Picosecond Observations of Some Ionic and Excited-State Processes in Liquids

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The design of a pulse radiolysis system for absorption and emission spectroscopy with a response down to 60 psec is described. Events which occur with response times of about 10 psec may also be observed by observing the development of these species during the radiation pulse. The system has been used to investigate the mode of formation of solute excited states in cyclohexane, the benzene excimer in pure benzene, and the rate of formation of solvated electrons in ethanol and 1-propanol. The data show that the excited singlet state of cyclohexane is formed rapidly (<10 psec) in radiolysis, and has a decay constant of 3.6×10^9 sec^{-1}. The state transfers energy to added solutes such as benzene, with $k = 2.2 \times 10^{11}$ M^{-1} sec^{-1}; CCl_4, $k = 2.5 \times 10^{11}$ M^{-1} sec^{-1}; and 9,10-diphenylanthracene, $k = 3.4 \times 10^{11}$ M^{-1} sec^{-1}. No significant yield of the triplet state of the aromatic solutes is observed in pseconds contrary to the large yields of triplets observed in nseconds. The anions and cations of the aromatic solutes are also observed, and exhibit rapid formation but little decay in pseconds. The excimer state of benzene is observed to appear with a delay of 10 psec, and this is considered to be the result of prior formation of the monomer singlet followed by the complexing time which is calculated to be 7 psec. The solvated electron in ethanol is formed rapidly but with a possible delay of 2–5 psec, while the solvated electron in 1-propanol is formed over 50 psec. The data are discussed in terms of current theories of radiation chemistry.

Introduction

Excited states both singlet and triplet are observed in the pulse radiolysis of aromatic solutes in cyclohexane solutions.[2-6] Nanosecond data show that the excited states are produced *via* two distinct processes which are characterized by quite different time dependences. In the concentration range 10^{-3}–10^{-1} M about 80% of the excited states are produced rapidly within 5 nsec while the remaining 20% are produced over about 100 nsec. It has been shown[6] that the development of the excited states over 100 nsec is matched by a decay of the solute anions, which are also observed in these experiments. Typical electron scavengers such as H_2O, SF_6, and alcohols reduce the yield of excited states, the former two scavengers also reducing the yield of anions. These experiments suggest that ion neutralization may lead to the formation of excited states. This is most probably the case for the excited states produced over 100 nsec, and it is suggested that a more rapid ion neutralization event may account for the rapid (<5 nsec) yield also. Schuler[7] and coworkers have suggested that the ion recombination is a geminate event leading to an initially rapid, followed by a slower, recombination. Indeed they can calculate a precise fit to the observed geminate recombination of biphenyl anions in the pulse radiolysis of 0.1 M biphenyl in cyclohexane.[6] This interpretation could certainly explain the faster production of excited states; however, the ion neutralization process could involve the solute cation and the electron, an event which is predicted to be very rapid.

Ion neutralization is very slow in alkane solutions at lower temperatures,[8] and in agreement with the mechanism that ion neutralizations lead to excited states, the excited states of an added solute are observed to grow in slowly while the ions decay.

Recent photochemical experiments by Holroyd[9] and Lipsky and Hirayama[10] show that excited states of cyclohexane and other alkanes can be produced by photochemical excitation at $\lambda < 2000$ Å. The lifetimes of the excited states are reported to be short (1 nsec), but the states are quenched by typical electron scavengers, *e.g.*, N_2O, CCl_4, and CO_2, and transfer energy to aromatic solutes such as, 2,5-diphenyloxazole and benzene, giving the characteristic fluorescence of these molecules. It is pertinent to inquire into the role of excited singlet states of alkanes in radiolysis.

With the above suggestions and conclusions in mind we have constructed a fast psecond pulse radiolysis apparatus which enables us to investigate events down to ten's of pseconds and hence to directly investigate the initial rapid development of the excited states in the radiolysis of alkanes.

Experimental Section

Our apparatus uses the fine structure of the electron beam of a linear accelerator to initiate the radiolysis, a technique which was first described by Hunt and coworkers.[11] But while they use Čerenkov light flashes to measure the concentration of absorbing species produced, and to perform a time transformation so that a low-frequency

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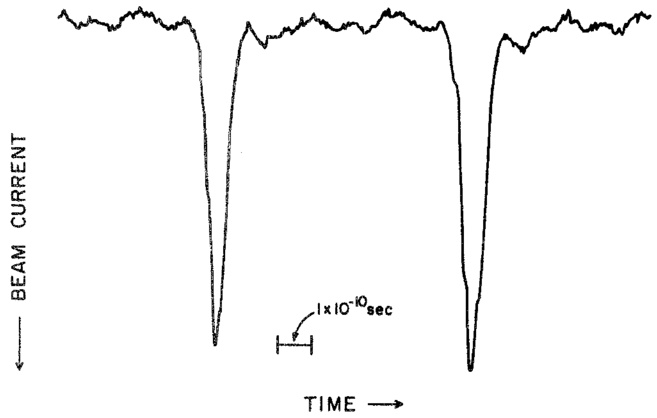

Figure 1. Fine structure pulses from the L-band linear accelerator as observed with a transmission line target.

detection system can be employed, we have developed a detection system with an over-all rise time (10–90%) of 60 psec which enables us to observe emissions as well as absorptions with corresponding time resolution.

The fine structure pulses from the Notre Dame linear accelerator (ARCO, Model LP-7) have an energy of 7 MeV and occur in bursts of 10 nsec total duration. The spacing, determined by the accelerating microwave, is 770 psec. Figure 1 shows typical fine structure pulses observed with a transmission line target[12] having a rise time of 18 psec. These pulses are approximately 45 psec (FWHM) in duration and have a peak current of about 60 A, the width depending very critically on the tuning of the accelerator which operates without a travelling wave prebuncher. The basic pulse radiolysis set-up shown in Figure 2 is conventional except for the light source and the detection system.

