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RADICAL IONS AND EXCITED STATES IN RADIOLYSIS.
OPTICALLY DETECTED TIME RESOLVED EPR

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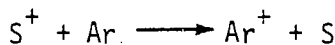
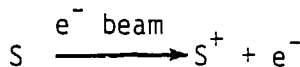
ABSTRACT

Excited-state production and radical-ion recombination kinetics in pulse-irradiated solutions of aromatic solutes in cyclohexane are studied by a new method of optical detection of time-resolved electron paramagnetic resonance (EPR) spectra.

INTRODUCTION

The EPR spectra of radical ion pairs that recombine to produce an excited singlet state can be detected optically *via* observation of a resonant change in the intensity of fluorescence arising from ion recombination. This not only permits the application of magnetic resonance to some very interesting problems, but also results in a major improvement in the specificity and sensitivity of time resolved EPR (1,2).

One area of current research (3,4) is the radiation chemistry of hydrocarbon solutions of aromatic molecules. Radical ion recombination is a major source of the excited states produced by pulse radiolysis. The recombination pathways for excited state production are summarized in the following scheme where S and Ar represent the solvent and aromatic solute, respectively.



MASTER (1)

(2)

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The primary products of ionization (1) are rapidly scavenged by solute molecules (2,3). Several ion recombination pathways (4-6) can then yield excited solute molecules. Experimentally, excited singlet state solutes(*) are observed *via* fluorescence and excited triplet states are most conveniently observed by triplet-triplet absorption.

The EPR spectra of radical ion pairs can be detected by observation of a resonant decrease in fluorescence following the application of a single (30-100 ns) microwave pulse. Here we will discuss several features of the fluorescence detected magnetic resonance (FDMR) technique.

METHOD, RESULTS, AND DISCUSSION

The experimental setup is illustrated in Figure 1. We use the same pulsed EPR spectrometer described previously. The light from excited state emission escapes through a hole in the bottom of the cavity and is detected at a selected wavelength. At some time after irradiation, a single microwave pulse is applied and the fluorescence is sampled during a subsequent time window selected by a boxcar averager. An EPR spectrum corresponding to a superposition of the spectra of the isolated radical ions that recombined to produce the excited state is obtained by measuring the fluorescence intensity as a function of the applied magnetic field. For each spectrum, the positions of the microwave pulse and boxcar averager sampling window are fixed with respect to the time of irradiation. Typical FDMR spectra obtained for kinetic studies (Figure 2) consist of a single peak with no resolved hyperfine structure. In some cases, the hyperfine structure of the FDMR spectrum can be resolved through the use of long (250-500 ns), low power ($H_1 \leq 0.4 \text{ g}$) microwave pulses (Figure 3). Although the hyperfine structure is resolved at the expense of some of the time resolution and sensitivity of the FDMR method, the spectra obtained in this way can provide useful data on the identity and structure of the radical ion precursors of excited states in more complex chemical systems. A plot of integrated FDMR intensity vs. time, obtained from a series of spectra similar to those in Figure 2, provides information about radical ion pair spin dynamics and chemical kinetics (Figure 4). The intensity of the FDMR signal increases for $\sim 70 \text{ ns}$ after application of the microwave pulse and

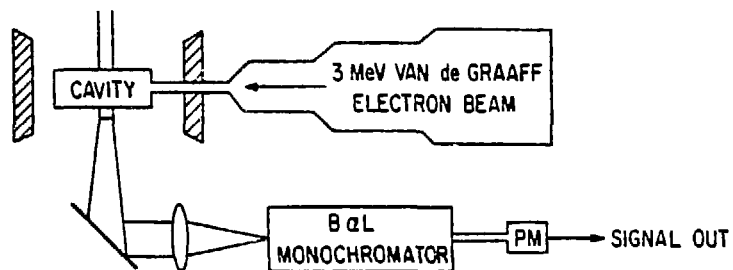


Figure 1. Experimental setup for optical detection of magnetic resonance showing the arrangement of the microwave cavity containing the sample cell; the electron beam and the light detection apparatus.

