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PICOSECOND PULSE RADIOLYSIS STUDIES TO UNDERSTAND THE PRIMARY PROCESSES IN RADIOLYSIS*

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Abstract

The use of pulse radiolysis to learn about processes which occur before the beginning of chemical times is discussed. Two examples, the distance distribution of positive and negative ions in hydrocarbons, and the state of the "dry electron" are discussed in detail.

Introduction

Much of the work in the radiation chemistry group at Argonne has been devoted to the understanding of the primary processes of energy deposition. The initial physics is well understood; however the interface between chemistry and physics is imperfectly understood[1]. Since the Born approximation breaks down at low energies, the physics is presently intractable and chemical measurements do not exist for such short times. It is these phenomena that we at Argonne are trying to understand. Very few complex systems have been studied in great detail - the aqueous system has been thoroughly studied and simple hydrocarbons have been less thoroughly studied. However much of what can be said about these systems is solely empirical; the fundamental chemistry and physics of the primary processes, which include reaction of electron precursors, distribution of geminate ions and the competition between reaction and solvation are unknown and so it is not possible to extrapolate to new systems, such as high-concentration protein systems, which are important in biological systems, or tri-butyl phosphate systems, which are important in nuclear fuel reprocessing. If the fundamental parameters which govern the transition from physics to chemistry were known, extrapolation to new systems would be more meaningful than that presently possible[2].

While our primary goal has been to understand the initial processes in radiation chemistry, the properties and reactivities of unusual species can also be studied. Thus, unstable ionic species in polar media and new species in hydrocarbon solvents can be determined. Also new and interesting processes can be found - for instance, we have recently submitted a paper which has suggested a new mechanism for high mobilities in hydrocarbons[3]. This proposal attempts to explain fast fluorescence, fast absorption and fast ESR measurements. We are not limiting ourselves to primary processes; we have also tried to understand the new and novel chemistry that comes at early times.

The primary processes in radiation chemistry can be described as follows: 1) The ionizing particle carries out the primary ionization and forms excited states. The electrons created by the ionizing particle often have fairly high energies. The excited state can also autoionize and create more

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electrons. 2) The electron will give up energy to the solvent. During this time the electron will translate in the solvent. The electron can also react with species in the solvent, either solutes which have been added or species that have been created by the electron beam. While most of the energy will be lost in this step, the energy loss process is highly efficient and may be faster than the following step where very little energy is lost. 3) The electron is thermalized. This step has been separated from the previous step because, while the energy range is small, this step may take a considerable number of collisions since the cross-sections for transferring energy to rotational and vibrational modes of the solvent are small. During this step, the electron may move through the solvent and can react with species within the solution, as was described above. The reaction may compete with the following step. 4) If there is a sufficiently strong dipole, either molecular or inducible, the electron will become localized within the solvent. During this step there will be the possibility of reaction as well as the possibility of electron reorganization that leads to the next step 5) of solvation. 6) Once the electron is in its most stable configuration in the solvent, reaction can occur with other species created by the ionization event[4],[5]. The time required for these reactions will give information about how far the electron has traveled, and what sort of scattering cross-sections are appropriate to explain the distribution of distances. 7) Finally reaction can occur with other species within the solution, possibly giving rise to time-dependent rate constants[6].

While it would be ideal to study all of these processes in a given solvent, this is not possible at present. For instance, it is difficult to determine distance distribution in polar media – the lack of the coulombic attractive potential means that the recombination time is controlled by a diffusive process and thus is not a strong function of distance; in nonpolar media the data are much easier to interpret[5]. If one tries to understand the reactions of the electron precursor, the so-called "dry electron"[7], it is necessary that the recombination kinetics be considerably slower than solvation times and observation times, something that is true in polar media, but not in nonpolar media.

We will discuss the determination of ion-recombination times in nonpolar media, showing how we have assigned the absorption spectra. We will then discuss what can be derived from the "dry electron" reaction; the mobility of that species and its possible importance.