As light source we utilize an Osram XBO 450-Watt xenon lamp which is pulsed for 120 μsec to a current of about 600 A with a repetition rate of 10 pps by a specially designed lamp pulser, or a 4-W argon ion laser (Coherent Radiation, Model 52B). The laser has the obvious advantage of single wavelength operation. It should be noted, however, that there is an inherent source of excess photon noise in any laser due to multimode operation. The laser cavity is resonant and hence may have output at all frequencies for which a standing wave can exist between the reflectors. For a 1-m cavity the so-called modes have a frequency separation of 150 MHz, and 10 to 30 of them may oscillate within the fluorescence line width giving rise to mode beating noise[13] which is very significant as the oscillations seem to occur in random sequence with amplitude fluctuations at each frequency. The amplitude of the noise observed is strongly dependent on the conditions in the lasing cavity and increases with increasing detector bandwidth. Using our fast detection system with 6 GHz bandwidth we observed typical values of 20% noise (peak to peak). To overcome this limitation of detectable absorption we have used the laser in single frequency operation by means of a tilted etalon incorporated in the cavity.

The light from the xenon lamp or the laser is focussed through the sample cell (1-cm optical path length) and *via* a lens and mirror system onto the entrance slit of a Bausch & Lomb monochromator (Model 33-86-02). An iris at the exit window of the cell limits the field of view of the detection system and a light chopper decreases the average light intensity falling on the cathode of an ITT F-4014 biplanar photodiode. This is mounted in a high-speed holder[14] which is designed to match the diode to a 50 Ω system and to allow operation of the diode up to 10 kV, as the response to an increase in light level is determined by the flight time of the photoelectrons between cathode and anode. Detailed consideration of the diode performance will be given elsewhere.[14] The linearity of the photocurrent *vs.* light intensity was checked with calibrated neutral density filters and by observing the Čerenkov radiation from cyclohexane with the analyzing light alternately on and off. With complete illumination of the cathode the linearity was better than 3% up to a cathode current of 120 mA. It should be noted, however, that some diodes showed considerable fatigue even at 4 μA mean current.

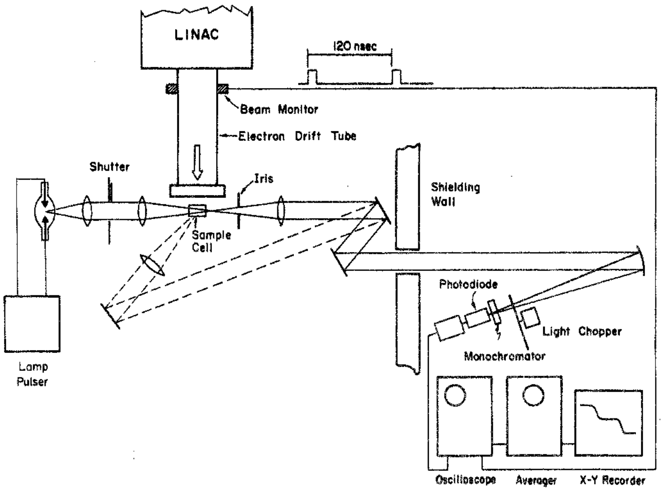

Figure 2. Schematic diagram of the pulse radiolysis system designed for picosecond time resolution.

The output of the diode is fed into a Tektronix S-4 sampling head (rise time 25 psec), stored in a NS-44 digital averager (Northern Scientific), and plotted on an X–Y recorder. An advance trigger for the sampling oscilloscope is provided by operating the linear accelerator in double pulse mode which results in two 10-nsec beam pulses in one rf envelope separated by 120 nsec. These pulses are sensed by a current loop which permits the oscilloscope to be triggered by the first pulse, while the radiolysis events of the second pulse are observed.

Figure 3 shows the response of the detection system to Čerenkov radiation from cyclohexane produced by two fine structure pulses. The diode was operated at 8 kV, corresponding to a flight time of 60 psec. The observed rise and fall times (10–90%) are 75 psec. The rise time in addition to the portion caused by the flight time is due to the pulse shape and trigger jitter.

Results

Water. A typical absorption *vs.* time trace is shown in Figure 4 for the development of the hydrated electron with two fine structure pulses in the radiolysis of a deaerated solution of 10^{-2} *M* $HClO_4$ in water. The wavelength of the observation was 520 nm which was achieved by using an interference filter with a band pass $W_{1/2}$ of 100

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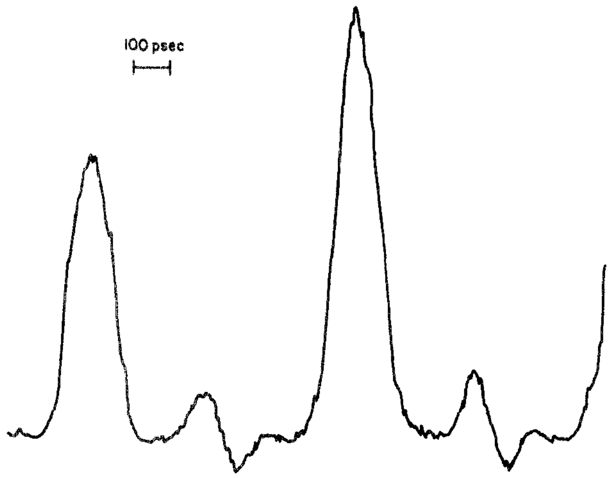

Figure 3. Cerenkov radiation from cyclohexane produced by two fine structure pulses as observed with the picosecond detection system.

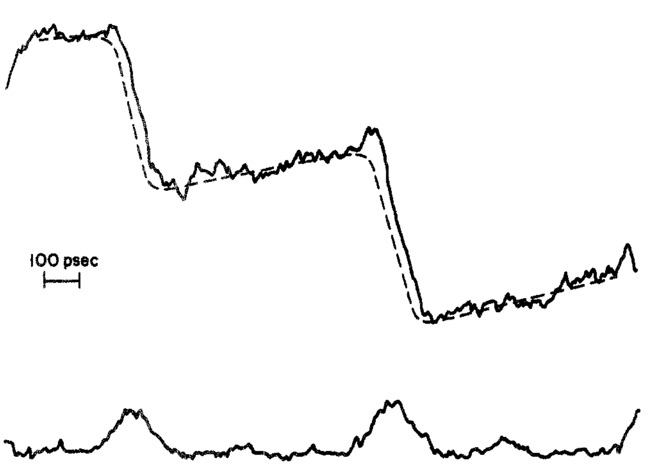

Figure 4. Absorption signal from e_{aq}^- produced by two fine structure pulses in a deaerated solution of 10^{-2} *M* $HClO_4$ in water observed at 520 nm: lower trace, Čerenkov radiation observed with analyzing light off. The dotted line is the true absorption signal and was obtained by subtraction. The averager (512 channels) was scanned four times.