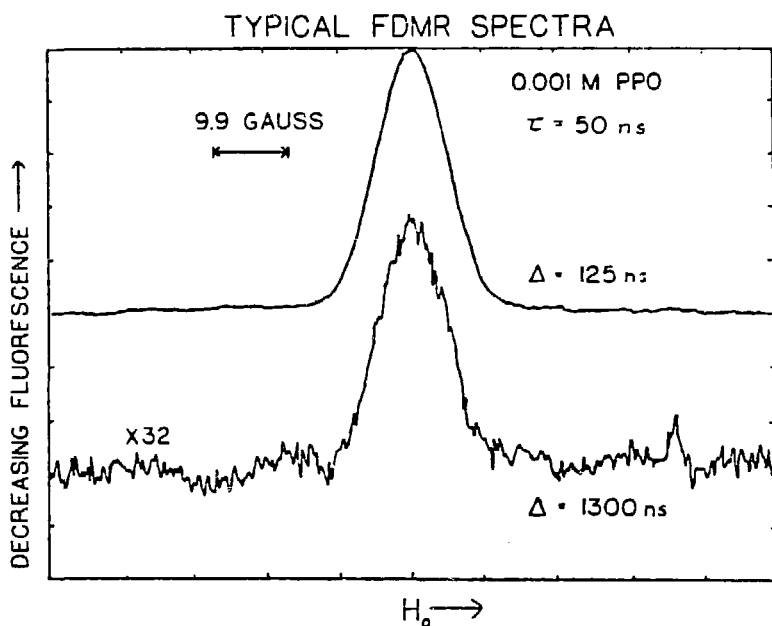


Figure 2. Typical FDMR spectra of 10^{-3} PPO (2,5 di-phenyloxazole) in cyclohexane. The microwave pulse was applied from 0 to 100 ns after irradiation with a 5 ns electron beam pulse. The fluorescence was sampled from 75-175 ns (upper trace) or 1250-1350 ns (lower trace) after irradiation.

then decays. The time dependence of the FDMR intensity is dominated by spin dynamics in the time domain immediately following the microwave pulse and by the recombination kinetics of the radical ion pair population at later times.

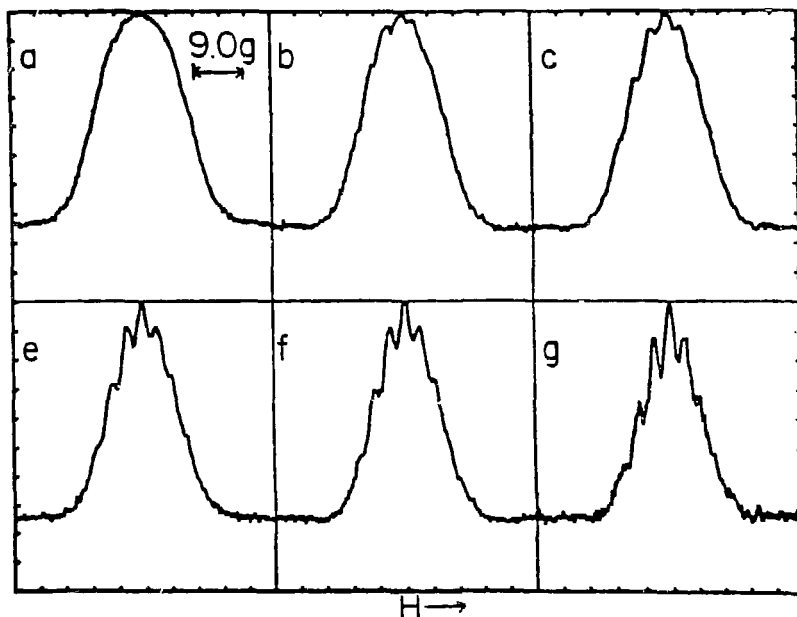


Figure 3. Microwave magnetic field (H_1) dependence of FDMR of 10^{-3} M biphenyl in cyclohexane. A microwave pulse of H_1 value 1.5 G (a), 0.74 G (b), 0.6 G (c), 0.47 G (d), 0.37 G (e) or 0.26 G (f) was applied from 0 to 500 ns after irradiation. The fluorescence was sampled from 500 to 600 ns after irradiation.