Experimental

The experimental system that was used has been well-described in the literature and thus a detailed description will not be given here[8],[9]. The system uses the basic pump-probe technique first suggested for pulse radiolysis by John Hunt[10], in which the probe light comes from Cerenkov light generated by the electron beam. The total dose that is deposited in the irradiation cell is approximately 8 krad, sufficient to give 70% absorption for the hydrated electron at 600 nm. The pulse width is approximately 25 ps – the width is limited by space charge broadening. This limitation is

not serious in our system, since this is approximately equal to the differ-ence in time it takes a light pulse and an electron pulse to traverse a 2 cm cell - 18 ps. Measurements are limited to the range of 250-750 nm at pres-ent. Short wavelengths are difficult because of the many reflections that the probe beam makes.

Results- Positive Ions

In figure 1 we show the decay of the absorption in n-hexane at 600 nm in the presence of an electron scavenger[9]. As the concentration of the electron scavenger is increased, the amount of absorption increases and the amount of decay decreases. This is consistent with the idea that the posi-tive ion is being observed. At low concentrations of electron scavengers, there is some decrease in the initial absorption; this decrease is probably due to the weak absorption of the electron in n-hexane at 600 nm.

To show that this description of the system is reasonable, it is neces-sary to show that we are looking at the same species. Since the absorption spectra are very diffuse, this is difficult to show unambiguously. In fig-ure 2 we show the absorption of the electron from 450 - 750 nm in n-hexane. Note that the spectra at late times in n-hexane are in exact agree-ment with the absorption seen in the presence of ethyl bromide and similar to the absorption seen in the pure n-hexane at the earliest times. This similarity strongly suggests that we are observing the same species in the presence and absence of electron scavengers and thus are observing a posi-tive ion in the solution.
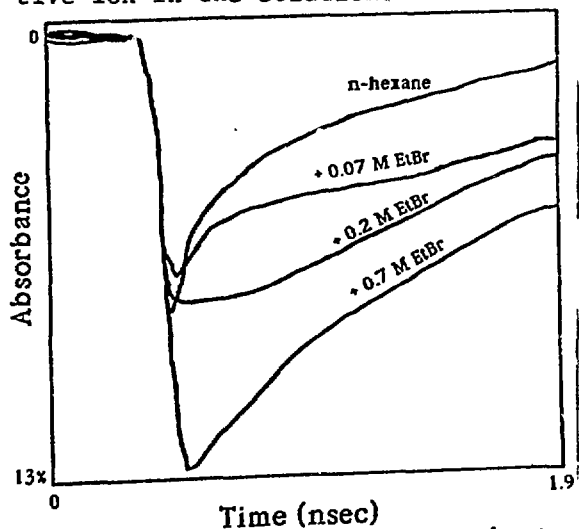

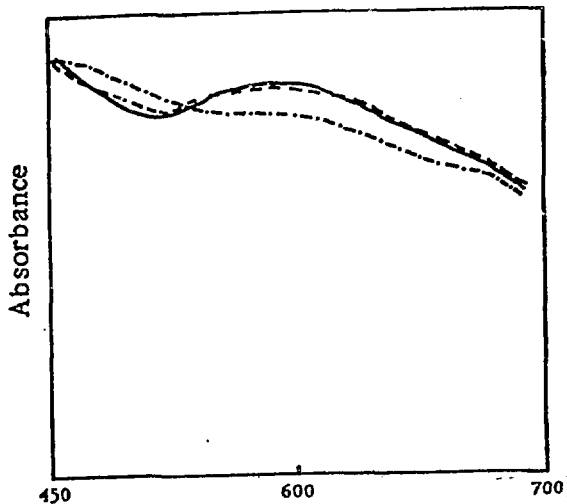Fig. 1. Absorbance at 600 nm in n-hexane, and in solutions of ethyl bromide in n-hexane.

Fig. 2. Spectrum of n-hexane and n-hexane in the presence of ethyl bro-mide ── neat n-hexane 50 ps after pulse. Full scale absorbance is .05 absorbance units. ── as above, but 500 ps after pulse. Full scale ab-sorbance is .02. ─·─ n-hexane + .7 M ethyl bromide at 50 ps after the pulse. Full scale absorbance is .08.

To derive the distance distribution, it is necessary to make certain corrections to the observed data. The major interference that we find in our experiment comes from the transient absorption created in the quartz windows by the electron beam. The amount of this correction is determined by making measurements in 4 M perchloric acid in water. The assumption is made that the only source of absorption after about 100 psec is due to the quartz windows. The magnitude of this correction has been confirmed by measuring the absorption of a 1 cm block of quartz.