Å. Starting at the left of the figure and moving to the right-hand side, the horizontal line of the top trace dips down with the first fine structure pulse, then shows some decay due to $e_{aq}^- + H^+$, then dips again when the second pulse appears. The bottom trace shows the Čerenkov radiation produced in the sample; this was taken with no analyzing light passing through the sample. The true hydrated electron signal is shown as the dotted line which is obtained by subtracting the Čerenkov from the absorption trace. Similar data are observed in pure water, but no decay or growth of e_{aq}^- is observed between the pulses. Usually acid is used in these samples to remove the absorption due to the e_{aq}^- produced in the trigger pulse.

The data from traces such as Figure 4 are plotted as an average e_{aq}^- absorption *vs.* time over the period of the radiation pulse in Figure 5. Hunt and coworkers[15] have shown that e_{aq}^- develops in a time that is short compared to 10 psec so that this trace illustrates the observation of a species that is produced with the radiation pulse, without delay or subsequent growth. These data are also used to measure the radiation dose in the sample by using the appropriate extinction coefficient for e_{aq}^- at the wavelength used and by noting that $G(e_{aq}^-)$ is 3.4 in this time region.[16,17]

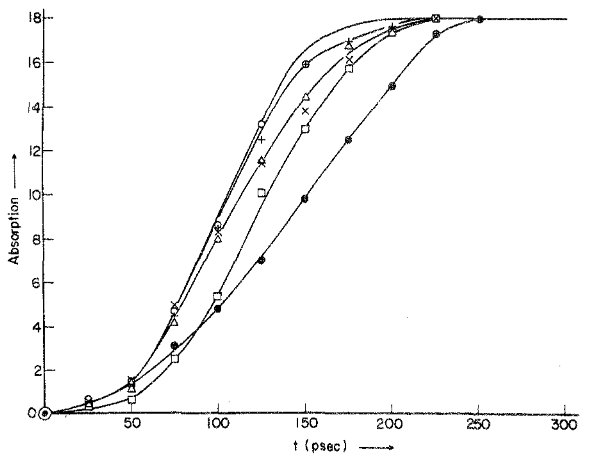

Figure 5. Development of the following species during a fine structure pulse: solid curve to the far left, water; +, ethanol; ●, 1-propanol; □, excimer in pure benzene; △, 10^{-2} *M* biphenyl/C_6H_{12}; ×, 3×10^{-3} *M* biphenyl in C_6H_{12}; ○, 0.1 *M* biphenyl/C_6H_{12}.

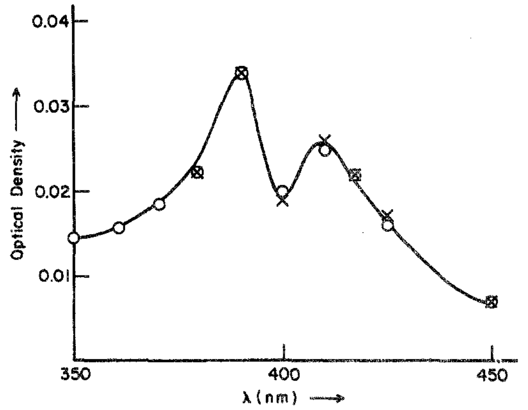

Figure 6. Transient spectrum observed in deaerated 0.1 *M* biphenyl in C_6H_{12} at 200 psec following the beginning of a fine structure pulse.

Alcohols. Similar experiments in ethyl and n-propyl alcohols show that the yield of e_s^- produced by a fine structure pulse is ~50% of that produced in water and that the signal is constant between the pulses over 770 psec. The absorption produced in these alcohols with the pulse is also shown in Figure 5 and compared to that in water. A slight lag amounting to a few pseconds is observed in ethanol, while a large lag of the e_s^- in alcohol behind e_{aq}^- in water is observed in 1-propanol.

Solutions of Biphenyl and Pyrene in Cyclohexane. Both the biphenyl and pyrene anion were identified in the pulse radiolysis of these solutes in cyclohexane, while the pyrene cation was identified by its absorption at λ 450 nm in the radiolysis of 10^{-2} *M* pyrene in cyclohexane saturated with SF_6. A typical spectrum for a solution of 0.1 *M* biphenyl (Ph_2) in cyclohexane (C_6H_{12}) is shown in Figure 6. This spectrum compares favorably with that observed in the radiolysis of Ph_2 in alcohol when Ph_2^- is formed alone.[18]

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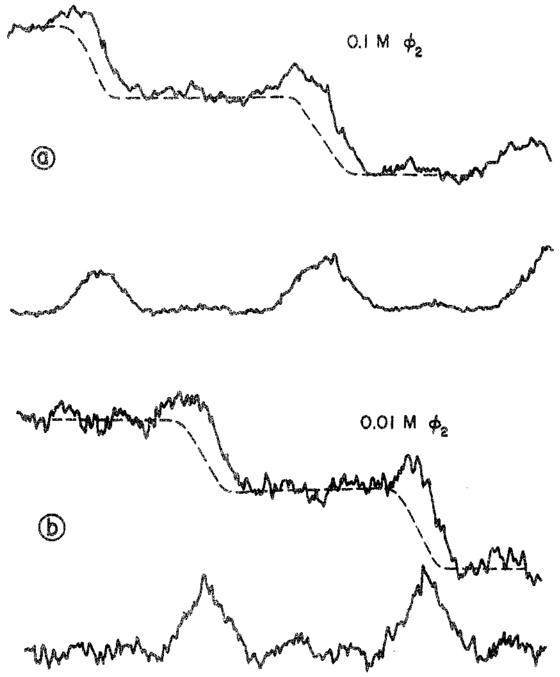

Figure 7. Absorption produced by two fine structure pulses in deaerated solutions of biphenyl (Ph_2) in cyclohexane observed at 404 nm. The dotted line is the true absorption and was obtained by subtraction: a 0.1 *M* Ph_2; b, 0.01 M Ph_2.