When the time dependence of the FDMR intensity is measured with higher time resolution (Figure 5), it is clear that most of the FDMR intensity develops after the microwave pulse has ended. Furthermore, compared with data for the corresponding deuterated solutes, the FDMR intensity observed in cyclohexane solutions of biphenyl- h_{10} or anthracene- h_{10} reaches a larger maximum value at an earlier time (5). This behavior can be understood in terms of the radical ion pair spin dynamics. Geminate radical ion pairs are created with purely singlet orientation of the unpaired electron spins. In a static magnetic field, the electron spin wavefunction Ψ rapidly evolves from its initial state where $|\langle\Psi|S\rangle|^2 = 1$ to a quasi steady state where $|\langle\Psi|S\rangle|^2 = |\langle\Psi|T_0\rangle|^2$ (6). Microwave radiation of the appropriate frequency connects states with T_0 character with states of T_{+1} or T_{-1} character and a decrease in $|\langle\Psi|T_0\rangle|^2$ results. After the microwave pulse, hyperfine induced S - T_0 mixing acts to re-establish the steady state at a rate determined by the magnitude of the hyperfine coupling constants. The S - T_0 mixing rate is given by:

$$\omega_{S-T_0} = (2h^{-1})[(g_1 - g_2)\beta H_0 + \sum_i a_{1i}m_{1i} + \sum_j a_{2j}m_{2j}] \quad (7)$$

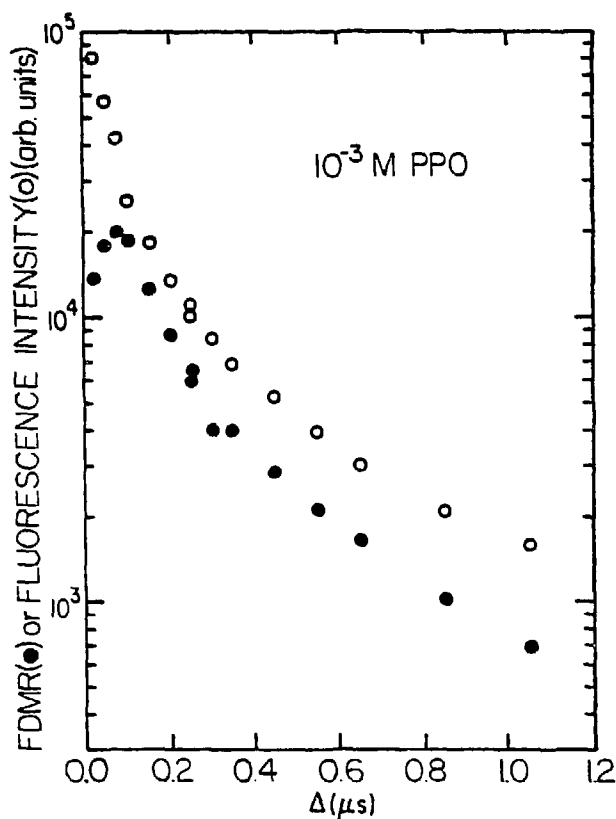


Figure 4. Comparison of fluorescence intensity (○) and FDMR intensity (●) observed in 10^{-3} M PPO-cyclohexane. A microwave pulse was applied from 0-100 ns after irradiation. The fluorescence was sampled at time Δ after the center of the microwave pulse. For comparison, the FDMR intensity has been scaled by an arbitrary multiplicative constant.

which is the familiar expression from treatments of CIDNP, CIDEP, and the magnetic field effect (7). Since usually there is no substantial g factor difference for aromatic radical cations and anions, the hyperfine coupling constants determine the S-T₀ mixing rate. Consequently, in the time domain immediately following the microwave pulse, we observe the decay of $|\langle \psi | S \rangle|^2$ as the steady state is approached. Due to the smaller hyperfine coupling constants of the deuterated radical ions, the rate of S-T₀ mixing, and thus the approach to the steady state is slower for deuterated solutes. After the steady state is established, the time dependence of the FDMR intensity is determined by the recombination kinetics of the radical ion pairs.