The results are displayed in figure 3. The inferred decay curve is very similar to that determined by Warman and coworkers[5] and Tabata and coworkers[11]. Those groups slowed the kinetic processes by scavenging the electron using an aromatic molecule and then watching the decay of the absorbance. These groups have analyzed their data based on theoretical treatments of the expected geminate reactions[12],[13].

This short discussion shows how information about the initial distribution of electron distances can be deduced from measurements made at longer times. Since the major driving force for understanding these distributions come from the radiation physicists, eventually these measurements must be transformed to water. This is a nontrivial problem and will be left as an exercise to the reader.
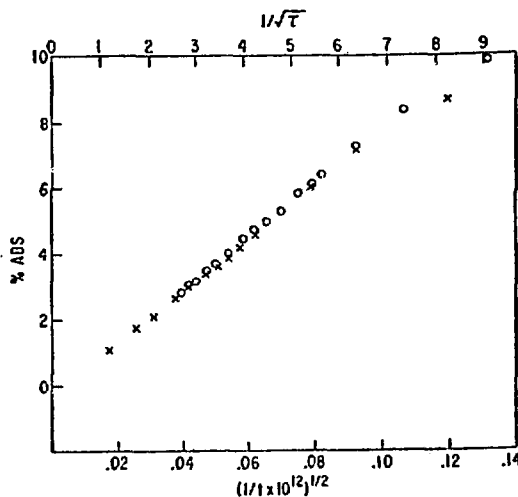

Fig. 3. Plot of absorption vs. reciprocal square root of time. $\tau = Dt/r_c^2$. X's and O's are for two different experiments on different time scales.

Results – "Dry Electron Studies"

Information about the precursor of the solvated electron has the potential of giving information about the way an electron loses energy. For instance, if one can show unambiguously that the electron precursor, if it is to react, must have an energy E, then it is clear that the electron must spend some time in that energy state. Bill Hamill first proposed that the precursor of the electron might react[7], named that species the "dry electron", and began studies of that system[14]. Studies followed by John Hunt[15], the Argonne group[16], and Gordon Freeman[17]. After a proposal by Mogensen[18], positronium chemists including Byakov[19] and the Strasbourg group[20] used positronium inhibition to gain information about the precursor of the electron. There is one major problem with the original proposal by Hamill, and that was that he named the precursor the "dry electron", a name which implies something about the state of the electron. Physicists seem to be better read than chemists – they name things out of Lewis Carroll or James Joyce. However to avoid confusion I shall refer to the electron precursor as the dry electron, since "dry electron" is more common and catchier.

The experiments described here are unique in that they are the first which allow an observation of spectral relaxation and dry electron reaction at the same time. The experiments were carried out in 1-propanol; 1-propanol was used since it remains a liquid over a wide temperature range. The measurements that will be discussed here were all made at -60C. At this temperature, the electron is solvated in about 500 psec; over this time scale the spectrum shifts to the blue. C_{37} values (the concentration of scavenger necessary to reduce the initial yield of the electron to 1/e of its initial value)[15] have been determined for a series of compounds. In general the C_{37} is about .6-.7 of the value at room temperature; in other words, reaction with the dry electron is more efficient at low temperatures than at room temperatures. This is similar to the conclusions of Hamill[21] but in contradiction to the results of Hunt[22].

Figure 4 shows the measured kinetic traces for acetone in 1-propanol at -60C. Note that the form of the trace in the presence and absence of acetone is virtually identical; the amount of the electron in the presence of acetone is only .75 of that in the absence of the electron. It appears as if any electrons which are initially formed, will then be solvated. In contrast, figure 5 shows the kinetic behavior in perchloric acid. The initial step for all concentrations of the perchloric acid are the same. However, some of the electrons will then react with the perchloric acid.
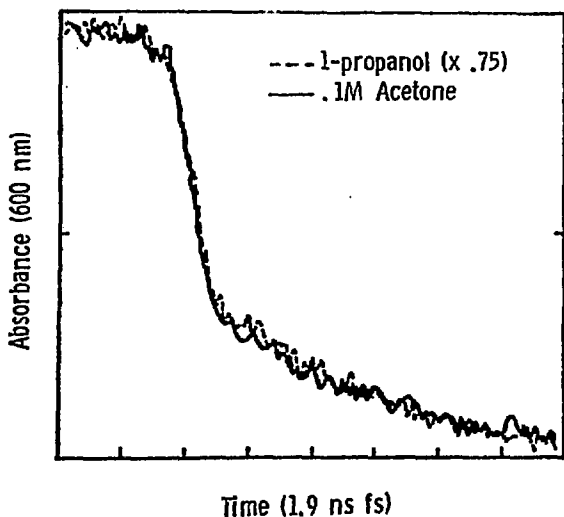
Acetone in 1-Propanol (-58C)