The biphenyl cation has a similar spectrum,[19] and the spectrum in Figure 6 is probably a composite of Ph_2^- and Ph_2^+. It is worthy of note that the absorption decreases toward λ 350 nm, which is contrary to the observation[20,21] at nsecond times where the absorption increases due to the formation of the triplet state Ph_2^T.

Figure 7 shows the development of the Ph_2^- absorption observed at λ 410 nm for 0.1 *M* and 10^{-2} *M* biphenyl in C_6H_{12}. The absorptions develop rapidly with the radiation pulse and show no change in the time interval before the next pulse appears. The absorptions during the pulse are compared to water in Figure 5. The 0.1 *M* Ph_2 in C_6H_{12} shows a development of Ph_2^- *vs.* time that follows the e_s^- in ethanol. The half-life of the electron in the 0.1 *M* Ph_2-C_6H_{12} solution is 2.7 psec,[22] while the half-life in 10^{-2} *M* Ph_2-C_6H_{12} is 27 psec. The development of Ph_2^- in the later solution shows a larger lag behind that of e_{aq}^- in water as expected. The *G* value of Ph_2^- in 0.1 *M* Ph_2 was measured as 1.1 molecules/100 W.

Similar data were obtained in the pulse radiolysis of pyrene in C_6H_{12} where the pyrene anion was observed with the 488-nm line of the 4-W argon ion laser. This trace is shown as insert B in Figure 8. In the presence of SF_6 the pyrene anion absorption is generally decreased but the absorption at 450 nm is unchanged. This is identified as the pyrene cation[23] and shows a slow growth between the fine structure pulses. In a 3×10^{-2} *M* pyrene/C_6H_{12} solution saturated with SF_6 the cation shows a faster growth with $t_{1/2} \sim 50$ psec indicating a $k \sim 4 \times 10^{11}\ M^{-1}\ sec^{-1}$ for the formation of the pyrene cation.

The singlet excited state of pyrene was observed in the pulse radiolysis of degassed solutions of pyrene in C_6H_{12}. The excited state showed a slow growth between fine structure pulses and will be considered in the next section.

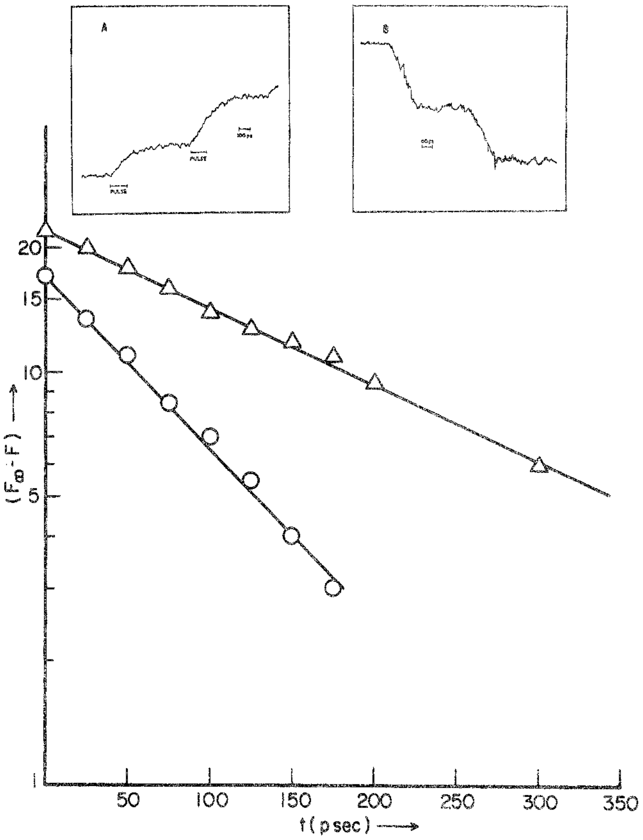

Figure 8. First-order growth of fluorescence in the picosecond pulse radiolysis of 9,10-diphenylanthracene (DPA) in cyclohexane: ○, 10^{-2} *M* DPA; △, 10^{-3} *M* DPA. Insert A shows an oscilloscope trace of the growth of fluorescence of 10^{-2} *M* DPA monitored at 423 nm. Insert B shows the absorption of the pyrene negative ion produced by two fine structure pulses monitored at 488 nm.

Fluorescence in the Radiolysis of C_6H_{12} Solution. The pulse radiolysis of aromatic solutes in C_6H_{12} leads to fluorescence which is characteristic of the added solute. Figure 9 shows the fluorescence from two fine structure pulses in the pulse radiolysis of 10^{-2} *M* 1,1′-binaphthyl in C_6H_{12}. It can be seen that the fluorescence rises with the pulse and then continues to rise to the next pulse, when the same behavior is repeated. Anthracene, biphenyl, *p*-terphenyl, 2,5-diphenyloxazole, 1,1′-binaphthyl, and 9,10-diphenylanthracene (DPA) all show this behavior. The most convenient molecule to use is the latter as the quantum yield for fluorescence is unity, the $t_{1/2}$ is 10 nsec[24] which means that little decay of the excited state occurs between pulses, and the fluorescence is situated in the visible part of the spectrum which minimizes the interference from Čerenkov radiation.

The growth of the fluorescence follows first-order kinetics as shown in Figure 8 where $\log(F_\infty - F)$ is plotted *vs.* time, where F_∞ and *F* refer to the fluorescence at the maximum growth time, *i.e.*, just before the next pulse appears, and *F* refers to the fluorescence at time *t*.