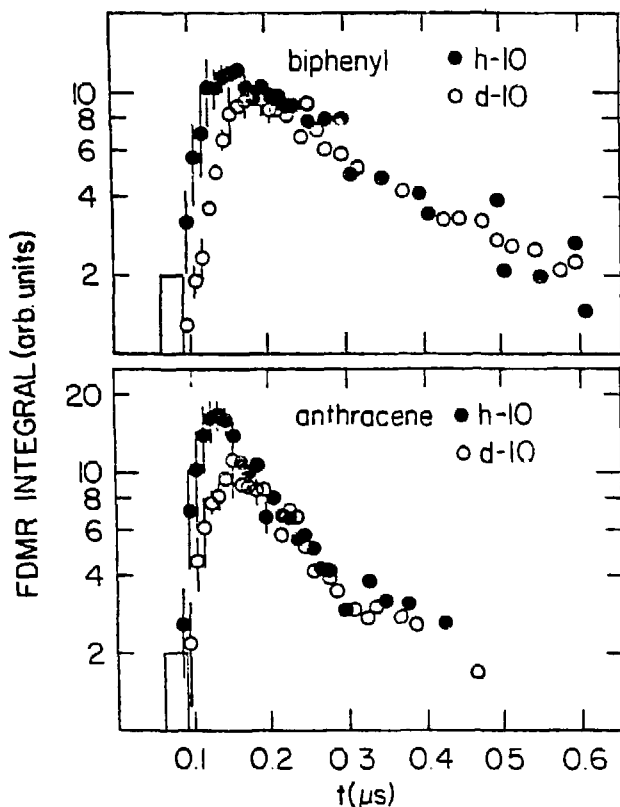


Figure 5. Time dependence of integrated FDMR intensity observed in cyclohexane solutions (0.001 M) of (a) biphenyl-h₁₀ (●) and biphenyl-d₁₀ (○) or (b) anthracene-h₁₀ (●) and anthracene-d₁₀ (○). Vertical bars represent standard deviation of the mean FDMR intensity for times where multiple spectra were measured. The rectangular box indicates the position of the 30 ns microwave pulse. The integrated area units of biphenyl and anthracene FDMR are not directly comparable.

The time and radiation dose dependence of the FDMR intensity establish that the FDMR phenomenon is a resonant change in the yield of excited singlets from geminate ion recombination. Time resolved absorption and conductivity measurements (8,9) have shown that the yield (G_{gi}) of geminate ion pairs decays according to

$$G_{gi}(t) = G_{fi} [1 + (\gamma/t)^{1/2}] \quad (8)$$

where G_{fi} is the free ion yield and γ is characteristic of the recombination reaction kinetics. If the FDMR effect is a resonant change in the yield of excited states arising from geminate recombination then the FDMR intensity should be proportional to $t^{-3/2}$

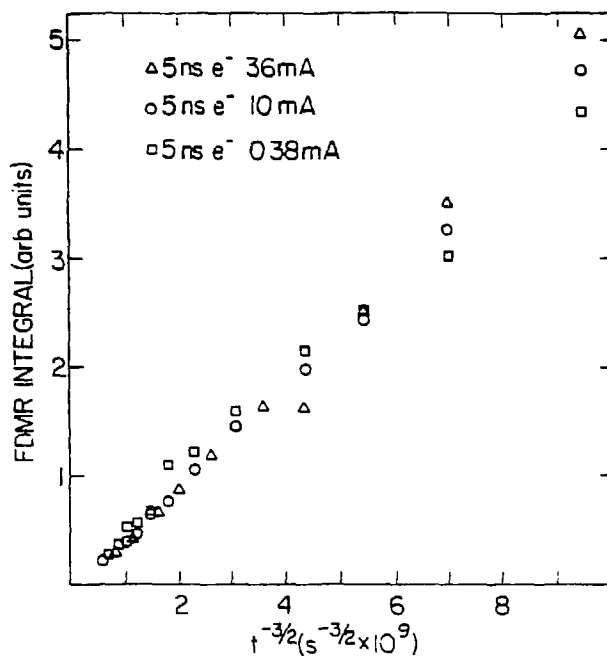


Figure 6. Radiation dose dependence of FDMR of 10^{-3} M PPO in cyclohexane plotted on a $t^{-3/2}$ scale. Samples were irradiated with 5 ns electron beam pulses with peak current values of 36 mA (Δ), 10 mA (\circ), and 0.38 m (\square). The microwave pulse was applied from 0 to 100 ns after irradiation and the fluorescence was sampled at time t after irradiation. Data for different doses were scaled so that all data sets had a common value at $t^{-3/2} = 4 \times 10^9 \text{ s}^{-3/2}$.

