radical Cation

X.-Z. Qin and A. D. Trifunac

Poster, Gordon Conference on Radiation Chemistry, Providence, Rhode Island

July 8-13, 1990

Cubane Radical Cation Fluorescence Detected Magnetic Resonance Study

X.-Z. Qin and A. D. Trifunac

Poster, Gordon Conference on Radiation Chemistry, Providence, Rhode Island

July 8-13, 1990

Recombination Fluorescence: Kinetics and G-Values

M. C. Sauer, Jr., C. D. Jonah, C. A. Naleway and R. Cooper

Poster, Gordon Conference on Radiation Chemistry, Providence, Rhode Island

July 8-13, 1990

Reevaluation of Hydrated Electron Thermodynamic Properties

D. M. Bartels

Solvated Electron 25 Years After, Argonne National Laboratory

July 16-18, 1990

Observations of the Solvated Electron by Fluorescence Detected Magnetic Resonance (FDMR)

M. G. Bakker, L. T. Percy and A. D. Trifunac

Poster, Solvated Electron 25 Years After, Argonne National Laboratory

July 16-18, 1990

Pulse Radiolysis of Cr(CO)₆ and W(CO)₆ in Alkane Solution

M. M. Glezen and C. D. Jonah

Poster, Solvated Electron 25 Years After, Argonne National Laboratory

July 16-18, 1990

Arrhenius Parameters for $H^+ + OH^- \rightarrow (e^-)_{aq} + H_2O$ and the Enthalpy and Entropy of Hydrated Electrons

P. Han and K. H. Schmidt

Poster, Solvated Electron 25 Years After, Argonne National Laboratory

July 16-18, 1990

Solvation Shells of the Hydrated Electron on the Classical Ions Li^+ and Cl^- from MD Simulations

Claudio Romero

Poster, Solvated Electron 25 Years After, Argonne National Laboratory

July 16-18, 1990

Electron Reactions in Irradiated Media

C. D. Jonah, invited talk

Gordon Conference on Water and Aqueous Solutions, Plymouth, NH

July 29-August 3, 1990

Reevaluation of Arrhenius Parameters for $H + OH^- \rightarrow e^-_{aq} + H_2O$ and the Enthalpy and Entropy of Hydrated Electrons

Ping Han and D. M. Bartels

Poster, Gordon Conference on Water and Aqueous Solutions, Plymouth, NH

July 29-August 3, 1990

Studies of Geminate Recombination by Fluorescence Detected Magnetic Resonance (FDMR)

M. G. Bakker and A. D. Trifunac

Invited Talk, Notre Dame Radiation Laboratory, Notre Dame, IN

August 9, 1990

Radical Ions in Photoionization

A. D. Trifunac, M. G. Bakker, invited talk

Sixth Interdisciplinary Laser Science Conference of the American Physical Society; Minneapolis, Minnesota

September 16-19, 1990

Early Events in Radiolysis: Radical Cation Reactions

A. D. Trifunac, invited talk (opening lecture)

5th Working Meeting on Radiation Interaction; Leipzig, DDR

September 24-28, 1990

Two-Photon Ionization in Hydrocarbons: Charge Pair Dynamics

Klaus H. Schmidt

Argonne National Laboratory Chemistry Division Monday Morning Seminar

October 1, 1990

Radiolytic Generation of Organic Radical Cations in Zeolite Na-Y

X. -Z. Qin and A. D. Trifunac

1990 Amoco/University Poster Session; Naperville, Illinois

October 5, 1990

Studies of Geminate Recombination by Fluorescence Detected Magnetic Resonance (FDMR)

M. G. Bakker and A. D. Trifunac, invited talk

22nd Southeast Regional Magnetic Resonance Conference, Tuscaloosa, Alabama,

October 12, 1990

Time-Domain Studies of Radical Ions Using Fluorescence Detection

A. D. Trifunac

Invited Seminar, Department of Chemistry, University of Tennessee, Knoxville, Tennessee

October 18, 1990

SEMINARS

Dr. Thomas Scott, Corporate Research, Exxon Research & Engineering Co.

"Picosecond Chemical Relaxations in Liquid Surface and Solid State Materials: The Influence of Local Relaxation Environments on Ultrafast Rate Processes"

October 30, 1989

Professor Paul Percival, Department of Chemistry, Simon Fraser University, Vancouver, British Columbia, Canada

"Intramolecular Motion in Organic Free Radicals Studied by Muon-Spin Rotation and Level-Crossing Spectroscopy"

November 6, 1989

Dr. Vadim Krongauz, E. I. du Pont de Nemours and Co. Inc., Wilmington, DE

"Polymerization Kinetics in Photopolymer Films"

January 29, 1990

Professor You-Cheng Liu, Lanzhou University, People's Republic of China

"The Radical Intermediates and Micellar Effect in the Reduction of Nitroxides by Ascorbic Acid"

June 14, 1990

Professor Yuri Molin, Academy of Sciences, Novosibirsk, USSR

"Optically Detected EPR Spectra of Radical Ion Pairs"

July 5, 1990

Professor Oleg Anisimov, Academy of Sciences, Novosibirsk, USSR

"Quantum Beats in Radical Ion Pair Recombinations"

July 6, 1990

Dr. Paul Krusic, E. I. du Pont de Nemours and Co. Inc., Wilmington, Delaware

"ESR Studies of Organic Triplets and Biradicals Relevant to the Design of Molecular Ferromagnets"

November 12, 1990