The rate of growth of the fluorescence increases with increasing DPA concentration, a plot of the rate constant

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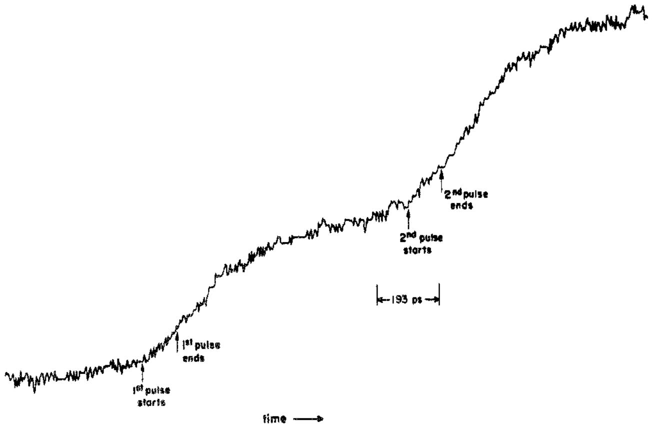

Figure 9. Fluorescence produced by two fine structure pulses in a deaerated solution at 10^{-2} *M* 1,1-binaphthylincyclohexane.

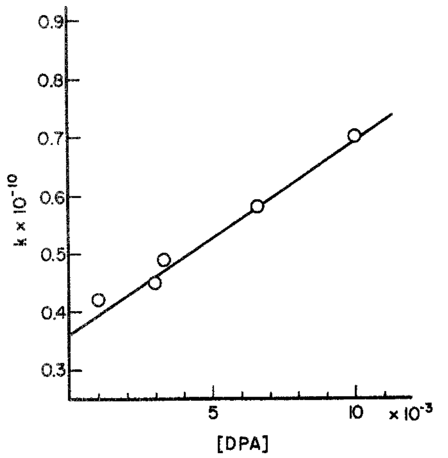

Figure 10. Rate constant for the growth of fluorescence for different concentrations of 9,10-diphenylanthracene (DPA) in cyclohexane.

vs. DPA concentration being linear as shown in Figure 10.

If it is assumed that the following mechanism applies in these experiments

$$C_6H_{12}^* \xrightarrow{\alpha}$$

$$C_6H_{12}^* + DPA \xrightarrow{\beta} DPA^* \longrightarrow h\nu$$

then the observed rate constant $k = \alpha + \beta[DPA]$. The data in Figure 10 then give $\alpha = 3.6 \times 10^9$ sec^{-1} and $\beta = 3.4 \times 10^{11}$ M^{-1} sec^{-1}.

Effect of Additives on the Fluorescence. Many additives such as ethanol, SF_6, CO_2, CCl_4, and benzene reduce the fluorescence of DPA in C_6H_{12}. In all cases the apparent rate of growth or formation of the DPA fluorescence also increases.

Effect of Benzene. At all concentrations of DPA used addition of 10^{-3}–10^{-2} *M* benzene progressively reduces the fluorescence to a plateau value. Typical data are shown in Figure 11. The plateau yield of fluorescence grows in directly with the radiation pulse and is unaffected by concentrations of CCl_4 up to 5×10^{-2} *M*. It appears that the DPA fluorescence is derived from at least two different processes, one rapid event and one that grows in between the pulses at a rate which increases with increasing DPA concentration. It is suggested that the slow development of fluorescence is due to an energy transfer to the DPA and that benzene also competes with the DPA for the C_6H_{12} singlet energy. The mechanism for the system is as follows

$$C_6H_{12}^* \xrightarrow{\alpha} \quad (1)$$

$$C_6H_{12}^* + DPA \xrightarrow{\beta} DPA^* \longrightarrow h\nu \quad (2)$$

$$C_6H_{12}^* + C_6H_6 \xrightarrow{\gamma} C_6H_6^* \quad (3)$$

and the fluorescence of DPA*, *F* follows the following relationship

$$\frac{1}{F} = \frac{1}{F_0}\left(1 + \frac{\alpha}{\beta[DPA]} + \frac{\gamma[C_6H_6]}{\beta[DPA]}\right)$$

In this case the fluorescence *F* is the difference between the measured fluorescence and the fluorescence at high benzene concentrations. The plot $1/F$ *vs.* $[C_6H_6]$ in Figure 12 is linear as demanded by the above equation and gives $\gamma/\beta = 0.65$, *i.e.*, $\gamma = 2.2 \times 10^{11}$ M^{-1} sec^{-1}.

If the resultant DPA fluorescence at high benzene concentration is subtracted from the fluorescence in the absence of benzene then it is possible to investigate the effect of [DPA] in reactions 1 and 2. The expression connecting *F* and [DPA] is

$$\frac{1}{F} = \frac{1}{F_0}\left(1 + \frac{\alpha}{\beta[DPA]}\right)$$

A plot of $1/F$ *vs.* $1/[DPA]$ in Figure 13 is linear and gives $\alpha/\beta = 1.05 \times 10^{-2}$, which is in excellent agreement with the direct measure of $\alpha = 3.6 \times 10^9$ sec^{-1} and $\beta = 3.4 \times 10^{11}$ M^{-1} sec^{-1}.

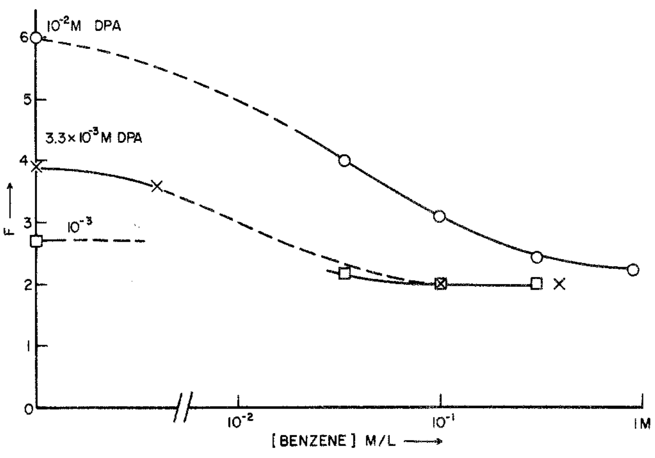

Figure 11. Reduction of fluorescence yield of DPA in C_6H_{12} by benzene: ordinate *F* = fluorescence yield; O, 10^{-2} *M* DPA; ×, 3.3×10^{-3} *M* DPA; □, 10^{-3} *M* DPA.