Fig. 4. Absorbance of the electron in 1-propanol at -60C in the presence of acetone. Absorbance is at 600 nm. The signal in the absence of acetone was multiplied by .75 to get the two curves to overlap.
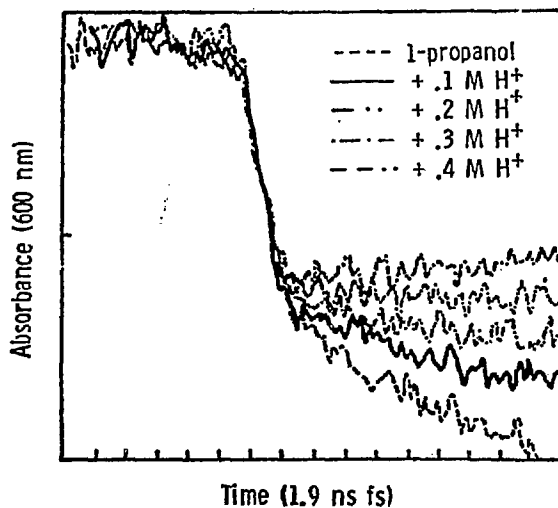
H^+ in 1-Propanol (-58C)

Fig. 5. Absorbance of the electron in 1-propanol at -60C in the presence of $HClO_4$. Measurement is at 600 nm.

The underlying reason for this difference in behavior seems to depend on whether the dry electron can react with the particular scavenger molecule. A simple explanation for these effects can be seen by looking at figure 6. In the top portion of the figure, it is assumed that there is a dry electron reaction and any nearby scavenger molecule will react with it. If there is no

scavenger molecule nearby, the dry electron will be solvated (as in the bottom portion of the figure). For the *acetone solution*, where there is a dry electron reaction, there will be no scavenger immediately nearby to react with the solvated electron, hence, no reaction. However, for perchloric acid, there is no dry electron reaction (as can be inferred from the constancy of the initial step) and thus solvated electrons can be formed which have near by scavengers and which can
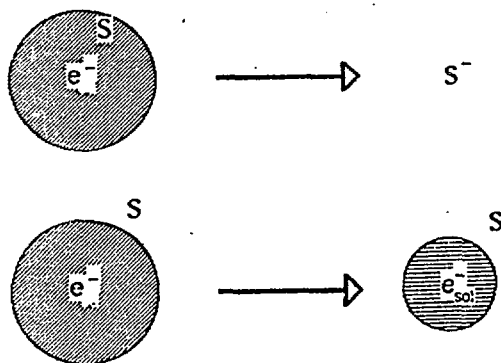

Fig. 6. Symbolic portrayal of precursor events. See text for discussion.

react without having to diffuse a long distance. This then explains why we see reaction for perchloric acid and not for acetone. It should be pointed out that the rate of the solvated electron with both scavengers are comparable.

Further information can be derived about the state of the reacting dry electron from these experiments. It must not be quasi-free and it does not have a very large mobility. If the mobility were large, there would be little correlation between the region in which the electron could react and the place in which it solvates. Since, as we saw above, there is a strong correlation between the reacting region and the region in which the electron solvates, the electron can not be highly mobile.

These experiments are continuing and will be made at different temperatures. Correlations between dry electron reactivity at room temperature and at low temperature are being made. From these correlations we hope to learn more about the dry electron reactivity. The ultimate goal is a fuller understanding of the initial processes of radiation chemistry. We have begun a program to try to model the solvation process using a mixture of quantum mechanical and classical mechanical techniques[23]. Using these techniques, formation of F centers in molten salts have been studied and we feel that these studies can give us new models and new ways of understanding the early radiation-chemical processes.

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