and scale linearly with the absorbed dose, since the fluorescence intensity is proportional to the number of recombination events per unit time. This behavior is observed for a broad range of radiation doses (Figure 6). At higher doses, an increased rate of decay of the FDMR intensity suggests a possible contribution by a dose dependent rate of spin lattice relaxation due to Heisenberg exchange (2).

The FDMR spectrum is sensitive to the structure of the radical ion precursors of excited states. Consequently, the FDMR technique could be used to distinguish the contributions of the various recombination pathways (4-6) to excited state production. The FDMR spectrum of the PPO-cyclohexane system at a low solute concentration shows the presence of broad "wings" in addition to a narrow central peak (Figure 7). The decay of the radical species responsible for the wings is somewhat faster than the decay of the species responsible for the central peak (2). This behavior is

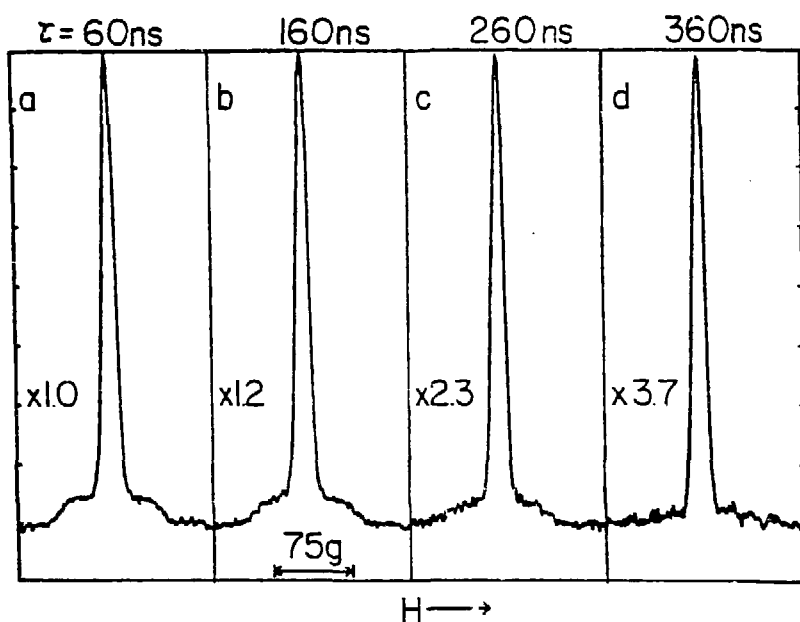


Figure 7. Dependence of the FDMR of 10^{-4} M PPO in cyclohexane wave pulse was started at 10 ns (a), 110 ns (b), 210 ns (c), and 310 ns (d) after irradiation. The fluorescence was sampled from 75 ns to 175 ns after the start of the microwave pulse. For comparison, the y axis values of the spectra have been multiplied by the factors indicated.

consistent with the idea that the wings are essentially the EPR spectrum of the cyclohexane radical cation or "hole." The kinetic properties of the species responsible for the wings are being actively investigated. If the FDMR method could be used to obtain quantitative data on the relative importance of solvent-solute or solute-solute recombination in excited state production, it could provide the first direct experimental check on theoretical calculations of the recombination kinetics (10,11).

Future applications of FDMR in radiation chemistry will explore excited state production in increasingly complex chemical systems where the sensitivity and specificity of the technique can be exploited to best advantage. Another potentially fruitful area of inquiry is the recombination of photoproduced ion pairs in liquid solution. Accordingly, we have recently undertaken an FDMR investigation of photoionization induced by an excimer laser excitation source.

SUMMARY

Time resolved pulsed EPR experiments utilizing optical detection were illustrated. The FDMR method provides a very sensitive and specific tool for the study of radical ion reactions that yield excited states.

ACKNOWLEDGMENT

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