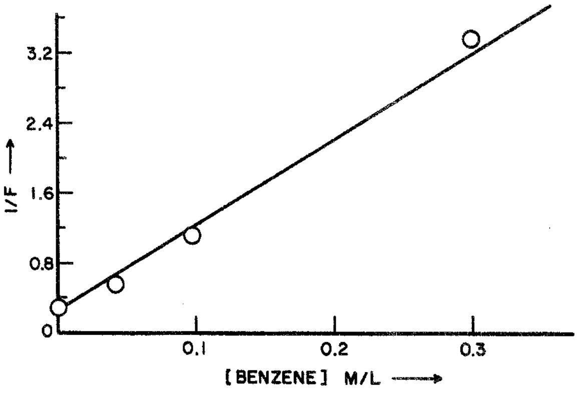

Figure 12. Stern–Volmer plot of the reduction of the fluorescence of 10^{-2} *M* DPA in C_6H_{12} by benzene.

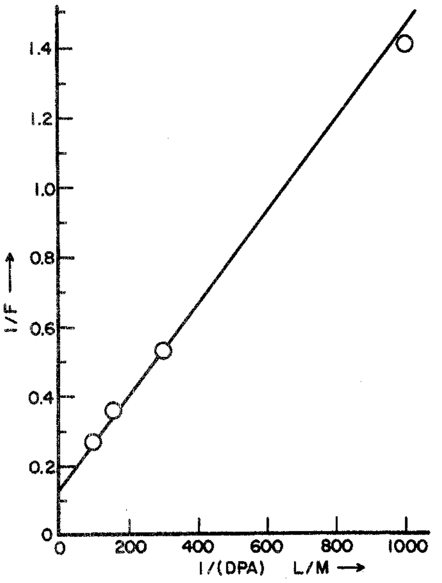

Figure 13. Plot of the inverse of DPA fluorescence *vs.* inverse of DPA competition for DPA in C_6H_{12}.

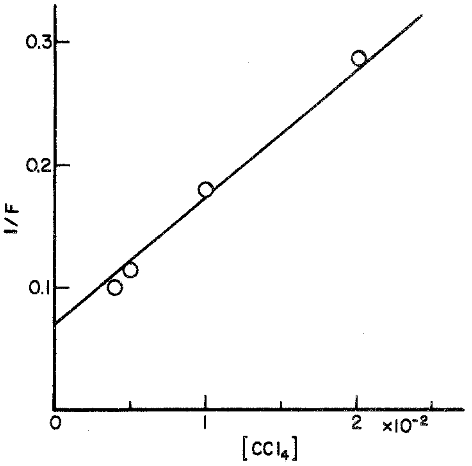

Figure 14. Stern-Volmer plot of the competition of 1,1′-binaphthyl and CCl_4 for the excited state of C_6H_{12}. The ordinate is the inverse of the 1,1′-binaphthyl fluorescence.

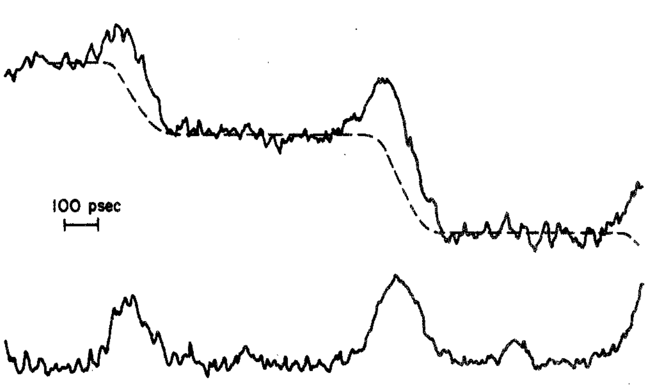

Figure 15. Absorption produced by two fine structure pulses in pure benzene monitored at 520 nm. The Čerenkov radiation shown in the lower trace was subtracted to yield the true emission *vs.* time curve which is shown as dotted line.

Effect of Carbon Tetrachloride. Carbon tetrachloride, CCl_4, reduces the yield of fluorescence of the aromatic solute, *e.g.*, DPA in C_6H_{12}, while the apparent rate of development of the fluorescence increases. On the basis that the CCl_4 and DPA compete for the excitation energy it is possible to measure a rate constant k for the transfer of energy from C_6H_{12} to CCl_4. The direct observation gives k is $3 \pm 1 \times 10^{11}\ M^{-1}\ \mathrm{sec}^{-1}$.

With the above mechanism it is also possible to calculate the ratio of two rates of transfer of energy from C_6H_{12} to DPA and CCl_4 from the decrease in the fluorescence yield with increasing CCl_4 concentration. The mechanism is reactions 1 and 2 with 4.

$$C_6H_{12}^* + CCl_4 \xrightarrow{\delta} \tag{4}$$

This mechanism is similar to that used in the benzene/DPA system and predicts a linear plot of $1/F$ *vs.* $[CCl_4]$, which is observed in Figure 14. The analysis of the data in Figure 14 gives $\delta/\beta = 0.75$, i.e., $\beta = 2.5 \times 10^{11}\ M^{-1}\ \mathrm{sec}^{-1}$, which is in agreement with the direct measurement of $\beta = 3 \pm 1 \times 10^{11}\ M^{-1}\ \mathrm{sec}^{-1}$.

Benzene. Previously the excimer excited state of benzene B_2^* has been observed in the pulse radiolysis and laser photolysis of pure benzene[25] and benzene in C_6H_{12}.[26] It is not certain how the excited monomer singlet, B^*, is formed, it could be formed by direct excitation to higher excited states followed by a cascade to B^*, or by ion recombination to give B^* directly. The excimer B_2^* is then formed by the process

$$B^* + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B_2^*$$

The half-life of this process in benzene is given by

$$t^{1/2} = \frac{0.69}{k_1[B_\delta] + k_2}$$

and is 7 psec at room temperature if $k_1 = 6 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$ and $k_2 = 3 \times 10^{10}\ \mathrm{sec}^{-1}$.[27]

Figure 15 shows that formation of B_2^* by two fine structure pulses monitored at 520 nm the λ of maximum absorption. The formation of the state *vs.* time during the pulse is shown in Figure 5. It can be seen that the formation of B_2^* lags 10 psec behind the formation of e_{aq}^- in water.

Discussion

In previous work[22] the rate constant for reaction of e^- with biphenyl in C_6H_{12} at room temperature was measured as $2.6 \times 10^{12}\ M^{-1}\ \mathrm{sec}^{-1}$. This rate parallels the high mobility of electrons in C_6H_{12} measured by electron drift studies. The rate constant predicts that the half-life $t_{1/2}$ of the formation of the biphenyl anion, Ph_2^-, should be 2.7 psec in 0.1 M Ph_2 and 27 psec in 10^{-2} M Ph_2 in C_6H_{12}. This is too rapid for a direct measurement in the present equipment, however, a reasonable observation of the rate of formation of Ph_2^- in such systems may be achieved by comparing the rate of development of Ph_2^- during the pulse with that of e_{aq}^- in water. The data are shown in Figure 5 for 0.1, 0.01, and 0.03 M Ph_2 in C_6H_{12}, when it can be seen that at 0.1 M Ph_2 the Ph_2^- absorption lags 2 to 4 psec behind the water curve while the data at 10^{-2} M Ph_2 is identical with that at 3×10^{-3} M and lag 10 psec behind the water. The absorption curves can be simulated by integrating a triangular voltage pulse

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with base 80 psec with various capacities and displaying the result on an oscilloscope screen. The triangular voltage pulse is equivalent to the actual radiation pulse, and the capacity integration corresponds to equipment distortion and late development of the observed entities. These rather crude computations provide the numbers quoted for the delayed absorptions and approximately conform to the actual radiolysis events. A more extended calculation is underway.

The observed half-life for development of Ph_2^- in 10^{-2} and 3×10^{-3} M Ph_2 solutions is shorter than that calculated from the measured rate constant for e^- plus Ph_2 in C_6H_{12}. We may conclude that the electrons may react prior to thermalization thus distorting the data, or that Ph_2 competes with the geminate recombination of the cation and e^-. This latter event may still play the controlling feature in the lifetime of the e^- in these systems, and will hasten the fate of the electron and effectively the development of Ph_2^-.

At first sight the lack of any significant decay of Ph_2^- between the fine structure pulses, as shown in Figure 7, does not agree with the geminate ion neutralization as described by Schuler and coworkers.[7] Indeed, the $G[Ph_2^-] = 1.1$ in solution at 0.1 M Ph_2 and greater agrees with the estimate of earlier nsec data.[6] This value of 1.1 would be larger however (1.6) if the initial $G(e_{aq}^-)$ in water is 5.0, which is predicted by diffusion theory. It is probably, although calculations have to be made to realize the effect quantitatively, that the initial ion neutralization of the cation and electron is extremely rapid so that at reasonable concentrations of Ph_2 (<1.0 M), it is not possible to capture more than 50% of the electrons. Alternatively, some of the Ph_2^- formed may still react too rapidly for direct observation. The point we wish to make clear for later discussion in relation to excited states is that the electrons all disappear very rapidly in the solutions used, in a time short compared with the observation time of excited states, *i.e.*, ~500 psec, and that the anions do not recombine rapidly in this time domain. We suggest that this is a general phenomenon for polycyclic aromatic solutes in C_6H_{12}, quoting the pyrene and biphenyl data to support it.

The data in solutions of pyrene in C_6H_{12} saturated with SF_6 suggest that the positive ion of the solute may be formed rapidly in the pulse radiolysis of these systems, with a rate constant of 4×10^{11} M^{-1} sec^{-1}. This rate constant is an order of magnitude smaller than the corresponding rate constant for the formation of the anion from electrons, but is in agreement with a ratio of 1/20 for these rates measured in steady-state experiment.[7] This suggests that the positive ion has an abnormally high mobility in alkanes, and is in keeping with the rapid formation of cations in the radiolysis of low-temperature alkane glasses containing aromatic solutes.[19]

The spectrum observed in 0.1 M Ph_2 in C_6H_{12} at 100 psec differs from that observed at 10 nsec in the region of λ 360 mμ. In the nsecond time domain an initial absorption is present a part of which grows in subsequently. This absorption is due to the triplet state of Ph_2 which has an extinction coefficient of 35,400[28] at λ 360 mμ. It is suggested[6,21] and in part observed that the cation–anion neutralization in the 10-nsec time domain leads to a significant yield of triplet excited state, the absence of Ph_2^T at 100 psec being due to the insignificant solute ion neutralization which occurs here.

Singlet excited states are observed to develop rapidly between the fine structure pulses with rates which increase with increasing aromatic solute concentration. The previous arguments and data show that these excited states are not formed by ion neutralization, and it is suggested that they are derived from an energy transfer process from cyclohexane. The observations by Lipsky and Hirayama[10] give concrete support to an excited state of cyclohexane with a lifetime in the nsecond region. The suggested mechanism of singlet energy transfer follows eq 1, 2, and 3 which suggest that the rate constant for the formation of fluorescence should be exponential. This is shown to be true experimentally in Figure 9 where the observed rate constant k is $\alpha + \beta[\text{solute}]$. A plot of k *vs.* the solute [DPA] is linear (Figure 10) and gives $\alpha = 3.6 \times 10^9$ sec^{-1} and $\beta = 3.4 \times 10^{11}$ M^{-1} sec^{-1}. The effects of other additives such as benzene and CCl_4 on the yields and rate of growth of the aromatic fluorescence can also be explained in terms of an energy transfer from C_6H_{12} to these solutes. The benzene data also show that a part of the singlet energy is derived by some other rapid process. If the yield of this rapid process is subtracted from the observed yield of fluorescence it is possible to set up Stern–Volmer plots as shown in Figure 12 which give the rate constants for energy transfer from C_6H_{12} to benzene and CCl_4 as 2.5×10^{11} and 2.2×10^{11} M^{-1} sec^{-1}, respectively.

Mechanism 1, 2, and 3 can explain all the experimental data in terms of excited states which have been observed in photochemistry. However, the lifetime of the excited state of C_6H_{12} is measured as 0.28 nsec in the present work, while Lipsky and Hirayama quote 2 nsec. However, they also quote a parameter $\alpha = t_1\beta = 67$ where t_1 is the lifetime of the excited singlet state of C_6H_{12}, and β the transfer constant to a solute. In our experiments we measure a similar parameter for benzene with $\alpha = 71$ in good agreement with the photochemical data. The difference in absolute t_1 must lie in the transfer constant β which Lipsky and Hirayama assumed to be diffusion controlled ~10^{10} M^{-} sec^{-1}. We measure this to be 20-fold faster. The conclusion is that the photochemical data and the psecond radiolysis data are in good agreement.

Our data show that 50% of the excited state of C_6H_{12} is captured in a solution of 10^{-2} M aromatic solute. The singlet yields in such a solution have been measured as 0.5[29] and 0.77.[30] If we take an average of 0.67, subtract the yield of rapid singlet which is 25%, then we may compute a $G(C_6H_{12}^*) = 1.0$. The total singlet yield is the 1.17 molecules/100 W. It is emphasized that these numbers are speculative until later precise measurements can be carried out.

The data in C_6H_{12} solution containing DPA and CCl_4 show that the rate of transfer of energy to CCl_4 is $3 \pm 1 \times 10^{11}$ M^{-1} sec^{-1} when measured by the increased rate of development of DPA fluorescence. The competition studies in the yield of fluorescence versus CCl_4 fit a good Stern–Volmer plot (Figure 14) and give a transfer rate constant of 2.5×10^{11} M^{-1} sec^{-1}. We conclude that up to 5×10^{-2} M CCl_4 the quenching of the singlet energy is due to direct reaction with the excited state of C_6H_{12}, and not with a precursor of an earlier reaction such as an electron. This suggests that the excited state of C_6H_{12} may be formed directly, or if formed *via* ion neutralization that this process must occur much faster than 40 psec. As

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shown in Figure 5, the development of the absorption of the solvated electron in ethanol and 1-propanol lags behind the production of e_{aq}^- in water. The delayed formations correspond to $t_{1/2}$ = 2-4 and 50 psec respectively for ethanol and 1-propanol. This may be due to a solvation time of the electron in these alcohols. Slower formation times have been observed in low-temperature ethanol glasses,[8] and alcohols at temperatures below −100°.[31] Here the relaxation is observed by a decrease in the spectrum in the infrared which parallels an increase in the yellow→red part of the spectrum, and is associated with the breaking of hydrogen bonding with subsequent orientation of the solvent dipoles to form deeper traps for the solvated electron. The present data may also be explained in this way, although a full spectrum was not observed. Microwave absorption measurements in liquid alcohols[32] show that the relaxation time for the rotation of free monomeric molecules is 21.9 psec in 1-propanol at 20°, which is close to that observed in the present work, while the relaxation time for H bond breakage is 430 psec.

Figure 5 also shows that the formation of the benzene excimer, B_2^*, is delayed 10 psec behind that of the e_{aq}^- in water. This is of the order of the time taken to form the excimer from the ground state and the first excited singlet state. The shape of the curve which shows a large initial delay cannot be calculated by the analog device used for the other curves. It would appear that the formation of the first excited singlet state is delayed with respect to e_{aq}^- in water and that the delay in the excimer formation is the resultant of this process together with the reaction of the excited singlet with ground state benzene. The initial delay in the formation of the excited singlet state could be due to a prior ion neutralization reaction or to the direct formation of a higher excited state with subsequent cascade to the first excited singlet state. These processes are short compared to the excimer formation time of 10 psec.

It is concluded that excited singlet states are formed rapidly in both cyclohexane and benzene in a time that is short compared to 10 psec. Rapid ion neutralization or direct excitation could explain this result. The differing subsequent chemistry in the two liquids lies in the different nature of the two excited states. In cyclohexane the state is short lived, $t_{1/2}$ = 0.2 nsec, has high energy, ~7 V, and transfers energy rapidly, $k = 2\text{-}4 \times 10^{11}\ M^{-1}\ \text{sec}^{-1}$. In benzene the first excited singlet state has a $t_{1/2}$ = 20 nsec, an energy of 4.7 V, and a transfer constant $k \sim 2 \times 10^{10}$. Unlike benzene the excited singlet state of cyclohexane is very reactive with conventional electron scavengers such as N_2O, SF_6, and CO_2, a feature which must enter into the treatment of the scavenging data in these systems.

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Radiolysis of Aqueous Methane Solutions[1]

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The γ-ray and electron pulse irradiation of aqueous methane and some ethane solutions is reported. The absorption spectra of the CH_3 and C_2H_5 free radicals have been measured in the wavelength range 210-270 nm. At 210 nm $\epsilon(CH_3) = 850\ M^{-1}\ \text{cm}^{-1}$ and $\epsilon(C_2H_5) = 520\ M^{-1}\ \text{cm}^{-1}$. The bimolecular recombination rate constants are $1.24 \pm 0.2 \times 10^9$ and $0.96 \pm 0.2 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ for CH_3 and C_2H_5, respectively. The rate constant $k(OH + CH_4) = 1.21 \pm 0.4 \times 10^8\ M^{-1}\ \text{sec}^{-1}$; $k(CH_3 + H_2O_2) = 3.5 \times 10^7\ M^{-1}\ \text{sec}^{-1}$. The yields $G(-CH_4)$, $G(C_2H_6)$, $G(H_2)$, $G(H_2O_2)$, and $G(N_2)$ for N_2O-CH_4 solutions are reported for some acid, neutral, and alkaline solutions. A radiolysis mechanism is also given.

Introduction

Whereas many investigators have studied the radiolysis of gaseous methane as was brought out in a recent review,[2] relatively few papers have appeared on the radiolysis of aqueous methane solutions.[3-7] The results of studies on oxygen-free[4,5] and oxygen-saturated solutions[4,6] demonstrate that only the OH free radical reacts with methane to any appreciable extent. By relative rate constant measurements $k(CH_4 + OH)$ has been established as $1.4 \times 10^8\ M^{-1}\ \text{sec}^{-1}$.[7] As expected, CH_3 is the product radical and its re-

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